Methods of electrode surface modification using porphyrin-type molecules combined with nanomaterials

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Porphyrin-type molecules such as phthalocyanines (Pcs) are employed as electrode modifiers in order to enhance electrode activity [1]. Nanomaterials such carbon nanotubes (CNTs), quantum dots and metal nanoparticles are employed together with Pcs to further enhance electrode activity due to the synergistic effect of these nanomaterials with Pc molecules. Methods of electrode modifications using Pcs alone or the nanocomposites include self-assembled monolayer formation, polymerization, adsorption, grafting or click chemistry. Characterization of the conjugates or surfaces modified by conjugates will be discussed. Methods of characterization include voltammetry, X-ray photoelectron spectroscopy, scanning electrochemical microscopy and other microscopic techniques. The applications of the nanocomposites as electrocatalysts will be discussed.

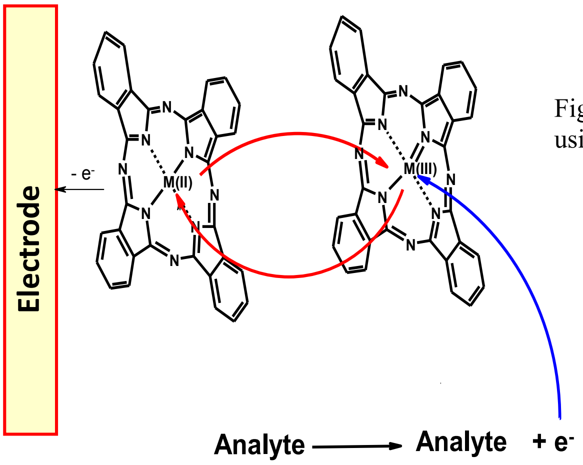

Figure 1. Electrode modification using metallophthalocyanines

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From bioelectrocatalysis to electrocatalysis. A contribution to sustainability of energy provision

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The provision of sustainably generated energy is of utmost importance for the future of our planet. Without any doubt, electrochemistry in general and especially the elucidation of fundamentals of (bio)electrocatalysis will be on the forefront to preserve a planet providing suitable living conditions for a growing population. Evidently, the access to energy may mean completely different things in a mega-city, in rural areas in Europe, or in growing arid areas in the sub-Sahara or villages in central Africa. However, in the one or the other way, provision of energy today has a substantial environmental impact by e.g. cutting the last trees leading to even more erosion or by emitting exceeding amounts of CO_2 for setting the air condition system to very low temperatures.

Despite big political decisions are urgently needed, electrochemists need to contribute to the scientific basis to make sustainable energy provision possible at each level. And it is probably even more important, that the next generation of electrochemists gets aware and contributes to this endeavor.

This presentation will make a journey from bioelectrocatalysis to electrocatalysis, seeking for similarities and differences and will present tools which are providing a better insight into fundamental features being the basis for highly selective reactions. This journey will show possibilities to use highly oxygen-unstable biocatalysts in biofuel cells and biosupercapacitors as well as to use gas-diffusion electrodes to increase the local availability of low soluble gaseous substrates. It will continue to locally arranged catalytic sites looking at similarities between enzymes and nanoparticles following the “nanozyme” concept and further to nanoelectrochemical tools for elucidating the electrocatalytic activity of single nanoparticles under conditions where mass transfer is not limiting. Finally, it will arrive at new noble-metal free catalyst materials for energy conversion reactions.

Acknowledgements: The author is grateful for the contributions of his PhD students and senior scientists, specifically among others Patrick Wilde, Thomas Quast, Tobias Löffler, Denis Öhl, Dr. Yen-Ting Chen, Dr. Harshitha Barike, Dr. Corina Andronescu, Tsvetan Tarnev, Dr. Justus Masa, Dr. Stefan Barwe, Dr. Alexander Botz, Julian Szczesny, Dr. Adrian Ruff, Dr. Felipe Conzuelo, Dr. Fangyuan Zhao, to the cooperation partners in the “Nanozyme project” from UNSW Sydney Dr. Tania Benedetti, Prof. Richard Tilley, Prof. J. Justin Gooding, Peter O’Mara, Johanna Wordsworth, the cooperation partners at Ruhr University Bochum namely the research groups of Prof. Martin Muhler (Industrial Chemistry), Prof. Matthias Rögner (Plant Biochemistry), Prof. Nicolas Plumeré (Molecular Nanostructures) as well as the group of Prof. Wolfgang Lubitz at the Max-Planck-Institute for Chemical Energy Conversion, Mülheim. The BMBF project “NEMEZU” (03SF0497B), the Humboldt foundation as well as the projects funded by the Deutsche Forschungsgemeinschaft (FOR 2397-1; CRC247; EXC-2033 – 390677874) are acknowledged for financial support.

Well-defined Pt(hkl)|solution interfaces: charge, ionic adsorption and acid-base properties.

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Abstract

The use of well-defined model electrodes benefits of the knowledge of the surface atomic density. This parameter is the key to correlate the charge transfer associated to any surface process to the stoichiometry of the corresponding electrochemical reaction. On polycrystalline materials, the number of surface atoms is unknown and the lack of this information makes difficult any quantitative analysis of data.

Comparison between different processes taking place at well-defined interfaces enables to gain information about the validity of Faraday laws in Surface Electrochemistry and validate charge density as a quantitative tool. Once understood, potentials of zero charge can be estimated for different single crystal Pt(hkl) electrodes and particularly for Pt(111), by using purely electrochemical techniques [2]. The results are corroborated by using more sophisticated auxiliary techniques.

The knowledge of the potential of zero free charge defines the adsorption of ions at the surface and the possible contribution of ionic pairs in this process. On the other hand, using electrolytes that do not contain to specifically adsorbed species enables to work at different pH values and approach interfacial properties related to acid-base equilibria [3, 4]

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Liquid Sunlight: *the evolution of Photosynthetic Biohybrid Systems*

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Accelerating technological development and population booms have intensified the ever rising demand on Earth's energetic and material resources. As the only energy input into the ecosphere, solar energy positions itself as the most promising solution to this relieving environmental strain. Efficient capture of sunlight can not only provide energy, but also power the recycling of waste materials, like CO_2, back into useful chemicals. Despite intense efforts in the fields of chemistry, biology, and engineering to develop such CO_2 fixation processes, comprehensive solutions remain elusive. Biology achieves CO_2 fixation to energy-dense multi-carbon compounds with impressive selectivity, yet suffers from poor photosynthetic light absorption. Integrating inorganic and biological materials together in a synergistic fashion to imbibe new and enhanced functionality in a hybrid system has been sought as an attractive pathway for the transduction of solar energy to high-value chemical targets.

Against this backdrop, our recent work focuses on a novel cyborgian design for solar fuel production: the Photosynthetic Biohybrid Systems (PBSs). These PBSs combine the strengths of inorganic materials and biological catalysts. Such systems exploit semiconductor broadband light absorption to capture solar energy and subsequently transform it into valuable CO_2-derived chemicals by taking advantage of the metabolic pathways in living organisms. Importantly, these systems now ascend to the high solar efficiencies of traditional semiconductor-based photovoltaic and photoelectrochemical devices and transfer over the captured sunlight to the robust and selective CO_2-fixing microorganisms responsible for the biosynthesis of a diverse, nearly limitless, array of chemical products. In this way, we may beat natural photosynthesis at its own game.

Oxygen Redox Electrochemistry - The Future of Lithium Batteries?

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The lithium-ion battery has transformed portable electronics. It has a key role to play in meeting the stringent CO2 emission targets necessary to slow global warming. However, it is clear that the world will need batteries that exceed the capabilities of today's lithium-ion technology; how to realise such batteries is much less clear. Advances in understanding the fundamental electrochemistry that underpins batteries are essential if progress is to be made. Two possible approaches to increasing the energy density of lithium batteries will be discussed, both depend on advancing our understanding of the fundamental electrochemistry of oxygen redox.

The intercalation cathode in a lithium-ion battery operates by the reversible removal and reinsertion of Li+ ions from/to the transition metal oxide host with charge compensation involving redox reactions on the transition metal ions, e.g. $Mn^{3+/4+}$ in $Li_xMn_2O_4$. If redox reactions could also occur on the oxide ions the capacity to store electrons and hence charge could exceed the limits of today's cathodes leading to lithium batteries with higher energy density. It is now known that O-redox does occur, however it is not truly reversible and there is much to be understood regarding the electrochemistry of O-redox in the solid state.

The Li-O2 battery has the highest theoretical specific energy of any battery, 3500 Wh kg^{-1}, compared with 800 Wh kg^{-1} for Li-ion. Its operation depends on mastering two of the most challenging electrodes, Li/Li^+ and O_2/Li_2O_2. The cell is composed of a Li metal negative electrode, an aprotic liquid electrolyte, e.g. $LiPF_6$ in tetraglyme ($CH_3O[CH_2CH_2O]_4CH_3$) and a porous carbon positive electrode open to the atmosphere. The reaction at the positive electrode involves reduction of O_2 to Li_2O_2 on discharge and its reversal on charge. Rendering this reaction reversible, with fast kinetics and low polarization, as well as minimal side-reactions and operating in ambient air is far from trivial. The role of redox mediating molecules in promoting reversible O_2/Li_2O_2, the reactivity of oxygen species with the electrolyte and electrode, the problems of operating in ambient air, will all be discussed.

Surface and bulk and Stability of Aqueous-Processed Ni-Rich NMC Cathode Materials

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Abstract

Despite recent advances in lithium-ion battery technology, further energy density improvements and cost reductions are necessary to achieve widespread adoption of electric vehicles. Low-Cobalt layered active materials are promising candidates for next-generation cathodes for lithium-ion batteries (LIBs). Co content is a significant cost issue for LIBs and is difficult to mine properly. Popular examples of these low-Co materials are $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC 811) and $LiNi_{0.85}Co_{0.1}Al_{0.05}O_2$ (NCA). However, these materials present processing and performance challenges such as compatibility with water during aqueous electrode formulation, unoptimized SEI/CEI formation conditions during cell assembly, and unstable capacity fade when cycled to upper cutoff voltages above 4.3 V vs. Li/Li^+.

Lithium nickel manganese cobalt oxide (NMC) has been developed as a promising high-energy-density cathode material, and aqueous processing offers significant environmental benefits and lower production expenses compared to traditional processing using N-methylpyrrolidinone (NMP). The effect of aqueous processing on battery performance was evaluated by comparing the rate capability and cycling performance of pouch cells made using aqueous- and NMP-processed cathodes. While both sets of cells perform well, the capacity retention of the aqueous-processed cells is slightly lower (Figure 1). This could be due to formulation differences, and we are currently exploring the use of different binders and additives to optimize aqueous electrode preparation. Correlating formulation and processing conditions with final electrochemistry could lead to the design of new approaches to improve the performance of aqueous-processed Ni-rich cathodes for high-energy-density batteries.

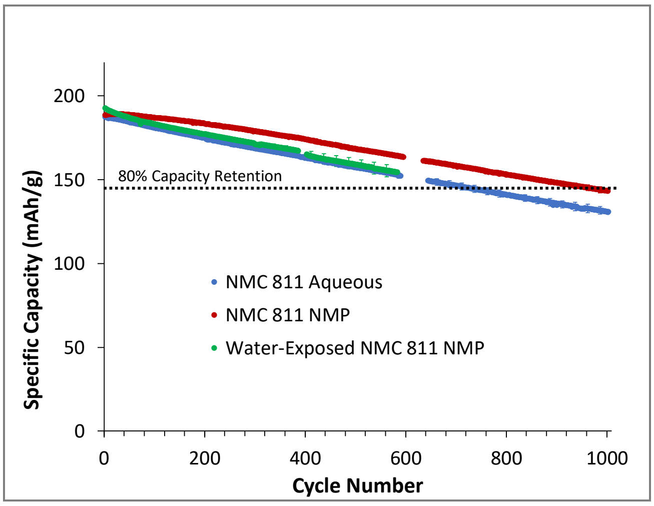

Figure 1. Cycling performance of NMC 811 single-layer pouch cells at 0.33C/-0.33C at an upper cutoff voltage of 4.2 V. Comparison between standard NMP/PVDF processing, water-exposed NMC 811 prior to NMP/PVDF processing, and aqueous processing.

Characterization of Electrode | Electrolyte Interfaces in Batteries

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The solid/liquid interfaces in battery, i.e. electrode | electrolyte interfaces, are critically important for the performance of batteries. Solid electrolyte interphase (SEI) is known as an electronically insulating but ionically conducting film formed on the surface of the anode in Li-ion batteries when the insertion potential of the anode is lower than 1.2 V versus Li+ /Li; similarly, cathode SEI (CEI) is formed on the surface of cathode when the lithium extraction potential of the cathode exceeds 4.2 V versus Li+ /Li. It is widely accepted that the physical and chemical properties of SEI and CEI films have significant impacts on the electrochemical performances of Li-ion batteries.

The mechanical property of SEI largely defines the cycling performance and the safety of LIBs. Great efforts have been made to modify the mechanical properties of SEI films by adding additives in electrolyte and/or modifying electrode surfaces, aiming at the formation of elastic and flexible SEI films to accommodate large volume variation during charging/discharging cycles. This is especially important for high capacity alloy or conversion reaction type anode materials in order to achieve excellent cycling performance and high Coulombic efficiency. However, the mechanical properties of SEI films have been rarely investigated. In this talk, we will report the qualitative imaging of SEI morphology and quantitative measurement of SEI's Young's modulus on a model MnO anode. The inhomogeneity of SEI film in morphology, structure, and mechanical properties provides new insights to the evolution of SEI on electrodes. Furthermore, the quantitative methodology established in this study opens a new approach to screen the effect of different additives on the mechanical property of SEI.

Furthermore, the formation of CEI on high voltage LCO is in-situ observed on different crystalline facets. The formation and stability of CEI is directly related to high-voltage cycling stability of corresponding coin cells. To fully characterize the structure and property of SEI and CEI, multiple techniques are needed. Examples of interface characterization in practical battery systems will be given to show the cross-talk effects between the cathode and anode.

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A need for better experimental and modelling approaches to understand and predict better corrosion of metals

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In the advanced materials industry, there is a clear trend towards more sustainable concepts, and this is certainly also the case for metals. They take a prominent position in the materials market thanks to their multifunctionality and structural and mechanical properties. However, metals are prone to corrosion, and therefore often organic coatings are applied to extend their lifetime. The search for organic coated metals with higher multifunctionality and extended lifetime goes together with the search for more sustainable material concepts in the context of the REACH regulation.

Nowadays, materials are developed for providing components with a lifetime ranging from 10 to 25 years. The lifetime of a material highly depends on its exposure to the environment inducing ageing processes. In the current state of the art, lifetime and ageing assessment are performed by means of experiments, combining accelerated and field testing. The limitation of the first is that the conditions of the accelerated tests are not representative for the real environmental conditions and that there is no proven relationship between accelerated laboratory tests and field performance data. The limitation of the second is that it takes several years (5 to 10 years).

The only way to realise a substantial decrease in the development time of new materials is to introduce modelling in the design cycle. What is needed to realize a breakthrough in this field is a tool that can predict quantitatively and dynamically the corrosion behaviour of (organic coated) metals. The long term scientific motivation of our research is to build a knowledge and technology platform to enable the prediction of durability behaviour and the estimation of lifetime of (organic coated) metals under long-term environmental ageing and corrosion conditions. This requires advanced research because corrosion of a (organic coated) metal is the result of an intense interplay between several physical phenomena that need to be characterized in real conditions and modelled. Within VUB and TUDelft research we try to focus on both aspects bringing in new advanced combined electrochemical & in situ surface analysis, advanced finite element electrochemical modelling and more recently quantum chemical modelling. During the lecture an overview will be given on our state of the art in the different domains, emphasizing some success but also bringing bottlenecks when it really comes to predictions of corrosion.

Acknowledgements: all VUB-SURF and TUDELFT-CTE colleagues for the excellent collaborations.
These instructions are an example of what a properly prepared meeting abstract should look like. Proper column and margin measurements are indicated.

Nanopore-Based Single Biomolecule Interface for Single Molecule Sensing

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The single molecule measurement has enhanced the precision and depth of our knowledge about living system. The million years of evolution have produced the membrane proteins which acts as a single biomolecule interface for capturing and identifying a single molecule of interests. In our study, we focus on the biological nanopore-based single biomolecule interface for single molecule measurements.1-3 We outline the design of nanopore-based single biomolecule interface which provides rich heterogeneities and stochastics information about each molecule. Then, we focus on the future areas beyond DNA sequencing including detecting rare species, resolving the hidden intermediates, depicting the spectra for the covalent/non-covalent interactions, tracing the dynamic pathways of single molecule proteins.4-6 A concept "single-molecule ionic spectrum" may potentially map the non-covalent interaction at atomic level in future. Since the characteristic interaction determines the sensitivity of nanopore, ideally the frequency analysis of nanopore data could potentially allow dis-criminate each amino acid.As ideally transferring the frequency-energy spectrum from the ionic current into the voice frequency, we illustrate that a nanopore-based single-biomolecule interface likes a tuba. When the single analyte flows into the 'tuba', its dynamic interaction with the pore could be modulated by the residue of the pore ('button') and the resonance space at the single-molecule interface ('tuba'). As a result, the beautiful music of a single molecule will be played with a typical rhythm and melody.

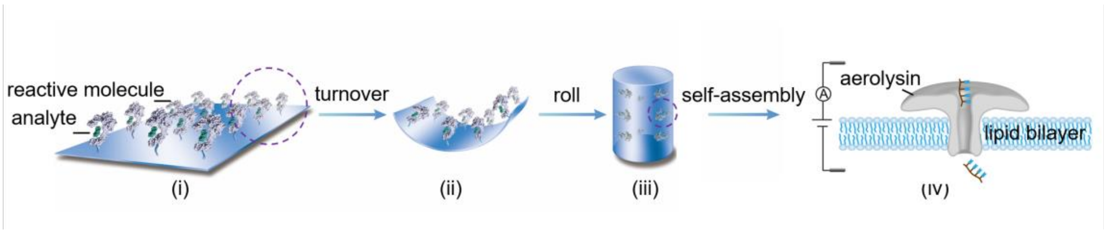

Figure 1. (a) The transformation of a sensing interface. (i) The macroscale interface with a sensing molecule for detection of the targeting analyte. (ii) The macroscale interface shrinks and turns over, (iii) then rolls into a channel as the micro-/nanoscale interface. (iv) A single-biomolecule interface derived from a single recognition molecule at the nano interface. A self-assembled aerolysin membrane protein is regarded as an example of a single biomolecule interface. The oligonucleotide is taken as an example for illustrating the analyte.

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Real-time Molecular Measurements in situ in the Living Body

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The availability of technologies capable of tracking the levels of drugs, metabolites, and biomarkers in real time in the living body would revolutionize our understanding of health and our ability to detect and treat disease. Imagine, for example, a dosing regime that, rather than relying on your watch ("take two pills twice a day"), is instead guided by second-to-second measurements of plasma drug levels wirelessly communicated to your smartphone. Such a technology would likewise provide clinicians an unprecedented window into organ function and could even support ultra-high-precision personalized medicine in which drug dosing is optimized minute-by-minute using closed-loop feedback control. Towards this goal, we are developing a biomimetic, aptamer-based electrochemical sensor platform that supports the high frequency, real-time measurement of specific molecules (irrespective of their chemical reactivity) in situ in the bodies of awake, freely moving subjects.

Energy Conversion and Storage:
Novel Materials and Operando Methods

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This presentation will deal with the development of new materials and *operando* methods for energy conversion and storage with emphasis on fuel cells and battery materials and technologies. The presentation will begin with a brief overview of the methods employed. Particular emphasis will be placed on the use of X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS) X-ray microscopy and tomography and transmission electron microscopy (TEM) under active potential control. The utility of these methods will be illustrated by selected examples including electrocatalysts for the oxygen reduction reaction (ORR), hydrogen oxidation reaction (HOR) and spectroscopic studies of Li/S batteries and Li metal deposition and dendritic growth. The presentation will conclude with an assessment of future directions.

Recent advancements in zinc-ion batteries based on Prussian Blue Analogues

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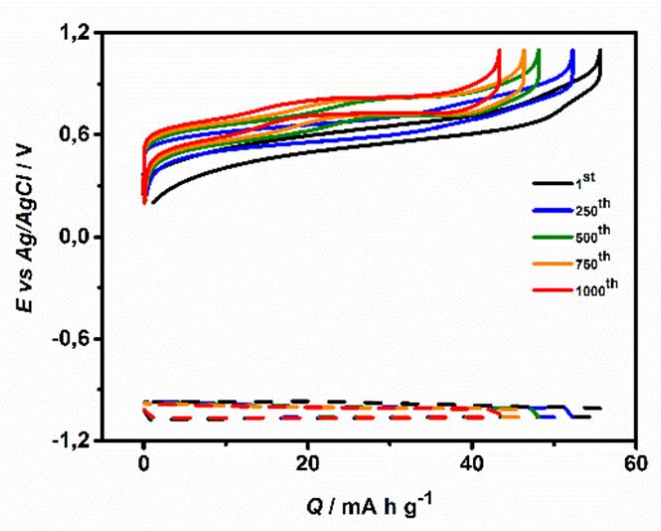
Aqueous zinc-ion batteries (ZIBs) are electrochemical energy storage systems based on a metallic zinc negative electrode and a zinc-intercalating positive electrode. The initially reported performances of ZIBs based on Prussian Blue Analogues have good shown potential for stationary application and storage of energy from volatile regenerative sources, such as wind and solar [1,2]; it was possible to reach a specific energy equal to 46 Wh kg^{-1} at 1C, a specific power equal to 480 W kg^{-1} at 10C, with a charge efficiency of more than 98%, and 100 cycles of life by using copper hexacyanoferrate (CuHCF). With the aim of reaching a longer cycle life, ideally 10000 cycles, the aging mechanism of CuHCF was investigated in details by electrochemical methods and post-mortem XRD. It was observed that the aging mechanism of CuHCF was not related to the dissolution of the active material, but rather to a phase transformation of the intercalating structure, probably caused by the intercalation-induced stress [3]. This mechanism appeared to be strongly dependent on the nature and concentration of the zinc salt in the electrolyte. Moreover, we observed that the intercalation of zinc ions was essential to this mechanism; this was strongly delayed in presence of abundant amount of sodium ions [4]. Based on this knowledge, the synthesis route of the active material has been modified in order to increase the stability of the battery, finally reaching more than 1000 cycles life (see figure).



Potential profile of modified CuHCF-based positive electrode in 100 mM ZnSO4 at 1C current rate.

Also the cycle life of metallic zinc negative electrode is challenging, as side reactions occur during the zinc electro-deposition. In particular, the coulombic efficiency of standard zinc electrodes is around 85% due to the parallel hydrogen evolution reaction (HER). In order to decrease the unwanted HER and improve the coulombic efficiency, two different strategies have been used: addition of surfactants [5]; addition of solid-state additives promoting the zinc electro-deposition [6]. Both strategies lead to an improvement of the coulombic efficiency up to 98%.
Here an overview of the recent advancements in the ZIBs will be shown, with particular care to the actual understanding of the aging mechanism, achieved results, and future challenges.

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Chemical modification of electrochemical energy storage materials

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Electrochemical energy storage can be carried out with two main classes of systems such as electrochemical capacitors and rechargeable batteries. These two electrochemical systems have distinct characteristics, properties and performance (energy and power densities). Electrochemical capacitors are based on capacitive charge storage with formation of an electrical double layer at the electrode surface between the charged electrodes and opposite charged ions from the electrolyte. Electrochemical capacitors are characterized by low energy density that is compensated by high power density. On the other hand, rechargeable batteries involved charge transfer processes and chemical reactions. Consequently, batteries are typically low-power devices compared to electrochemical capacitors but they are characterized by a significantly higher energy density.

There are currently considerable research efforts to improve the performance and stability of these energy storage systems. An approach that we have investigated in our laboratory in order to mitigate these two issues is the chemical modification of the components of a composite electrode. More specifically, the general aim was to modify active electrode materials to increase the energy density of electrochemical capacitors and the stability of rechargeable battery. The more recent systems investigated in our group will be presented and discussed.

Sunlight-Assisted Electrocatalytic CO_2 Conversion to Valued Added Chemicals Using Nanostructured Metals and Metal Oxides

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Artificial photosynthesis of value-added chemicals from CO_2 and water has received renewed attention, and diverse technical solutions for high-efficiency and durability durable systems have been explored.[1] Photoelectrochemical (PEC) systems have long been demonstrated to be technically viable with a number of semiconductor photoanodes coupled to metal or metal oxide electrodes and photocathodes coupled to metal/metal oxide anodes.[2-9] Although they are promising, however, these single absorbers (photoanode or photocathode) exhibit significantly lower efficiencies than the solar conversion limit and require external biases, primarily because of energy losses arising from overpotentials in the O_2-evolution and CO_2-reduction reactions. Recently, photovoltaic-assisted electrocatalytic (PV-EC) systems are considered alternatives to the conventional PEC systems while reporting significantly higher efficiencies than the PEC.[10] In this study, we will show three types of photosystems (PEC, PV-EC, and PV-PEC tandem) with various metals and metal oxides electrodes synthesized in our group, and compare the systems in terms of solar-to-chemical conversion efficiency and durability. Finally, possible applications of the synthesized materials will be presented.[11,12] This research was supported by the National Research Foundation of Korea (2014M1A8A1049354, 2018R1A6A1A03024962, 2016M3A7B4908169, and 2018K2A9A1A01090462) and the Korea Ministry of Environment as Waste to Energy-Recycling Human Resource Development Project (YL-WE-17-001).

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Wiring of Bacterial Cells to Electrodes through Redox Polymers

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We have throughout the years since 2004 pioneered "wiring" both Gram-positive and Gram-negative bacteria [1-3] (and thylakoid membranes [4]) to electrodes using osmium redox polymers (Os RPs) that will strongly facilitate extracellular electron transfer (EET). Because of the cationic nature of the Os RPs they will electrostatically interact very strongly with the cells and form hydrogels that will precipitate on the electrode surface and will allow substrates and products to freely diffuse in and out of the hydrogel. We have investigated the influence of E°'-value and structure of the Os-complexes of the Os RPs on the rate of the EET. However, only recently we have obtained a much more clear picture on how the RPs and the cells interact and how the interaction changes with time. In these recent investigations we have "wired" wild type and some mutants of *Enterococcus faecalis* with both 4 different Os RPs as well as with a quinone RP [5-8]. These recent results will be shown and discussed.

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Following in Prof Conway's footsteps: 3- and 2-Dimensional materials for (super)capacitive energy storage

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In 1999, Prof Brian Conway published a book entitled "Electrochemical supercapacitors: scientific fundamentals and technological applications" [1] which became the reference in the field of supercapacitors and a source of inspiration for a generation of scientist.

This presentation will give an overview of the research work we achieved on capacitive (porous carbon) and pseudocapacitive materials and the challenges/limitations associated with the development of these materials. Starting with porous carbons, we will present the state-of-the art of the fundamental of ion adsorption mechanism in porous carbons and its practical applications before moving to solid-state supercapacitor electrodes and devices, which are currently focusing a lot of interest. A second part of the talk will be dedicated to pseudocapacitive materials, starting with an introduction where we will remind some key difference between battery and pseudocapacitive materials. Key results obtained with 2-D MXene carbides and metal oxides materials will be presented and discussed. A last part of the talk will be dedicated to the development of micro-devices for Internet of Things (IOT), which is supposed to be one of the most promising application for microdevices. Exemples of on-chip and flexible micro-devices will be presented and discussed.

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Electron Charge and Spin Transfer in Films of Biomolecules

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Experimental studies of electron charge and spin transfer through monolayer films of biomolecules on electrodes will be presented. The dependence of protein and peptide film structure, as well as medium polarization effects, on the charge transfer and charge transport will be discussed. Experimental results on the single molecule conductance through nucleic acid duplexes as a function of the length, sequence, and duplex flexibility will be described and their charge transfer mechanism will be contrasted with that found for peptides and proteins. Experimental results on a new type of electrode measurement that probes the spin polarization of chiral molecules by the magnetization that they generate on an electrode surface and their ability to spin filter the electron current will be described. The implications of this work for enantioselective electrochemistry will be demonstrated.

Opportunities of Electrochemical Reaction Applications in Solid State Devices and Circuits Fabrication

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Integrated circuits (ICs) and Thin Film Transistor Liquid Crystal Displays (TFT LCDs) are the two largest electronic industries now a days. The former progresses toward packing a very large number of nano-sized devices into a small chip, e.g., near 1 billion MOSFETs in a 1” x 1.5” die. The latter is developed toward fabricating micrometer sized TFTs on a giant piece of substrate, such as the 3 m x 3m generation-11 glass. These products are made of mixed dry and wet processes, such as plasma deposition, plasma etching, sputtering, solution cleaning, and solution etching. Electrochemical reactions exist in every process step. For example, the plasma deposition or etching process starts from the dissociation of feed gas molecules through collision with high energy electrons. Subsequently, the generated ions and radicals arrive the substrate surface where they react to form products. Therefore, the plasma process can be taken as a dry electrochemical reaction process. The plasma reaction has to be carried out in vacuum, which is a drawback with respect to the cost and throughput.

Electrochemical reactions have been used in the manufacture of solid state products, e.g., electroplated copper interconnect lines and anodized aluminum or tantalum oxide dielectric. However, they are not widely used in modern electronics manufacture. In this paper, the author will show examples on possible applications of electrochemical reactions in the manufacture of advanced devices and products. Critical production issues, such as impurity, defects, morphology, and reliability, will be discussed. Figure 1 shows an advanced 3D IC structure where TFTs are made from electrochemical reactions and embedded in the interconnect structure. The detailed process will be discussed. Ultimate challenges in electronic and optoelectronic device fabrications will also be presented and discussed.

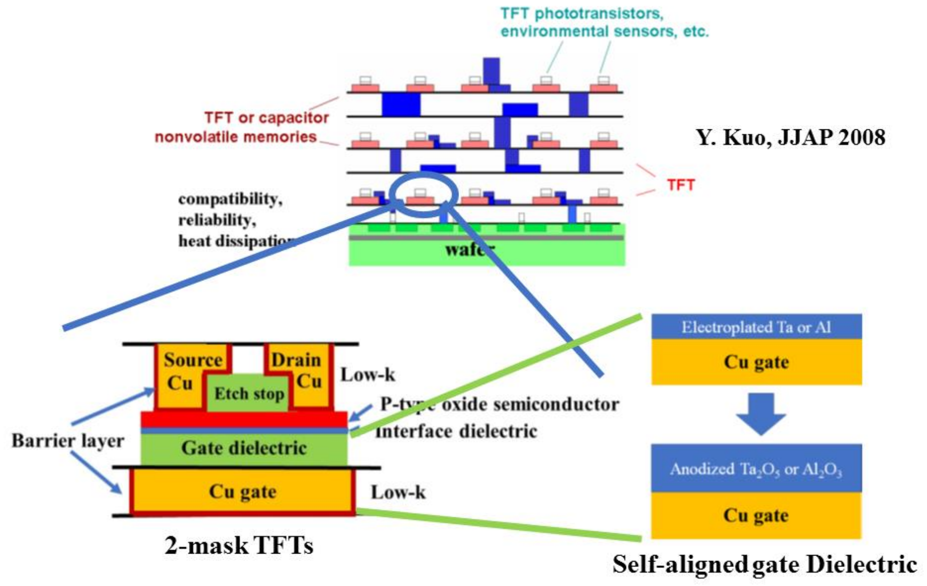

Fig. 1. A 3D IC with electrochemical reaction fabricated TFTs embedded in interconnect structure.

Hybrid Carbon/Graphene Electrodes for Energy Storage in Supercapacitors

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The utility of supercapacitors for both fixed and portable energy storage would be greatly enhanced if their energy density could be increased while maintaining their high power density, fast charging time, and low cost. This study describes a simple, solution-phase, scalable modification of carbon materials by electrochemical reduction of a double diazonium reagent to form a covalently bonded "brush" of hydrogen-terminated graphene ribbons (GRs) with layer thicknesses of 2–20 nm.[1] The hybrid electrode exhibits 20–100 times higher areal capacitance than the unmodified electrode,[2] with a large Faradaic component resulting from nitrogen doping of the graphene ribbons. On a flat sp^2 carbon surface modified by GRs, the capacitance exceeds 1200/μF cm in 0.1 M H$_2$SO$_4$, which can be increased further to >18 mF/cm^2 by altering deposition conditions. Modification of high surface area carbon black electrodes with GRs yields projected capacitances of 950–1890 F/g, power densities >40 W/g, and minimal change in capacitance during 1500 charge/discharge cycles at 20 A/g. A capacitance of 1890 F/g affords an energy density of 318 Wh/kg operating at 1.1 V and 590 Wh/kg at 1.5 V. The projected energy density of a hybrid GR/carbon supercapacitor greatly exceeds the current 10 Wh/kg for commercial supercapacitors and approaches that of lithium ion batteries. In addition, an aqueous supercapacitor has greater safety than lithium batteries, much lower cost, higher power density, and much faster recharge rate due to more efficient ion transport.

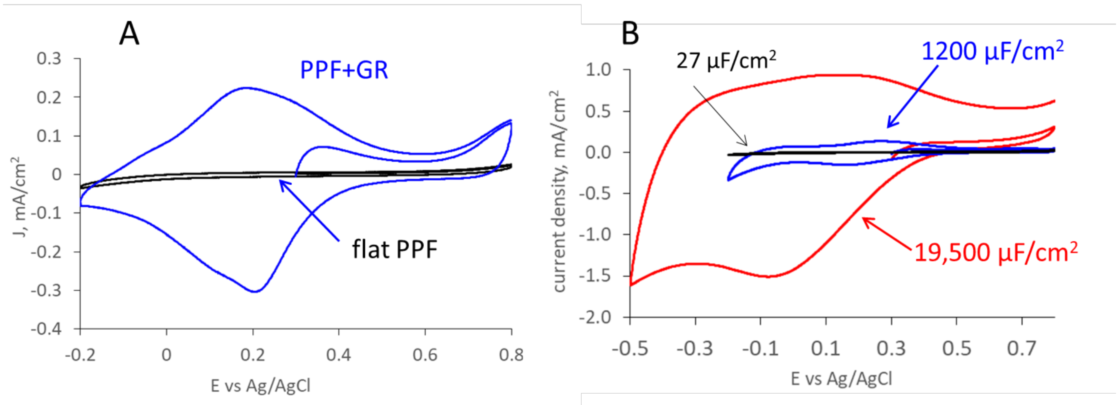

Figure: Voltammetry (50 mV/sec) in 0.1 M H$_2$SO$_4$ of flat sp^2 hybridized carbon surfaces (PPF) before and after graphene modification. A. bare PPF (black curve) and PPF modified with a ~15 nm thick film of graphene ribbons (blue curve). B. same electrodes as panel A (black and blue) plus a modificd surface using different conditions (red).

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Platinum Electrochemistry and Electrocatalysis. From Hydrogen Adsorption to Platinum Dissolution

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Platinum is amongst the most important transition metals due to its catalytic properties and also one of the most studied electrochemical systems. Despite over fifty years of extensive research, many aspects of its electrochemical behavior and electrocatalytic properties remain a mystery. This presentation summarizes our contributions to Pt electrochemistry and electrocatalysis, and discusses the adsorption of H (the under-potential deposition of H, UPD H), surface electro-oxidation, and (electro-)dissolution.

Temperature-dependent cyclic-voltammetry (CV) research on the UPD H on polyoriented and monocrystalline Pt electrodes in aqueous acidic media combined with theoretical data analysis allowed us to determine the thermodynamic state functions ($\Delta_{ads}G°$, $\Delta_{ads}S°$, $\Delta_{ads}H°$) of the process and to evaluate the Pt–H_{UPD} surface bond energy ($E_{Pt\text{-}Hupd}$). Comparison of the value of $E_{Pt\text{-}Hupd}$ to that of the Pt-H_{chem} surface bond under gas phase conditions ($E_{Pt\text{-}Hchem}$) resulted in establishing a relationship between these two species, and deduction of a possible surface adsorption site of H_{UPD} [1].

Our research on the surface electro-oxidation of Pt electrodes in aqueous acidic media employed CV, chrono-amperometry (CA), Auger electron spectroscopy (AES), and electrochemical quartz crystal nanobalance (EQCN). The results led to the conclusion that anhydrous PtO was the first stable surface compound formed and its development was followed by the formation of PtO_2 on top of the PtO layer. Examination of the PtO growth under well-defined polarization potential (E_p), polarization time (t_p), and temperature (T) conditions within the framework of oxide growth theories allowed us to conclude that the early development of PtO (up to one equivalent monolayer of O) was limited by the interfacial structural transformation (the so-called place exchange) between the surface Pt atoms and the electro-adsorbed O. Beyond this thickness, the process was limited by the escape of the Pt^{z+} cations from the metal into the oxide at the inner metal/oxide interface. Theoretical treatment of these processes made possible evaluation of the Pt–O_{chem} surface dipole moment, the potential drop across the oxide layer, and the electric field operating across the oxide [2-4].

Our recent EQCN measurements employing polycrystalline Pt electrodes of gradually increasing surface roughness (R) allowed us to determine the interfacial mass changes associated with the UPD H, PtO development, and the double-layer charging at atomically flat, polycrystalline Pt surfaces. Analysis of the results led to the estimation of the number of H_{UPD} species, H_2O molecules, H_3O^+ cations, and anions interacting with each Pt surface atom during these interfacial processes [5].

Finally, our most recent experimental efforts focus on the (electro-)dissolution of Pt materials (polycrystalline, nanoscopic) in aqueous acidic media at well defined potential conditions. The results revealed that the process is strongly surface-structure dependent. Application of polyoriented spherical single crystal electrodes allowed us to simultaneously evaluate surface-structural changes associated with Pt (electro-)dissolution taking place on twenty-five facets. The results demonstrated that Pt(531) reveals the greatest stability upon repetitive potential cycling in the potential region of surface oxide formation-reduction and (electro-)dissolution [6,7]. These results suggest that Pt nanoparticles possessing the (531) surface orientation of atoms are expected to be the most stable for the oxygen reduction reaction (ORR).

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Understanding and Controlling Reaction and Transport Mechanisms in Prussian Blue Analogues for Faradaic Deionization

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Electrochemical desalination technologies using cation intercalation reactions within nanoparticulate host compounds show potential for energy-efficient water treatment with high water recovery and low pumping pressure. While the theoretical charge-storage capacity of such materials can exceed the levels needed to desalinate seawater salinity levels, removal levels at finite-rate operation are limited by transport phenomena that range from atomic to device scales. In this talk we address this challenge by characterizing and controlling the rate-limiting processes within porous electrodes containing Prussian blue analogue (PBA) nanoparticles, a material with facile kinetics and cation-specific preference for intercalation. We first use the potentiostatic intermittent titration technique (PITT) to characterize both thermodynamic equilibrium and apparent diffusion of PBA nanoparticles (NPs) incorporated within porous electrodes. By combining atomistic modeling with PITT results, we find that the measured variation of equilibrium potential with the degree of intercalation (DOI) results from repulsion between interstitial vacancies in nearest-neighbor sites within the PBA host. We also discover that the apparent diffusion coefficient of cations within PBA porous electrodes varies non-monotonically between 10^{-11} cm^2/sec (at 50% degree of intercalation, DOI) and 10^{-10} cm^2/sec (at DOIs of 0% and 100%) that we show is a signature of electron-conduction limitations in PBA NP agglomerates. Galvanostatic cycling of electrodes with different average NP-agglomerate sizes reveals that two-fold higher rate capability is achievable when agglomerate radius reduces two-fold, despite having the same NP size distribution. By way of comparison with theory and by characterizing the effective conductivity of PBA-NP compacts, we show that apparent cation diffusion in PBAs is limited by electronic conduction through NP agglomerates. Building on these findings, we also measure the effective electronic and ionic conductivity and hydraulic permeability of porous electrodes that incorporate insulative nanoparticles from which we build processing/structure/property relationships to inform materials selection for Faradaic deionization devices using cation intercalation materials. We subsequently identify optimal electrode formulations using electrochemical Ashby diagrams with guidelines determined using device-level metrics for electrochemical desalination.

Washing-Free Electrochemical Biosensors

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Washing processes, essential in most heterogeneous labeled assays, have been a big hurdle in simplifying the detection procedure and reducing assay time. Nevertheless, less attention has been paid to washing-free heterogeneous labeled assays. I present purely washing-free biosensors that allow fast, sensitive, and single-step detection of biomarkers in serum with low interference. Proximity-dependent electron mediation of an electron mediator between an indium–tin oxide (ITO) electrode and an enzyme label allows us to discriminate between a bound and an unbound label: a bound label offers faster electron mediation than an unbound one. The new biosensors are highly promising for the simple, sensitive, and rapid point-of-care detection of proteins, small molecules, and nucleic acids.

Electrografting Beyond Diazonium Salts

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Aryl diazonium salts (but also iodoniums) have been widely used for modifying surfaces (many forms of carbon, metals, semiconductors and polymers) with a variety of substituents on the aryl group (from simple organic groups to proteins). This reaction can be performed in many ways: spontaneously on reducing surfaces or in basic medium, by electrochemical reduction, by photochemistry (under UV or visible light in the presence of a photo sensitizer). The key species is the very reactive aryl radical that is produced close to the surface and binds to it. The modified surfaces have been characterized in a number of ways (electrochemistry, IR, XPS....) and more recently by STM. In order to extend the number of structures that can be attached to surfaces one has to look for molecules that, upon activation by electrochemistry, provide a reactive radical and a leaving group that should be quite inert (that does not react competitively on the surface).

Alkyl halides provide such molecules, the C-I bond is weak and can be easily broken to give an alkyl radical and a iodide anion that is not very reactive. In this way, it was possible to attach alkyl or perfluoro alkyl groups to different surfaces (Au, GC, Cu, Fe). Iodo and bromoacetonitrile have also be grafted in this way. However,the reduction of idohexane that leads to its surface reaction takes place at quite negative potential (-2.8 V/SCE in ACN).

2,6-dimethyl benzenediazonium (2,6-DMBD) as other diazonium salts can be easily cleaved by electrochemistry, to give the 2,6-dimethylphenyl radical, but due to the steric hindrance of the radical, it does not react with surfaces. However, this radical is able to abstract an hydrogen or halide from another molecule present in the solution, this leads to the formation of a new radical that can react with a surface. This reaction has been used to attach hexyl or perfluoroalkyl chains to the surface of GC. As 2,6-DMBD is very easily reduced this indirect grafting of an alkyl group it achieved with a potential gain of -1.7 V. Electrografting of acetonitrile is also possible by this method. This reaction can be extended to bromo compounds, to other surfaces such as aluminum, gold and polymers, but also to the formation of mixed alkyl-aryl films. A similar gain of potential is obtained when electrografting aryl iodides, this makes the reaction possible with some aryliodides that would not be possible directly.

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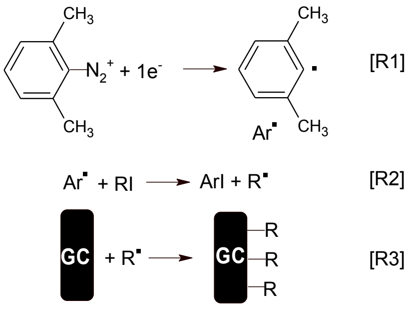

Scheme. Mechanism for the grafting of alkyl and perfluoroalkyl films.

These instructions are an example of what a properly prepared meeting abstract should look like. Proper column and margin measurements are indicated.

The abstract **should not exceed ONE PAGE** of text, references, tables and figures. Abstracts exceeding this limit may be cut without consideration of content after the first page.

Type the title single-spaced in 14-point Times Roman bold, upper and lower case and NOT in ALL CAPITAL letters.

Type the author(s) name(s) single-spaced in 10-point Times Roman regular.
Type the affiliation(s) and address(es) single-spaced in 10-point Times Roman italic.

Type the body of the abstract text (including references and tables) single-spaced in 10-point Times Roman regular.

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Fuel Cell Activity from Non-Precious Metal Molecular Catalysts

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The development of non-precious metal PEM fuel cells is important for their widespread application. Many synthetic molecular catalysts have been prepared, inspired by the high rates and efficiency of hydrogenases, with the potential for providing high performing, non-precious metal fuel cell catalysts. Mimicking not only the active site, but also the protein scaffold has resulted in synthetic H_2 oxidation catalysts with amino acids, $[Ni(P^{Cy}{}_2N^{Amino\ acid}{}_2)_2]^{2+}$, with TOFs and overpotentials for H_2 oxidation approaching those of enzymes. Importantly, their best performance is under acidic conditions and elevated temperatures, conditions optimal for PEM fuel cells. Further, the COOH providing at attachment point to surfaces, these complexes have shown promise for incorporation in real fuel cells. Activity, efficiency, and stability on surfaces and in fuel cells show promise for synthetic non-precious metal catalysts.

Asymmetric pseudo capacitors using water-in-salts as electrolytes

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A strategy to increase the energy of supercapacitors is to use electroactive polymers, which have a pseudocapacitive process, that is, the redox reaction is so fast that the process resembles the loading of the double layer. However, since the process is faradaic, the amount of energy is greater than the charge of the double layer [1]. When electroactive polymers are used as the electrode for pseudo-capacitor, they are coupled to a carbon electrode, the polymer being the positive electrode and the carbon being the negative electrode (or vice versa, depending on the electro-active potential range of the polymer). The most concentrated water-in-salt (WiSE), ie 21 mol kg^{-1} of Li[Tf$_2$N], is being used as electrolyte for pseudocapacitors with the PCz and PEDOT polymers, both using active carbon as an auxiliary electrode. PCz presents its redox reactions in positive potentials, and in turn, PEDOT is electroactive in negative potentials. Therefore, carbon will be negative and positive for PCz and PEDOT, respectively. Initially, the maximum operating voltage was evaluated, that is, with a method similar to that proposed for double layer capacitors, we evaluated to what potential each polymers presents their reversible redox reactions. Figure 1a shows the determination for each of these polymers, and it is possible to observe that both have a good electrochemical stability. Two characteristics are noteworthy: first, PCz is stable up to 1.3 V, and this class of polymer usually presents low electrochemical stability in the presence of water; second, PEDOT presents high current when compared to PCz and also high electrochemical stability (-1.6 V). In turn, Figure 1b shows the determination for activated carbon using WiSE as electrolyte. The total window is 2.6 V, which is much larger than that observed in aqueous electrolytes. Using PEDOT and active carbon, it can reach 2.9 V, practically the voltage observed in capacitors with electrolytes containing organic solvents. The mass balance of the pairs, PEDOT / Carbon and Carbon / PCz still needs to be performed, so that the two electrode devices are tested and all the electrochemical behavior will be discussed.

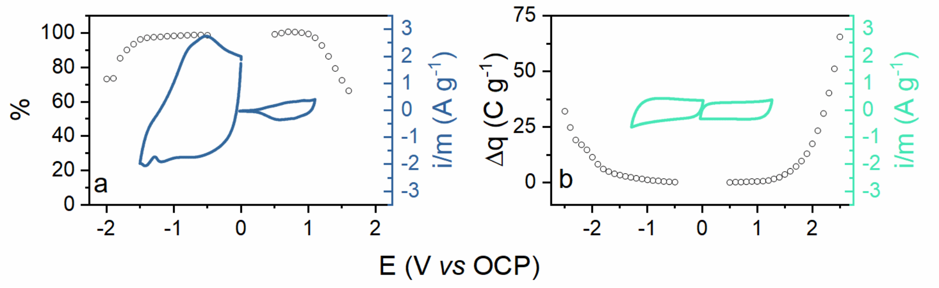

Figure 1. (a) determination of the maximum operating voltage of PEDOT (negative) and PCz (positive) and (b) active carbon (positive and negative) using 21 mol kg-1 of Li[Tf$_2$N] in water as electrolyte.

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Electrochemical Behavior of Superlattice films Based on DNA and Metal Nanoparticles

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The electrochemical systems involving self-assembled nanoparticle arrays are a subject of great interest. Most studies involving nanoparticles uses drop casting technique on an insulating barrier, although this method does not allow the control the deposition process. The strategy based on the self-assembly of programmable atom equivalents consisting of AuNps with complementary DNA strands is a novel and interesting way to assembly nanoparticles on electrode surface [1, 2]. The use of DNA to assembly metal nanoparticles into specific crystalline lattices is a topic of high interest in the moment. The possibility to build any kind of structure with DNA also mixing with metal nanoparticles opens novel procedures to synthesized different material with wide applications. Due to the DNA self-assembly it is possible not only to control the crystal symmetry, but also control distance between particles, rigidity, dynamics and actuation of these systems [3]. In this way those nanoparticles superlattices are interesting for a broad range of applications, including plasmonics, catalysis and electronics [4]. In the presentation some electrochemical behavior with the structures prepared on the electrode surfaces will be shown that the 3D structure as well as the nature of the DNA influence electrical conduction. Some results showing how the conduction is dependent on the organization and thickness of the superlattice film will be presented and discussed. The results demonstrating the formation of a hybrid electroactive device with a well-organized structure composed of different nanoscopic entities that function synergistically will be also discussed. The results showing that methylene blue intercalate into the DNA double helix, and that the obtained films are conductive, with k_{ET} values reaching ~230 s^{-1}, moreover it will be shown that the body centered cubic structure in (110) orientation have a higher k_{ET} compared to the (100), indicating that not only the DNA and the nanoparticle are important for the conduction but also how they are organized is also essential to understand the way that the charge is conducted.

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Active Modulators of Mg Surface Reactivity: from Corrosion Control to Primary Batteries

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Magnesium and its alloys are among the lightest structural metallic materials and also considered as promising materials for resorbable implants and energy storage. However, the high reactivity and the corrosion susceptibility of Mg in aqueous environments significantly limits the application range. However, the reactivity of the Mg surface can be controlled from both the metal and the electrolyte sides. In this paper, the chelating agents able to form complexes with Mg cations and the cations of impurity elements are discussed as potential modulators of Mg surface reactivity.

The compounds capable to form strong insoluble complexes with Mg^{2+} can confer an efficient inhibition of Mg dissolution blocking the surface by a dense layer of products [1]. In turn, the modulators forming highly soluble complex can strongly affect formation of the corrosion products on the metal surface shifting the process towards faster dissolution of Mg, which can be relevant for the optimization of discharge properties of metallic Mg-based anodes [2].

Recently, different authors have demonstrated that noble impurities present in the Mg-based materials can play a detrimental role for corrosion resistance making the degradation process hardly controllable. The shown enhanced cathodic activity at the corrosion front can be associated to an iron re-deposition mechanism [3]. In this work, it is demonstrated that adding strong Fe^{3+} complexing agents to the electrolyte is a way to prevent the Fe-redeposition process and in turn drastically suppress the corrosion of Mg-based materials or self-discharge of Mg anodes in batteries. A correlation between the complex stability and inhibition efficiency can be established [4]. Applicability of this concept to control the degradation of Mg-based implants and to boost performance of primary Mg-air batteries is demonstrated.

This paper will also discuss the possibility to use complexing modulators to stimulate the surface treatments processes on Mg. As a result, LDH (Layered Double Hydroxide) conversion layers, capable to function as smart nanocontainers, can be formed at mild conditions [5].

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Hydrophobic Species Activating the Oxygen Reduction Reaction on Single Crystal Electrodes of Pt

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The activity for the oxygen reduction reaction (ORR) strongly depends on the surface structure of Pt [1-4]: the existence of the (111) terrace edge activates the ORR activity of Pt [4]. Studies using vibrational spectroscopy show that Pt oxides (PtOH and PtO) are blocking species of the ORR on Pt electrodes [5-7]. Theoretical calculation predicts that structure of the adsorbed water changes at the (111) terrace edge of Pt [8]. The change of the water structure destabilizes the Pt oxides, giving the higher activity for the ORR on the surfaces with (111) terrace edge. Hydrophobic species can also affect the structure of adsorbed water and the stabilization energy of Pt oxides. In this Keynote Lecture, we summarize the effects of hydrophobic species on the ORR of single crystal electrodes of Pt.

Alkyl amines enhance the ORR activity and durability of Pt nanoparticles [9]. We extended the study to single crystal electrodes of Pt. The ORR activity on Pt(111) modified with alkyl amines is 2.5 times higher than that on bare Pt(111). However, the alkyl amines deactivates the ORR on Pt(100) and Pt(110) markedly [10]. IR spectra show that smaller cluster of ice-like water is formed on Pt(111) modified with alkyl amine, whereas larger cluster of ice-like water is found on Pt(100) and Pt(110). Cluster size of ice-like water can affect the ORR activity strongly.

The ORR on Pt(111) modified with tetraalkyl ammonium cation is activated with the increase of the alkyl chain length. The activity on Pt(111) with tetra-*n*-hexylammonium cation (THA^+) is 8 times higher than that without THA^+[11]. THA^+ is not adsorbed on Pt(111) and prevents the formation of PtOH according to IR spectra. Non-specifically adsorbed hydrophobic THA^+ provide active surface for the ORR on Pt(111).

Melamine activates the ORR on Pt and PtPdCo nanoparticles significantly [12]. We have studied the structural effects on the ORR using Pt single crystals modified with melamine. The ORR activity of melamine modified Pt(111) is 3 times higher than that of bare Pt(111). Melamine markedly activates the ORR on Pt(331) = 3(111)-(111), giving the highest activity among Pt single crystals examines.

We will discuss the mechanism of the ORR activation due to the adsorbed species.

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Continuum in Abiotic, Enzymatic and Microbial (Bio)-Electrocatalysis in Fuel Cells

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Redox reactions at electrodes may be catalyzed by the electrode material itself, synthetic molecules, biological macromolecules such as (inert) oxidoreductase proteins, or by living and self-replicating microorganisms like bacteria. In this communication the continuum between the inert (materials, molecules and enzymes) and living (microbes) biocatalyses at electrodes is delineated. The motivation for catalysis is first discussed with simple case-study redox reactions at electrodes. Then, enzymatic biocatalysis of these illustrative redox reactions is addressed. The need for redox mediation is explained together with the possibility of direct enzymatic bioelectrocatalysis. In this context, the effect and value of modifying the electrode surface is introduced. Cellular bioelectrocatalysis with living microorganisms is then considered and illustrated for electroactive bacteria or yeast at anodes and cathodes. The specificity of microbial bioelectrocatalysis is stressed. Similarly to the case of enzymes, several electron transfer mechanisms to/from the electrode are discussed and the possible effect of modified electrodes emphasized. Finally the pros and cons of the different types of catalysts are addressed with a discussion of possible specific applications.

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Photo-Induced Charge Carriers Dynamics in Solar Semiconducting Systems

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High-performance conversion of solar light to different types of energy which might be subsequently released in diverse ways remains an unsaturated need for interruptedly growing global demand for energy. However, currently the field of renewable energy suffers from lack of an ideal material able to drive conversion of the solar energy with high quality and quantity and being stable enough to provide a long-term productivity. Therefore, multi-directional efforts including a development of new materials and catalysts, incorporation of plasmonic nanostructures or creation of low-level sub-stoichiometry are continuously undertaken and devoted to minimisation of the required bias voltage, improvement of light capture or charge transport properties. Our recent achievements regrading employment of different in structure polyoxometalates as catalysts, sub-stochiometric semiconducting oxides, newly designed and engineered crystal structures in solar driven arrangements as well as their performance for photo induced processes such as oxidation or reduction will be presented and discussed in detail. Besides the extensive characterization of the above-mentioned systems, the kinetic assessment of the transient absorption phenomena will be approached. Use of transient absorption spectroscopy to study charge carrier behaviour in semiconductors-based systems allows to relate a photoelectrode architecture to the charge carrier origin, separation, collection, trapping, lifetime and therefore to the final efficiency. Presentation and comparison of the charge carrier dynamics occurring in semiconducting systems: bare, modified as well as mixed oxides, will be shown as particularly useful in clarifying the observed differences in in their photoelectrochemical performance.

Electrochemical Tip-enhanced Raman Spectroscopy & Microscopy

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The structure of the electrochemical interfaces determines the performance of electrochemical devices and systems, which requires a better understanding for the rational design of the electrochemical systems. Tip-enhanced Raman spectroscopy (TERS), which is an organic integration of scanning probe microscopy (for the nanoscale control and obtaining the morphology of sample), Raman spectroscopy (offering molecular fingerprint information), and localized surface plasmon resonance (LSPR, producing enhanced electromagnetic field to offer TERS with sensitivity down to single molecules), appears to be an ideal tool for studying the complex electrochemical interfaces.

We will first introduce the challenge in the field and the key development in TERS. We then focus on our recent efforts on electrochemical TERS (EC-TERS) instrumentation. With the uniquely designed spectroelectrochemical cell, we were able to synergistically control the reaction by both the electrode potential and laser power and characterize the reaction at the nanometer spatial resolution on STM–based EC-TERS. We found that the excited plasmon can lead to generation of reactive holes to a region of 30 nm in radius close to the mean free path of electron in Au. We further developed AFM-based EC-TERS to characterize the defects of MoS_2 with a spatial resolution better than 10 nm and identified very interesting spectral behavior of MoS_2 defects during electrocatalytic processes as a signature of electrochemcial active sites.

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Hard Carbons for Sodium-Ion Batteries: Structure, Analysis, Sustainability and Electrochemistry

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Hard carbons are extensively studied for application as anode materials in sodium-ion batteries, but only recently a great interest has been focused toward the understanding of the sodium storage mechanism and the comprehension of the structure-function correlation. Although several interesting mechanisms have been proposed, a general mechanism explaining the observed electrochemical processes is still missing, which is essentially originating from the remaining uncertainty on the complex hard carbons structure. The achievement of an in-depth understanding of the processes occurring upon sodiation, however, is of great importance for a rational design of optimized anode materials.

In a recent review, we provided a comprehensive overview of the up-to-date known structural models of hard carbons and their correlation with the proposed models for the sodium-ion storage mechanisms. Targeting the eventual commercialization of hard carbon anodes for sodium-ion batteries a careful evaluation of their sustainability needs to be performed, since this is undoubtedly a crucial parameter to take into account for the future large-scale production of hard carbons.

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Designing Lithium-sulfur Batteries with Practically Necessary Parameters

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Sulfur has become appealing as a cathode in recent years as sulfur is abundant, is environmentally benign, and exhibits an order of magnitude higher charge-storage capacity than the currently used lithium-ion battery oxide cathodes. However, lithium-sulfur cells suffer from a few formidable challenges: (i) poor electronic and ionic conductivity of sulfur and its discharge product Li_2S, (ii) dissolution in the liquid electrolyte of the polysulfide intermediates and their shuttling between the cathode and anode, (iii) large volume changes occurring during charge-discharge cycling, and (iv) lithium-metal degradation during cycling due to continuous solid-electrolyte interphase (SEI) formation and electrolyte consumption. Efforts to overcome these difficulties around the world have shown enormous improvements in cycle life, but a vast majority of the published work has been with low sulfur content, low sulfur loading, and a high amount of liquid electrolyte, which will drastically reduce the practical energy density and make the lithium-sulfur technology uncompetitive with the current lithium-ion technology.

This presentation will focus on designing lithium-sulfur cells with practically necessary parameters to be competitive with lithium-ion technology. Innovative sulfur cathode architectures and novel cell configurations will be presented to realize the practically necessary parameters. For instance, lithium-sulfur cells with a coaxial-graphene-coated cotton-carbon as a substrate for sulfur cathode that display high performance with simultaneously a high sulfur loading (~ 50 mg cm^{-2}), high sulfur content (75 wt. %), and a low electrolyte/sulfur ratio (4.2 μL mg^{-1}) will be presented. Such a cell exhibits remarkably a high areal capacity (31 mA h cm^{-2}) and areal energy density (66 mW h cm^{-2}) with a capacity-retention of 68% over 200 cycles, exceeding the areal capacity (4 mA h cm^{-2}) and areal energy density (10 mW h cm^{-2}) of commercial $LiCoO_2$ cathode. Besides the challenging cycle life, lithium-sulfur cells also suffer from rapid self-discharge. With novel cell configurations, self-discharge data collected over an extended period of one year will be presented. Moreover, the roles of the porosity, electrical conductivity, and chemical interaction with sulfur of various carbons used in lithium-sulfur cells will be presented, which will help to choose the appropriate carbons. Finally, the areas that need to be addressed in the future to make the lithium-ion technology practically viable will also be presented. In addition, a comparison of the lithium-sulfur technology with other metal-sulfur batteries will also be provided.

Electroanalysis and Electrocatalysis of Gold Based Nanomaterials and Nanocomposites

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Gold-based nanomaterials and nanocomposites have received increasing attention in a wide range of energy, environmental and medical applications due to their unique physicochemical properties, chemical robustness, and distinct catalytic activities. Recently, my research team has designed and synthesized a variety of gold-based nanostructured materials [1-5]. In this presentation, we mainly focus on the synthesis and modification of nanoporous Au electrodes as well as their promising environmental and biological applications.

Nitric oxide (NO) plays important roles in myriad biological processes and is considered as a biomarker of cardiovascular disease, hypertension, symptoms of vaginitis, and cancer. A nanoporous gold (NPG) microelectrode, fabricated via an electrochemical alloying/dealloying process, exhibits a high electrochemically active surface area and can effectively monitor NO with a high sensitivity and a very low detection limit (1.43 nM). Mercury poses serious risks for human health and the environment; thus, it is of critical importance to develop a facile approach for the sensitive detection of Hg(II). The NPG microelectrode was further modified with FeOOH nanoflakes; the resulting FeOOH/NPG microelectrode shows excellent electrochemical performance for the detection of Hg(II) with a high sensitivity of 123.5 $\mu A\ \mu M^{-1}\ cm^{-2}$ and a low detection limit of 7.81 nM. The critical roles of nanomaterials in electrochemical sensing are discussed.

There is a growing interest in developing high-performance catalysts for the electrochemical reduction of carbon dioxide (CO_2) to address the increasingly serious impacts of global climate change. Recently, we have demonstrated a facile electrochemical alloying/dealloying approach in conjunction with an acid treatment to fabricate a unique three-dimensional nanoporous Au network structure with a large electrochemically active surface area, which serves as a high-performance electrocatalyst for the efficient and selective conversion of CO_2 to CO. The formed NP Au showed a superb Faradaic efficiency (over 95%) and a high CO production rate at the applied potential of -0.6 V vs. RHE in a CO_2-saturated 0.1 M $NaHCO_3$ solution. The significant impact of surface structures on the electrochemical reduction of CO_2 is highlighted.

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Unifying ORR structure-activity-stability relationships of shape-controlled and highly defective PtNi/C electrocatalysts

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Due to strain and ligand effects, the simultaneous presence of concave and convex surfaces and their highly-defective nanostructure (atomic vacancies, grain boundaries), highly defective hollow PtNi/C electrocatalysts have proven to enhance remarkably the oxygen reduction reaction (ORR) kinetics [1,2]. Likewise, PtNi aerogel [3], jagged PtNi nanowires [4,5] feature both high concentration of structural defects and enhanced ORR activity. On the other hand, and inspired from single crystal approach, nanostructured octahedral-shaped PtNi/C electrocatalysts exhibiting only Pt(111) facets are among the most active ORR electrocatalysts [6,7]. This presentation will show how structure-activity-stability relationships of this two classes of materials can be unified *via* a unique descriptor, the Surface Distorsion, derived from a physical parameter, the microstrain obtained from X-ray diffraction patterns [8].

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Trial of realization of electrochemical nanotechnologies to advanced manufacturing

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The transfer of the new technologies from our university to industries will be introduced, in particular, sensing systems on biosensors and batteries. A biosensing system is commercialized based on a concept of physiological balance for healthcare. The addition of low-cost biochemical sensors to the sensing system would help with scientific prescriptions based on contemporary medicine. As a candidate for a low-cost and robust chemical sensor platform, the ion-sensitive field-effect transistor (ISFET) has long been examined. Besides, we introduced an approach related to battery evaluation by Electrochemical impedance spectroscopy (EIS). After reviewing past our research, our two approaches for new business trials are discussed. One approach is based on the progressiveness of technology that relies on public finance with existing big companies. Another approach is a lean startup based on a customer development model for entrepreneurs.

The first approach involved a public finance start-up with an existing large company. This approach is usually effective when a technological breakthrough is required. Universities were expected to play a key role in organizing a joint venture by combining several existing enterprises, and thus this was included in the objectives of the Radical Innovation and Entrepreneurship Program (COI STREAM) of the Center of Innovation Science and Technology that was launched by the Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT). A wireless multi-target ISFET system that detected, analyzed and provided feedback on physiological substances in biological barriers was developed. This program involved a collaboration between our university and two private enterprises (Riken Genesis Co., Ltd., and Toppan Printing Co. Ltd). Certain key molecules for monitoring the balance sensing such as cortisol do not possess electric polarization. Hence, the role of aptamers that deformed to change the charge distribution within a Debye length was investigated for the detection of these non-polarized molecules by ISFET. [1] In other cases, a technology transfer of battery evaluation by EIS is progressing. EIS has been utilized to characterize each elemental process of electrochemical devices because it enables us to analyze the dynamics of each elemental process sensitively and separately without destruction of the cell. A measuring device of EIS is used by employing a combination of a potentio/galvanostat and a frequency response analyzer with a sinusoidal waveform as the input signal for the measurement. However, these instruments are expensive, especially for EIS measurements that involve a large number of battery cells in an energy storage system. In our study, application of square wave potential for input signals of EIS was investigated in simple electrochemical reaction to verify a new technique called “Square-current electrochemical impedance spectroscopy (SC-EIS)” which is a method for EIS without using the frequency response analyzer systems. We applied SC-EIS to evaluate a state of a commercial stationary storage battery system with LIB. [2]

Another approach included a small startup from Waseda University in the Enhancing Development of Global Entrepreneur (EDGE) program of MEXT. The first trial of the startups was a pet business, which served a skin monitoring system by using an ISFET sensor for pets. A wireless ISFET system was developed for animal skin care and it included a simple and quick skin pH measurement method applicable to both humans and dogs. As part of the first stage in customer discovery, students interviewed several dog-owners and their pets who participated in a dog run at a big park by showing a prototype as the minimum viable product (MVP). None of the dog-owners were interested in the MVP, as all the pets were young and healthy. Since there were no true customers, alternative areas were explored. The next target entailed animal hospitals with unhealthy dogs. However, veterinary doctors did not want to purchase the products as they believed in the accuracies of their diagnoses. The next area explored was dog-grooming services. In these services, there were constant complaints that customers did not accept their suggestions despite being informed about symptoms of a cutaneous disease. Hence, the dog-grooming services could be the early adapters of the first product.

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Probing Surface Reactions and Intermediates using In Situ Raman Spectroscopy

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The rational design of highly efficient catalysts relies on the fundamental understanding of the structure-activity relationships and reaction mechanisms at a molecular level. Surface-enhanced Raman scattering (SERS) can provide rich structural information of molecules with "fingerprint" sensitivity at a single-molecular level thus is a promising tool for the in-situ study of surface catalysis. However, only few noble metals such as Ag, Au, or Cu with roughened surfaces can generate strong SERS enhancement, which had greatly limited the practical applications of SERS. To break the long-standing limitation of SERS, we developed a technique named shell-isolated nanoparticle-enhanced Raman spectroscopy or SHINERS. In SHINERS, the Au/Ag core as plasmonic antenna provides strong electromagnetic fields to enhance targets' Raman signals, while ultra-thin, uniform and pinhole-free silica shell separates the Au/Ag cores from the system under study and ensures no interference from processes involving the SERS-active cores. SHINERS can be used for the trace analysis over surfaces with diverse compositions and morphologies by simply spreading the shell-isolated nanoparticles (SHINs) on these surfaces.

Using SHINERS, we have achieved the in-situ monitoring of the dynamic reaction processes of surface catalysis occurring on model single crystal surfaces or practical nanocatalysts for the first time, which cannot be realized by traditional SERS. Combining with electrochemical methods and DFT simulations, we have in-situ studied the surface electro-oxidation, CO electro-oxidation, CO_2 reduction, and oxygen reduction reaction at Au(hkl) or Pt(hkl) surfaces. Hydroxyl, peroxide, and superoxide were directly observed as intermediates, which proved the long-standing speculation in electrochemistry. Furthermore, two structural transitions of interfacial water at different atomically flat single crystal Au and Pd electrodes surfaces were also comprehensively investigated. The observations indicate that the component of different structured interfacial water changes when sweeping the potential from the potential of zero charge to very negative, which may relate to the HER reactivity.

On the other side, a SHINERS-satellite strategy has also been developed to in-situ monitor the heterogeneous catalytic processes occurring on practical nanocatalysts, and the reaction mechanisms and structure-activity relationships for CO oxidation and selective hydrogenation are revealed at a molecular level. The concept of shell-isolated nanoparticle-enhancement is being applied to other spectroscopies such as fluorescence, IR, SFG, and tip-enhanced spectroscopies to improve the sensitivity or spatial resolution. Such advanced techniques also have great potentials for the in-situ study of reactions/catalysis, at single atoms or a single molecule.

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Electrocatalysis on gold

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Gold is a surprisingly good electrocatalyst for certain electrochemical reactions [1]. In this talk, I will summarize our older as well as more recent results on the electrochemical activity of gold single-crystal electrodes for the oxidation of CO and small organic molecules, as well as the electrochemical reduction of carbon dioxide. In most cases, the electrocatalytic activity is highly sensitive to pH and prefers alkaline media. I will explore the idea that gold is a good catalyst for certain reactions because it binds many intermediates weakly.

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Voltammetry Nanomembranes Coupled to Ferrocene Monolayers for Creatinine Detection

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The importance of knowing creatinine (CRE) levels in the human body is related to its possible association with renal, muscular and thyroid dysfunction, among others. Thus, the accurate detection of CRE indirectly provides information surrounding those functional processes, therefore contributing to the management of the health status of the individual and early diagnosis of acute diseases. This analysis is currently accomplished in hospitals by means of spectrophotometry in centralized clinical laboratories after serum extraction from the patient's blood (i.e. the Jaffe's method). Nonetheless, this strategy possesses a number of drawbacks that are trying to be overcame by the so-called modern CRE (bio)sensing.**[1]** In this context, it seems that the interaction between CRE and certain metals, such as iron, platinum, manganese and nickel, provides a reliable manner for quantitative CRE sensing.

CRE interaction with Fe(II) centres immobilized in a self-assembled monolayer comprising well-defined ferrocene moieties (Fc-SAM) on glassy carbon electrode is here explored for the first time. These moieties display a reversible and gaussian-shaped voltammetric peak in organic solution containing hexafluorophosphate anion (PF_6^-): an anodic potential scan oxidizes Fe(II) to Fe(III) centres that are energetically stable owing to iron pairing with PF_6^- at the Fc-SAM|sample interface.**[2]** In the presence of CRE, this interacts with the Fe(II) in the monolayer and the voltametric peak decreases as the available Fe(II) to be oxidized decreases. This Fe(II) blocking caused by the CRE is manifested in a linear decrease of the peak current and the integrated charge with the CRE concentration in the solution. While this concept may be used for CRE detection in any biological fluid, analogous Fe(II) blocking is also showed by chloride ion (Cl^-), constituting hence a strong interference towards the real application of the sensor.

In order to supress this Cl^- interference in CRE detection using Fc-SAM electrodes, a nanometre-sized ion-selective membrane (n-ISM) is incorporated on top of the monolayer. The n-ISM contains the cation exchanger sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (Na^+ $TFPB^-$), which allows for controlled cation-exchange processes across the membrane|solution interface.**[3]** Thus, an anodic potential scan oxidizes Fe(II) moieties to Fe(III) that are stabilized by the $TFPB^-$ in the membrane with the concomitant expulsion of Na^+ to the solution to keep the electroneutrality of the system. This cation transfer is manifested in a reversible gaussian-shaped peak that is totally independent of the Cl^- amount in the sample solution.[2] Whether CRE is added to the solution, this is partially solved into the membrane according to its partition coefficient (membrane/water) and reaches the Fc-SAM therefore interacting with Fe(II) centres, and blocking them for a further oxidation. As the area of the voltammetric peak depends on the number of Fe(II) centres that are oxidized, both the peak current and charge linearly decreases with the CRE concentration in the solution. This strategy is now being explored for CRE detection in real samples, such as urine and blood. Furthermore, as far as the preparation of the Fc-SAM is reproducible, the developed electrode will be of calibration-free type.

After the exhaustive laboratory and clinical validation of the CRE sensing concept, the fabrication of a point-of-care device is foreseen. Further fundamental studies are necessary to optimize the working range displayed by the Fc-SAM sensor as well as technical development to translate the sensor into an appropriate clinical platform.

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Towards Green Solar Batteries

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The integration of solar energy conversion and energy storage functions is critical to prevent possible energy shortages related, among others, to the increase of the world population. In our group, we actively study the possibility to integrate the solar energy conversion and electrochemical energy storage functions using multi-functional, organic, bio-sourced materials featuring suitable optical absorption properties and redox activity.

The cases of study we will discuss include quinone-based biopigments from the melanin family (responsible for skin photoprotection) as well tannin and lignin derivatives.

Modified Oxide Catalyst Structures and Active Species for the Oxygen Evolution Reaction (OER)

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The oxygen evolution reaction (OER) is a major cause of energy losses in photocatalytic systems for solar fuels, but also in a number of other emergent technologies such as rechargeable metal-air batteries, water splitting devices, and unitized regenerative fuel cells. The low energy efficiencies of OER are the result of its sluggish reaction kinetics and large overpotentials. Significant improvements to the OER activity of transition metal oxides (TMOs) have been made by tailoring the morphology and crystal structure of the catalysts, incorporating dopants, as well as using conductive supports. However, clear structure-activity correlations remain elusive because of the complex composition and structure of TMO catalysts. Further understanding of these relationships for these promising catalysts for oxygen evolution may lead to additional developments that will enable TMOs to replace precious metal-based OER catalysts (e.g. IrO_x and RuO_x). Insights from two recent examples of our studies will be discussed. We have utilized a range of spectroscopic techniques for characterization of Ce-modified copper oxide (CuO_x) and Ni-modified cobalt (oxy)hydroxides to reveal the OER active species and structures of these catalysts. In the case of Ce-modified CuO_x, Ce incorporation (6.9 at%) into CuO_x led to 3.3 times greater OER activity compared to pure CuO_x and this was coincident with significant structural changes due to an increasing amount of disorder. By combining X-ray photoelectron and Raman spectroscopy techniques, a strong correlation between OER performance with tetravalent Ce (Ce^{4+}) ions was observed up to a concentration corresponding to CeO_2 phase segregation. We propose a strong promoting effect of Ce^{4+} for OER in this system. [1] In the case of Ni-modified CoO_xH_y, operando Raman spectroscopy and electrochemical techniques were used during the oxygen evolution reaction to identify the composition and local structure of electrodeposited CoO_xH_y and $NiCoO_xH_y$ catalyst films. In these studies, several unique initial catalyst structures and crystallinities were prepared by subjecting the samples to a variety of thermal and electrochemical conditioning procedures before evaluation. During oxygen evolution, Ni-modified CoO_xH_y films with lower initial crystallinity underwent substantial structural evolution that began with an irreversible transformation of a spinel local structure to an amorphous CoO structure at low anodic potentials. Increasing anodic polarization with elevated oxygen evolution rates caused additional structural conversion of the amorphous CoO structure to a complex phase that can be described as an amalgamation of NiOOH and layered CoO_2 motifs (NiOOH-h-CoO_2). The formation of this active structure was correlated with improved OER activity. Formation during oxygen evolution of the same NiOOH-h-CoO_2 structure independent of the initial cobalt oxide structure suggests that this active phase identified in these studies could be the universally active structure for $NiCoO_xH_y$ catalysts. [2-4] These two examples, i.e. the promoting effect of Ce^{4+} and the formation of active OER structures in Ni-modified CoO_xH_y, reveal the importance of chemical state and local structure considerations for the rational design of improved oxide-based OER catalysts.

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Visible Light Driven Photoelectrocatalytic Semiconductor Heterojunction Anodes for Water Treatment Applications

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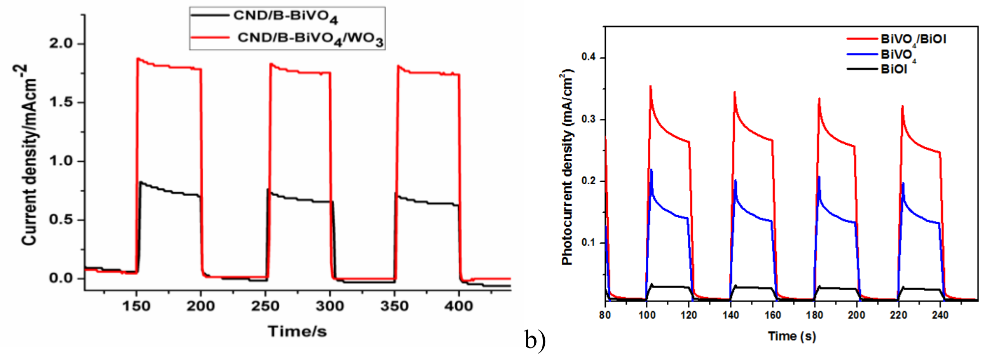
Contamination of water bodies by harmful and recalcitrant organic substances is a global challenge. A promising technique for removing these organics from water/wastewater is photoelectrocatalytic oxidation which combines electrolytic and photocatalytic processes. In the quest for sustainability and green technologies, it is important to fabricate photoanodes that can respond to solar light. One of the various ways of preparing such visible light driven photoanodes is through semiconductor heterojunction alignment. This paper presents an overview of our research in this domain. We have prepared different visible light driven photoanodes such as carbon nanoparticle/boron doped $BiVO_4/WO_3$, ZnO, Cu_2O/TiO_2, WO_3, $BiVO_4$/BiOI etc. A typical study involves the degradation of emerging pharmaceutical pollutants – acetaminophen and ciprofloxacin – at a $BiVO_4$/BiOI photoanode under visible irradiation via photoelectrocatalytic process (PEC). The $BiVO_4$/BiOI was electrodeposited on a FTO glass and characterised with XRD, SEM, EDS and diffusive reflectance UV-Vis. The results confirmed the successful electrodeposition of $BiVO_4$/BiOI on the glass substrate. Mott-Schotty plots confirmed the formation of p-n heterojunction between the two electrodeposited semiconductors. The calculated charge carrier density of $BiVO_4$/BiOI was higher than those of pristine $BiVO_4$ and BiOI. The binary electrode also gave improved photocurrent response compared with unitary electrodes. Degradation efficiencies of 68% and 62% were achieved upon the application of the prepared photoanode (FTO/$BiVO_4$/BiOI) in PEC degradation of acetaminophen and ciprofloxacin respectively using a bias potential of 1.5 V within 2 h. A synthetic pharmaceutical wastewater containing a mixture acetaminophen and ciprofloxacin was also treated with the photoanode. The photoanode was also effective in the degradation of dye. The findings of this study suggest the suitability of the prepared photoanode for the photoelectrocatalytic degradation of organic pharmaceutical pollutants in wastewater.



a) b)

Photocurrent response in the presence of visible light for a) carbon nanodot (CND)/B-$BiVO_4$ and CND/B-$BiVO_4/WO_3$; b) BiOI, $BiVO_4$ and $BiVO_4$/BiOI photoanodes

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The Electrocatalytic Properties of Underpotential Deposited Metals for the Reduction of Selenate in Aqueous Electrolytes.

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Selenate, SeO_4^{2-}, ranks among the most difficult oxyanions to reduce in aqueous environments making their detection particularly challenging. As was reported recently, underpotential deposited Cu, Cu(UPD), on polycrystalline gold, Au(poly) can promote reduction of SeO_4^{2-}(aq), in aqueous acidic electrolytes to yield, following Cu stripping, a layer of elemental Se, which can then be oxidized at more positive potentials.[1] This contribution will present an extension of such studies to include the low index faces of single crystal Au electrodes and, in addition, describe the ability of Cd(UPD) to carry out the same reaction on Au(poly). Evidence for the role of the surface microstructure was obtained by comparing linear potential scans (LPS) recorded for Au(111), Au(100) and Au(110) in a solution of 0.1 M $HClO_4$ + 1.2 mM $Cu(ClO_4)_2$ + 1 mM purified Na_2SeO_4, upon holding the potential E at 0.325 V vs RHE for a time τ_{hold} = 100 s (see Panel A, Fig. 1), which yielded features associated with Cu stripping in the range $0.35 < E < 0.7$ V and with Se oxidation for $1.0 < E < 1.25$ V. Also shown in this figure in the dashed black line are corresponding data collected with a Au(111) electrode in a 1 mM Na_2SeO_4 solution devoid of $Cu(ClO_4)_2$, for τ_{hold} =1000 s, for which no activity for SeO_4^{2-}(aq) reduction was discerned. Similar results were found in experiments performed with Au(poly) in 0.1 M $HClO_4$ containing 1 mM purified SeO_4^{2-}(aq) (black), 1.2 mM $Cd(ClO_4)_2$ (blue) (see Panel **B**, Fig. 1), for which the amount of Se produced, as determined from the integration of the Se oxidation peak, Q_{Se} (black solid symbols, left ordinate) was found to be proportional to the time at which the electrode was held τ_{hold} for E_{hold} = -0.25 V vs Ag/AgCl. Various aspects of this interesting electrocatalytic process, including in situ spectroscopic and microgravimetric data aimed at identifying the factors that control the mechanism will be discussed.

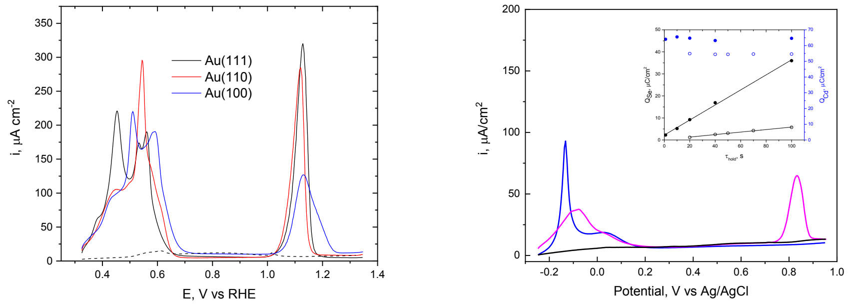

Fig. 1. **Panel A**. Linear potential scans (LPS) conducted at 0.1 V/s on the indicated single crystal faces of Au after holding the potential at 0.325 V vs RHE for 100 s in deareated 0.1 M $HClO_4$ containing 1.2 mM $Cu(ClO_4)_2$ + 1 mM Na_2SeO_4. The dashed black line represents the equivalent data collected after holding for 1000 s with a Au(111) electrode in a 1 mM Na_2SeO_4 solution devoid of $Cu(ClO_4)_2$. **Panel B.** LPS (ν =0.1 V/s) with a Au(poly) disk electrode in deareated 0.1 M $HClO_4$ containing 1 mM purified SeO_4^{2-}(aq) (black), 1.2 mM $Cd(ClO_4)_2$ (blue), and a mixture of 1 mM purified SeO_4^{2-} (aq) and 1.2 mM $Cd(ClO_4)_2$ (magenta) for E_{hold} = -0.25 V for τ_{hold} =100 s. **Insert:** Plot of the charge associated with Se oxidation, Q_{Se} (black solid symbols, left ordinate), and Q_{Cd} (blue solid symbols, right ordinate) vs. τ_{hold}.

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Singlet Fission and Electrochemistry

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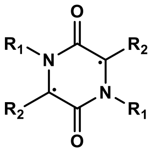
Singlet fission (SF) is a photophysical process in which an organic chromophore in excited singlet state shares its excitation energy with a neighbouring ground-state chromophore and both are converted into two triplet states.[1,2] Singlet fission has attracted attention because it promises to increase the maximum theoretical efficiency of inexpensive single-junction solar cells. Although up to now, it has not found its way into practice, the synthetic, photophysical, electrochemical and computational research is running.

Singlet fission is possible to describe as an exchange of electrons between two molecules which does not require change of spin of any from the molecules. The most important criterion in the selection of chromophores, assures that the SF process is isoergic or even better, somewhat exoergic, by demanding that the first singlet excitation energy be at least the double of the first triplet excitation energy. This criterion is quite unusual. A class of compounds that are likely to meet the requirement are biradicaloids, species formally derived from perfect biradicals by sufficient but not excessive covalent perturbation [3].

Besides their crystalline form and molecular packing, two of the molecular properties are especially important when looking for new candidates for efficient SF: (i) the relative energies of the S_0 (lowest singlet), T_1 (lowest triplet), and S_1 (first excited singlet) states, and (ii) the potentials of one-electron reduction and one-electron oxidation. Redox properties of molecules for SF are thus critical for their use, therefore electrochemistry is important approach to the investigation of promising compounds.

These considerations that led to the choice of 2,5- and 2,6-diketopiperazines (**1,2**) [4] and 1,3-diphenyl-isobenzofuran derivatives (DPIBF, **3**) as molecules suitable for SF. In the present contribution the first electrochemical studies of diketopiperazines (**1,2**) will be presented. Besides that various DPIBF derivatives (**3**) will be discussed[5], where covalent dimers are formed either directly through various positions or are linked via various alkyl chains. The other study is focused on a series of fluorinated derivatives of DPIBF where the influence of number and position of fluorine atoms in the molecule on the redox potentials and mechanism is followed. For electrochemical characterization of all these molecules classical electrochemical techniques (polarography, CV and RDE) were used and combined with *in situ* UV-vis and EPR spectroscopy[6].



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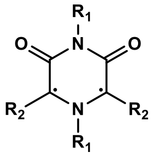

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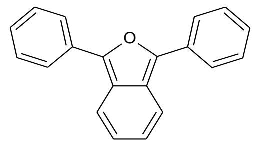

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Impact of Nanobioelectrochemical Sensing and Signalling of Disease Biomarkers on UN's Sustainable Development Goal

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Goal 3 of the 17 United Nation's Sustainable Development Goals (SDGs) for 2015-2030 proposes to ensure healthy lives and promote well-being for all at all ages by the year 2030. According to WHO, the prevailing circumstances are that: 1 billion people worldwide do not have access to health care systems; 36 million deaths each year are caused by noncommunicable diseases, such as cardiovascular disease, cancer, diabetes and chronic lung diseases; and tuberculosis (TB) kills 1.7 million people, and there are 9.4 million new cases, yearly. This grim health reality calls for intensive research on the development of very creative ways to provide affordable modern healthcare services for all, in order to attain the SDG for health as envisaged by the UN. In this contribution, we explore how SensorLab researchers are harnessing the unique properties of smart electroanalytical materials to develop affordable clinical diagnostic technologies and devices. Biocompatible quantum dot materials that have shown promise in novel nanobioelectrochemical sensing and signalling of breast cancer, HIV and tuberculosis, will be discussed. Accordingly, the presentation will include discussions on the development and signalling mechanisms of (i) genosensors for human epidermal growth receptor-2 (Her2) and telomerase breast cancer biomarkers; and (ii) TB biomarker-based impedimetric phase angle-transduced interferon-gamma (IFN-λ) aptasens and electro-LAM (lipoarabinomannan) immunosens. Also, to be presented are b-cancerphenosens protocol for phenotyping breast cancer drug metabolism.

Nanoscale Visualization of Structure-Activity at Complex Electrodes

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Electrode surface structure-activity relationships have never been more important, with electrochemistry at the heart of energy storage and conversion technologies, and gaining renewed interest in areas from organic synthesis to sensor systems.[1] Yet, the intrinsic activity of electrodes of practical importance is usually characterized by classical macroscopic electrochemical techniques, which are unable to detect and analyze the spatially heterogeneous fluxes that govern the electrochemical response of complex interfaces. At Warwick, we advocate new approaches to the study of electrochemical and electrocatalytic phenomena, whereby nanoscale information on activity is obtained by electrochemical microscopy in the form of **"activity maps"** and **"activity movies"**.[2] These high resolution data are then related to **co-located** electrode structure and properties obtained from complementary high-resolution microscopy and spectroscopy techniques applied in the same area as the electrochemical imaging. This new age of ***correlative electrochemical multi-microscopy*** seeks to resolve electrode structure and activity unambiguously by identifying and characterizing the structural features that constitute an active surface. This contribution will highlight the use of nanoscale scanning electrochemical cell microscopy (SECCM), scanning ion conductance microscopy (SICM) and combined scanning electrochemical microscopy (SECM)-SICM as key techniques for the synchronous acquisition of electrochemical activity-electrode topography,[3,4] coupled with a wide range of microscopy techniques, spanning electron microscopy and electron backscatter diffraction, micro-Raman spectroscopy and atomic force microscopy to pinpoint the nature of particular active sites. Illustrative examples of this general approach will include investigations of layered materials (2D and 3D), structurally and/or compositionally heterogeneous surfaces such as polycrystalline metals, and ensemble electrodes comprising of nanoparticles on an electrode support surface. We will demonstrate that, in essence, complex electrode surfaces can be broken down and studied as set of "single entities" (*e.g.*, individual steps, terraces, defects, crystal facets, grain boundaries, single particles),[1,5] and that the resulting nanoscale understanding of reactivity can be used to create rational models for electrochemical interfaces that are self-consistent across broader lengthscales and timescales. This roadmap for future electrochemical investigations will ultimately facilitate the rational design of functional (electro)materials.

Dozens of talented PhD students, postdocs and colleagues at Warwick and elsewhere have made outstanding contributions to our work on nanoscale electrochemical imaging over the past decade and their work will be referenced throughout this contribution.

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The Challenge of Large Energy Storage

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The general field of electrochemical power sources faces today 4 main challenges, related to major applications: powering mobile electronics, electro-mobility, very high energy density for robotics, drones, unmanned vehicles/airplanes and large energy storage. The commercial and practical success of Li ion batteries as the major power sources for mobile electronic devices, promotes this technology to its next challenge – electrochemical propulsion of ground transportation. For this application, high energy and power densities, together with prolonged durability, appropriate safety and long cycle life are mandatory. Aside this important application, there are needs for propelling unmanned vehicles and drones, where very high energy density is a major demand, compromising on durability and cycle life. In parallel to electro-mobility, large energy storage (LES) is becoming a major challenge of modern electrochemistry and the world of rechargeable batteries. LES is important for promoting the extensive use of sustainable energy – solar and wind. It is important also for load leveling in electricity production. It should be noted that there are hundreds of millions of people living in remoted places in the world, having no chance to be connected to a continuous electricity supply during the next decade. For this large population, living in very hard conditions, the availability of modular energy supply packages that include solar panels, effective batteries for energy storage and appropriate electronic control units, will be a great help and a great improvement of daily life. We see in recent years a great progress in the development of energy harvesting technologies – wind turbines, effective and relatively cheap solar panels, while the lack of effective electrochemical storage technologies seems to be the "Achilles heel" for the intensive use of them as major sources of electrical power supply. Here, energy density is much less important compared to the other above mentioned major applications of rechargeable batteries. In turn, durability for decades of continuous use, low cost, the use of most abundant elements (in order to meet the large scale of devices required) and effective energy turnover per cycle (i.e. very low hysteresis in the electrochemical charge-discharge processes) are the most important properties. The aim of this presentation is to review relevant electrochemical energy storage devices that can be applied for large energy storage.

There are 4 major relevant electrochemical technologies for such purposes: Hydrogen based systems in which sustainable energy can be stored and converted via water electrolysis that forms hydrogen which in turn is used in fuel cells for electricity production;Flow batteries;Stationary batteries and Supercapacitors. This presentation concentrates in stationary batteries and supercapacitors. We provide herein a few examples.

Li ion battery technology can offer excellent systems for load leveling and LES applications. For instance, combining $Li_4Ti_5O_{12}$ (LTO) anodes and $LiFePO_4$ (LFP) cathodes with simple organic electrolyte solutions forms very stable and fast 2 V batteries with very prolonged (nearly unlimited) cycling, excellent safety features and excellent energy turnover per-cycle. The latter advantage results from the fact that both LTO and LFP undergo lithiation / delithiation processes via first order phase transition reactions, which hysteresis is very low. However, Li batteries cannot be considered as main technology for LES because if the electro-mobility revolution will succeed, lithium will be needed for EV batteries. We may not have enough lithium for both large scale applications. A follow-up to the success of Li-ion battery technology is the development of Na ion batteries. These batteries cannot rival Li ion batteries in terms of energy density. In light of the unlimited abundance of sodium in earth crust, they can be relevant for LES, provided that it will be possible to develop very stable Na ion batteries.

Another important battery technology for LES may be lead-acid batteries. For this application, their durability and cycle life at high DOD operation must be improved. This goal can be achieved. We will outline ways to reach it.

The presentation will include also description of hybrid supercapacitors which combine pseudo-capacitive negative electrodes which charge storage capability is amplified by surface treatments, and intercalation positive electrodes. They are based on aqueous electrolyte solutions, what ensures excellent safety features and relatively low cost. Such systems can also be very suitable for load leveling and LES applications.

Modified conductive colloidal AFM probes towards sensing at the single entity level

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Atomic force – scanning electrochemical microscopy (AFM-SECM) is a highly attractive hybrid technique for studying biomedically relevant samples at the single entity level. Within recent years, research was targeted towards innovative approaches enabling high resolution topographical and electrochemical imaging, but also toward expanding AFM functionality beyond mere imaging[1]. Our group recently introduced a new type of AFM-SECM probe having a conductive colloid instead of a sharp AFM tip. As this spherical probe, which is located at the end of an electrically insulated AFM cantilever, is conductive, it can be easily modified with e.g., conductive polymer, which allows single cell force spectroscopy studying adhesion properties at an electrified interface[2]. Cell adhesion is a crucial parameter not only for developing new materials serving as substrates for neural scaffolds, electrodes, and biomedical devices. In addition, due to the fairly low spring constant ($k \approx 1$ N/m), such probes offer high force control and are suitable e.g. for mechanical stimulation of cells with defined force or pressure.

Within this contribution, we present various modification strategies of these conductive colloidal AFM-SECM probes with functional polymers such as polydopamine (PDA) using pulse deposition[3] or electrocatalytic layers such as platinum black or Prussian blue or with boron-doped diamond as interesting electrode material providing an extended potential window and high physical and chemical inertness[4]. We can tune the properties of such probes e.g., for single cell adhesion studies, by applying potential to e.g., the PDA modified probes. In dependence of the potential, the redox properties of PDA can be altered (e.g., quinone/phenolic moieties), which will influence the adhesion properties. Platinum black or Prussian blue modified probes are highly attractive for the localized detection of hydrogen peroxide (H_2O_2), which is an endogenous reactive oxygen species (ROS) leading to protein oxidation, lipid peroxidation, and DNA damage at higher concentration levels, but also function at lower physiological levels as an intracellular signaling molecule regulating kinase-driven pathways[5]. Given the high surface area, these colloidal probes are also interesting as transducer for enzymatic biosensors providing highly spatially resolved information on signaling molecules e.g., at the single cell level. An overview on modification schemes along with the characterization and applications in biomedically relevant research will be presented.

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Concepts for Electrifying Organic Synthesis

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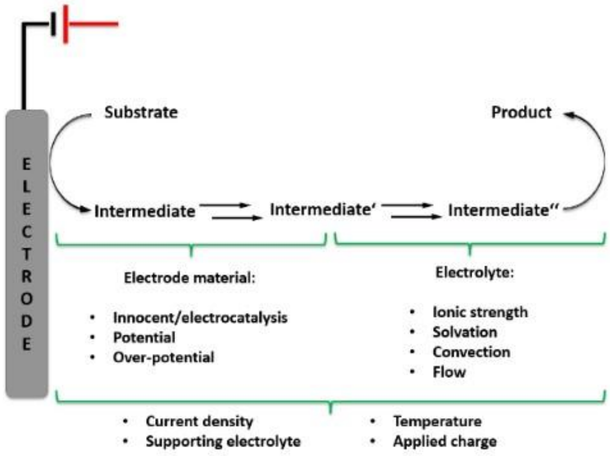
The use of electrochemistry for the generation of reactive intermediates can have major advantages towards conventional synthetic strategies.[1] Less or no reagent waste is generated and new reaction pathways are accessible.[2] In order to exploit the electricity driven conversions for synthetic purposes and to install unique selectivity two modern approaches will be outlined:

1) Solvent-controlled selective dehydrogenative cross-coupling reactions: A key for this is the use of boron-doped diamond anodes and fluorinated alcohols within the electrolyte.[3] This methodology opened new pathways for innovative and scalable arylation reactions.[4]
2) New electrode systems for the anodic and cathodic conversion to value-added organic compounds. These systems are capable to go beyond common limits in electro-organic synthesis.

The working horse to identify suitable electrolytic conditions is the electrosynthetic screening approach. This strategy gives also rise to fast optimization and subsequent scale-up.[5]



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Degradation mechanisms in Li_2VO_2F Li-rich disordered rock-salt cathodes

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A new class of materials, Li-rich disordered rock-salts, are promising candidates for next-generation cathodes due to their ability to reversibly cycle more than one Li-ion per transition metal. Recently, several new variations of these Li-rich cathode materials have been developed with promising initial capacities. Challenges, however, include capacity fade and voltage decay during cycling. These are detrimental process that need yet to be overcome. The mechanisms behind the significant capacity fade must be understood to allow for the design of new materials where the detrimental reactions are mitigated. In this study the origin of the capacity fade in the Li-rich material Li_2VO_2F is investigated.

The Li-rich disordered rock-salt Li_2VO_2F, consists of the multivalent V^{3+}/V^{5+} redox couple with the incorporation of ideally two Li^+ per TM. This gives a theoretical capacity of 462 mA h g^{-1}. Not all of the lithium can be extracted from the structure due to stability constraints, but previous studies have shown experimental capacities as high as 420 mA h g^{-1} (i.e. 1.8 Li^+ per TM). Li_2VO_2F exhibits small volume expansion and no crystalline phase transitions during charge/discharge, resulting in little stress within the material lattice.

Based on careful photoelectron spectroscopy studies using the advantage of tuning the photonenergy of the bombarding beam depth profiles of the surface of the particles can be obtained. The experiments were performed at I09 beamline at Diamond light source, UK. The samples were cycled vs. lithium as the counter electrode and with an electrolyte of 1M $LiPF_6$ in EC/DMC 1:1. Electrodes cycled one, five and fifty times were investigated.

The results show the degradation to begin at the particle surface and then spreading inwards with continued cycling. A schematic figure of the result for each electrode is shown in Fig.1. There is both a redox reaction of the vanadium taking place at the surface as well as the build up of a surface layer resembling the Solid Electrolyte Interphase on a typical anode. The presentation will compare these results with those from other lithium rich cathode materials.

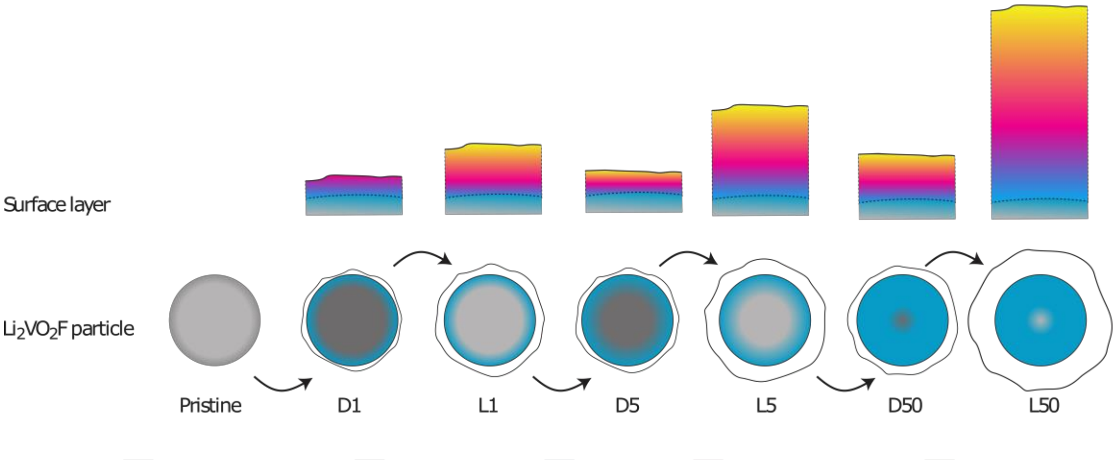

Fig. 1. A schematic drawing depicting the results of the photoelectron spectroscopy measurements.

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Electrochemically-Controlled Hydrogen Bonding: Complications and Opportunities Resulting from Proton Transfer

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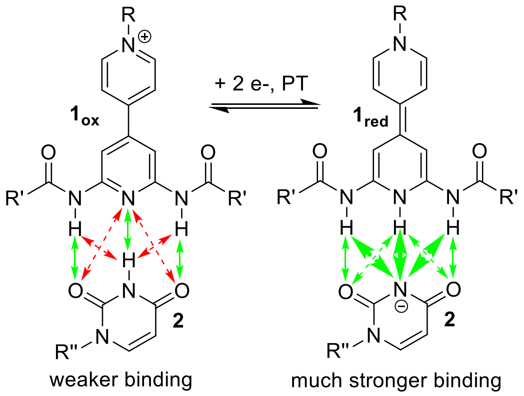
An important goal in supramolecular chemistry is the development of stimuli-responsive systems in which the strength of the intermolecular interactions can be altered by external signals such as changes in light, temperature, pH or voltage of an electrode. Our group is exploring the latter possibility, primarily by developing systems in which electron transfer perturbs the strength of H-bonding interactions between molecules. The underlying principle is straightforward: an oxidation that decreases the negative charge on a H-acceptor (A) or a reduction that decreases the positive charge on a H-donor (D) will weaken a H-bond. Alternatively, reduction that increases the negative charge on a H-acceptor or oxidation that increases the positive charge on a H-donor will increase the strength of a H-bond. However, in the latter case, it is possible that oxidation or reduction could also lead to full proton transfer. If this occurs across the H-bond, the primary H-bonds will remain, but the secondary H-bonds will change. This can lead to an increase in unfavorable secondary interactions, which counteracts the effect of the initial proton transfer. However, with proper design, proton transfer can lead to an increase in favorable secondary interactions, which enhances the effect of the initial electron transfer.

In this presentation, several examples will be presented illustrating complications arising from proton transfer. One example involves a ferrocene urea, which forms a DD type H-bond array that is complementary to AA type guests. Oxidation of the ferrocene increases the H-donor ability (acidity) of one of the urea NH's. This would be expected to increase H-bonding strength, which is indeed observed with a cyclic diamide AA guest in CH_2Cl_2 (K_{red} = 39 M^{-1}; K_{ox} = 680 M^{-1}). However, with the more basic AA guest naphthyridine, the increase in binding strength is far smaller (K_{red} = 18 M^{-1}; K_{ox} = 58 M^{-1}). This can be attributed to proton transfer resulting in an AD-DA type interaction. The strength of one of the primary H-bonds has increased, but the secondary interactions are now all unfavorable, counteracting the effect of the initial oxidation.



While in the above case proton transfer works against electron transfer, it is also possible to flip things around and make proton transfer work with electron transfer. This can be done by starting out with a H-bond dimer that has unfavorable secondary interactions and utilizing the proton transfer to convert them to favorable secondary interactions. The principle is illustrated by the monoquat-based host **1** which presents a DAD array of H-bond sites complementary to the ADA guest **2**. The primary H-bonds are all favorable (green) but the secondary interactions are all unfavorable (red). This results in a modest K_b of 650 M^{-1} under electrochemical conditions (0.1 M NBu_4PF_6/CD_2Cl_2). In the absence of **2**, initial cyclic voltammetry studies of **1** display the expected two, sequential, 1 e^- reduction waves of the monoquat redox couple in CH_2Cl_2, corresponding to reduction of **1** to the radical and then the quinoidal anion. Addition of **2** results in no change in the $E_{1/2}$ of the first reduction, but the second reduction shifts 0.30 V positive. Further addition of **2** causes only small change in the $E_{1/2}$, consistent with a 1:1 complex. The 0.30 V positive shift indicates an ~10^5 increase in binding strength upon overall 2 e^- reduction of **1**. Combined with the initial association constant of 650 M^{-1}, this indicates an association constant of ~10^8 M^{-1} in the fully reduced state. The most likely explanation of such strong H-bonding in a 3 H-bond array is that the second reduction induces proton transfer across the central H-bond in the complex, thus converting the DAD-ADA array to a DDD-AAA array. The latter is expected to have significantly stronger H-bonding because all of the secondary interactions, in addition to the primary interactions, are favorable

Electrochemical Advanced Oxidation as Wastewater Treatment Technology – From Kinetics to Modeling and Engineering Aspects

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Electrochemical advanced oxidation processes (EAOPs) have emerged in middle of the nineties as alternative to the chemical advanced oxidation processes (AOPs) by *in situ* generating strong oxidants such as hydroxyl radicals ($^{\bullet}OH$) ($E°(^{\bullet}OH/H_2O) = 2.8$ V / standard hydrogen electrode (SHE)), limiting the addition of chemicals [1,2]. These oxidizing species are responsible for the degradation and mineralization of various organic compounds present in wastewater. This is attributed to high reactivity of $^{\bullet}OH$ and its different mode of actions. Until recently, three mechanisms of $^{\bullet}OH$ action were considered [3]: (i) hydrogen atom abstraction, (ii) electrophilic addition to unsaturated bond, and (iii) electron transfer. In 2018, a fourth mechanism of action has been highlighted, which consists of the ipso-substitution on perhalogenocarbon compounds [4]. The problematic of water is a major of concern for stakeholders and decision-makers to face the increasing water demand in contrast to the water stress, while the water resource quality is degrading. One of the proposed solution is to favor non-potable and potable water reuse in the different sectors (agricultural, industrial and domestic). The water quality is generally not suitable for non-potable purpose because of the release of micropollutants in natural water at the outlet of wastewater treatment plants (WWTP), being not designed for the removal of such complex and lowly concentrated matrices. The addition of a complementary treatment in WWTP is therefore more and more considered.

EAOPs-based technologies are one of them. Numerous efforts have been devoted for kinetic studies at laboratory scale. Still, EAOPs need further studies to be developed at industrial scale. Modeling studies are required for reactor design optimization. The competition between mass transfer and charge transfer has been assessed recently in a paired electrocatalysis process by considering three reaction rates, i.e. anodic oxidation at anode surface, Fenton oxidation (through electro-Fenton process) in bulk solution and mediated oxidation in the bulk and anode surface [5]. This brings new scientific insight compared to the Comninellis' team model developed in the early 2000s [6], since two more reaction rates are considered (Fenton and mediated). Also, the mass transfer constants were depending on the electrolysis time, since the viscosity of solution was increasing with the surfactant degradation. This non-stationary condition makes the reaction orders more complex than the one developed previously [6,7]. In addition, a new global current efficiency has been proposed which permit to fit the experimental data in electro-Fenton combined to anodic oxidation process.

Another challenge for the upscaling of EAOPs is their drawbacks such as energy requirement and the need for a supporting electrolyte. Thanks to electrochemical microfluidic reactors there is the possibility to reduce ohmic drop and the cell resistance, which reduce the conductivity requirement and the energy consumption. The short interelectrode distances involved in the range of 50 to 500 µm allow for transfer intensification and have shown promising results for EAOPs application in wastewater treatment [8]. The optimization of micro-reactor design through mass transfer and specific energy efficiency studies will be exposed as well.

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Plasmonic Photocatalysts with Nanoparticles Free of Noble Metals

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Water splitting and artificial photosynthesis are becoming increasing popular routes to access renewable fuels. In order to perform such reactions, plasmonic photocatalysts have been the object of intense scrutiny because they can enhance photocatalytic activity by acting as (i) "electron-sink" to attract electrons generated under UV irradiation, or (ii) as visible-light harvesters by injecting "hot" electrons to the semiconductor conduction band induced by their classic surface plasmon resonance (SPR) effect. However, these plasmonic photocatalysts usually require a plasmonic particle which is most often constituted of gold or silver.

In this communication, we will present our attempts to generate high activity photocatalysts based on non-noble metal plasmonic particles. In a first example, we present our results on copper nanoparticles. In order to prevent these particles from being oxidized, the particles are encapsulated in 2 to 5 layers of graphene. The communication will present the performance of these photocatalysts in water splitting and in CO_2 photoreduction. An alternative construction will be presented, where titanium nitride nanocubes will be used as plasmonic nanoparticles. The performance of such catalyst will be presented and will be compared to other photocatalysts prepared in our groups in the recent years.

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Superconcentrated KFSA Solutions for Non-Aqueous and Aqueous Rechargeable Batteries

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Non-aqueous potassium-ion battery (KIB) has attracted much attention as a potential high-voltage and high-power secondary battery due to the lower standard electrode potential of K/K^+ in carbonate ester solutions and smaller Stokes radius of slovated K^+ ions compared with the lithium case.[1] We first demonstrated a high voltage KIB with graphite//$K_2Mn[Fe(CN)_6]$ configuration.[2] However, most of the reported KIBs including ours suffer from large irreversible capacity and capacity degradation due to anodic/cathodic decomposition of carbonate ester-based electrolyte. Our previous work revealed that superconcentrated $KN(SO_2F)_2$ (KFSA) / 1,2-dimethoxyethane (G1) electrolytes realized high coulombic efficiency of graphite electrode.[3] Although $K_2Mn[Fe(CN)_6]$ positive electrode also showed higher coulombic efficiency of ca. 96% in KFSA/DME electrolyte than KPF_6 / carbonate ester one, the coulombic efficiency of $K_2Mn[Fe(CN)_6]$ electrode is needed to be improved. To improve the coulombic efficiency, we here study superconcentrated KFSA/glyme electrolytes using longer glyme such as diglyme (G2) and triglyme (G3) as solvent.

Figure 1 a show charge/discharge curves of K//$K_2Mn[Fe(CN)_6]$ cells filled with 5.5 mol kg^{-1} (≡ m) KFSA / G1, 5.6 m KFSA / G2, and 5.6 m KFSA / G3. All cells exhibit reversible capacity of ca. 110 mAh g^{-1}. Notably, G2 and G3 electrolyte showed much higher coulombic efficiency than G1 electrolyte as shown in Fig. 1b. Raman spectroscopy data indicates that pronounced interaction between K^+ ion and G2 or G3, which results in negligible amount of free solvent, is a key to high oxidation stability.[4]

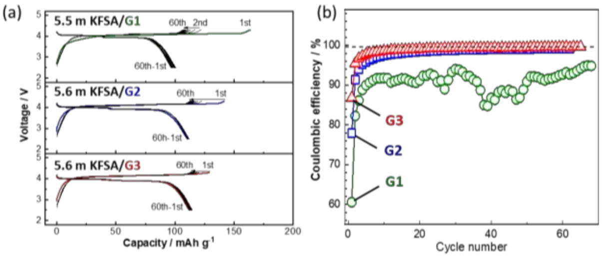

Fig. 1 Electrochemical performance of non-aqueous K//$K_2Mn[Fe(CN)_6]$ cell filled with superconcetrated KFSA/glyme electrolytes: (a) charge discharge curve and (b) coulombic efficiency.

Based upon the fact that KFSA is highly soluble in water up to 31 m, we found that multi-cation FSA system enables higher solubility of 33 m $K_{0.55}Na_{0.45}FSA$ / H_2O, which realizes high voltage operation of aqueous Na/K multi-ion batteries because of the widened potential window of 3.5 V. We confirm that the mixed electrolyte is applicable to $NaTi_2(PO_4)_3$ carbon composite (NTP), $Na_3V_2(PO_4)_3$ carbon composite (NVP), and $K_2Mn[Fe(CN)_6]$ electrodes. Furthermore, we assembled NTP//$K_2Mn[Fe(CN)_6]$ and NVP//$K_2Mn[Fe(CN)_6]$ full cells demonstrating reversible charge/discharge with an average discharge voltage of 1.4 V and 1.9 V, respectively (Figs. 2a and 2b). From these results, we will present our future insight into high voltage non-aqueous and aqueous potassium-ion based batteries.

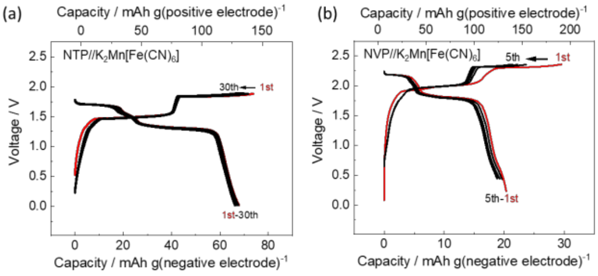

Fig. 2 Charge/discharge curves of aqueous multi-ion cells of (a) NTP//$K_2Mn[Fe(CN)_6]$ and (d) NVP//$K_2Mn[Fe(CN)_6]$ filled with 33 mol kg^{-1} $K_{0.55}Na_{0.45}FSA$ / H_2O electrolyte.

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Intermediates in PEC Water Oxidation. How They Come and How They Go

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Atmospheric oxygen that we live on is the result of a fundamental evolutionary step in photosynthesis, which occurred on Earth 2-3 billion years ago [Biello 2009]. The water oxidation in natural photosystem II accounts for 50% of this oxygen. The man-made analog to this natural process is water oxidation in photoelectrochemical cells - one of the most complex processes in physical chemistry. I will showcase how modern x-ray spectroscopy methods have assisted in the understanding of the molecular pro-cesses which occur in natural [Bora 2013, Ralston 2000, Visser 2001] and in man-made "photosystems". A most recent example is the element and orbital specific identification of transient electron holes in iron oxide [Braun 2012], chemical surface intermediates [Bora 2011] and changes in the water molecules in the electrochemical double layer during photoelectrochemical water oxidation [Braun 2016]. I will also demonstrate how the electronic structure evolution is quantitatively paralleled by the electric transport properties of the electrodes during operation.

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Biomolecular Sensing via Electrochemistry at Oil-Water Interfaces

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The electrochemical behavior of biological molecules at the interface between two immiscible electrolyte solutions (ITIES) provides a simple strategy for the detection of target analytes such as proteins in a label-free manner. Such detection is based on protein-anion complexation at the interface and adsorption of the complex [1] Exploiting the adsorption can enable detection of nanomolar cocnetrations of model proteins, while exploitation of enzymatic activity of specific biomarkers has enabled detection of sub-picomolar concentrations. This approach can be applied to other biomolcules such as sulfated carbohydrates [2,3] and aptamers [4], as a generic strategy for the non-redox detection of bio(macro)molecuels involving polyelectrlyte-counter ion binding at the interface.

To-date, however, relatively little has been reported on the structural changes in biological molecuels following their adsorption, under electrochemical control, at this interface. Building on initial studies udsing infra-red (IR) spectroscopy to probe the secondary structure of a range of proteins [5], this presentation will focus on the structural properties of insulin at the interface. Detection of insulin is a useful sensing target as it's detection opens a new route to understading aspects of diabetes. In this case, electroadsortion at the gelled ITIES followed by IR spectroscopy is used to probe changes in the structure of the protein at the interface. Finally, on-going studies into the detection of enzymes, using glucose oxidase as a model, will be discussed.

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Oxygen Redox and Singlet Oxygen in Non-aqueous Battery Chemistries

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The redox chemistry of O_2 moieties has come into the focus of much of the forefront battery research such as metal-O_2 batteries and Li-rich layered oxides (*Nature Mater.* **2012**, *11*, 19. *Science* **2015**, *350*, 1516). O_2 evolution is in either case a critical yet not fully understood phenomenon (*JACS* **2016**, *138*, 11211). For example, operation of the rechargeable metal-O_2 batteries depends crucially on the reversible formation/decomposition of metal (su)peroxides at the cathode on discharge/charge. So far these parasitic reactions have been ascribed to the reactivity of superoxide and peroxide. Yet, their reactivity cannot consistently explain the observed irreversible processes. Only better knowledge of parasitic reactions may allow them to be inhibited.

Here we discuss our recent insights into irreversible parasitic reactions caused by the highly reactive singlet oxygen ($^1O_2$) during cycling of non-aqueous batteries that have so far been overlooked. A major reason for this is the difficulty to detect $^1O_2$ in batteries. I discuss the set of methods we developed for its identification. $^1O_2$ accounts for the majority of the parasitic products during cycling of metal-O_2 cells (*Nature Energy* **2017***,* 17036. *Angew. Chem. Int. Ed.*, **2017**, 56, 15728). We report on the formation mechanism of $^1O_2$, materials stability (*Nature Commun.*, **2019**), and a new class of high-voltage stable quenchers (*Angew. Chem. Int. Ed.*, **2019**), and ways to suppress its formation. Moreover, $^1O_2$ forms upon oxidizing Li_2CO_3 above 3.8 V vs Li/Li^+ (Angew. Chem. Int. Ed. 2018, 57, 5529). Li_2CO_3 is a universal passivating agent in Li-ion battery cathodes and decisive in interfacial reactivity. Li_2CO_3 formation, even at impurity levels, will deleteriously affect the stability of all Li batteries that operate beyond 3.8 V vs Li/Li^+, which includes most currently-studied cathode chemistries. Awareness of singlet oxygen gives a rationale for future research towards achieving highly reversible cell operation.

The Impact of Biocatalysis on Current Fuel Cell Technology

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The enzyme laccase has been reported to completely reduce oxygen to water at a turnover number of 200 *e*– site^{-1} s^{-1} at 0.8 V/RHE, pH 5. This rate is comparable or even favorable to supported platinum when metal utilization is taken into account. Current fuel cells are limited to low molecular-weight fuels such as hydrogen and methanol, whereas biological metabolism is capable of complete oxidation of carbon-rich fuels such as sugars, at high efficiency albeit low power density. Such comparisons encourage us to challenge our current understanding of electrocatalysis to encompass the broad range of evolution-derived "technologies" that are available in nature.

This talk will describe advances in applying biological and biomimetic technology in current fuel cell technologies, including the development of molecular catalysts for fuel cell reactions in acidic, alkaline, and neutral environments, and the opportunity for multistep oxidation of biofuels. A particular focus will be on computational understanding of multistep reaction cascades with efficient control of intermediate transport. Such approaches could lead to future application of the technologies demonstrated by enzymes such as laccase.

High-rate Pseudocapacitive Energy Storage in MXenes with Fast Intercalation

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Pesudocapacitive materials are promising candidates for fast electrochemical energy storage with high energy density, as the pseudocapacitive intercalation is accompanied by fast, surface-confined redox reactions. MXenes, a family of two-dimensional (2D) transition metal carbides and nitrides, have shown their potential as pseudocapacitive electrode materials due to their 2D morphology, metallic conductivity (>8,000 S/cm) and redox active surfaces. [1] Different MXenes are available with a large variety of surface chemistries, all of which have demonstrated high performance in energy storage applications. Especially titanium carbide MXene showed a high volumetric capacitance of 1500 F/cm^3 in acidic aqueous electrolyte. The high capacitance of MXenes in acidic aqueous electrolyte is due to the reversible partial-electron transfer between the intercalated protons and the surface groups on MXene. [2]

Unlike typical porous materials, the interlayer space between MXene sheets is expandable, accommodating ions of different kinds, sizes and polarities. A wide variety of cations with various charges, such as H^+, Na^+, K^+, Mg^{2+}, Al^{3+} and even bulky ionic liquids, are capable to intercalate between MXenes sheets. The co-existence of solvent molecules with intercalated ions in the MXene layers has shown profound effects on the charge/discharge process of MXene electrodes. In aqueous electrolyte, the water molecules confined between the MXene nanosheets enable ultrahigh ion transport rate, which is superior to other pseudocapacitive materials, such as conductive polymers and metal oxides. In organic electrolyte, the chemical nature of the electrolyte solvent can influence the arrangement of electrolyte molecules/ions between the Ti_3C_2 layers, which correlates directly to the total charge stored. [3] A large interlayer space has been observed in a sulfoxide-based solvent, which allows ions intercalate with low resistance. On the contrary, the intercalated Li ions are fully desolvated in a carbonate-based solvent system, allowing the MXene electrode to store almost twice the charge compared to the same salt in a nitrile- or a sulfoxide-based solvent. Hence, properly matching the electrolyte composition to the pseudocapacitive electrode material is essential for controlling the ions intercalation process and is necessary for achieving superior electrochemical performance.

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Electrochemical and electrochemiluminescent biosensor platforms based on screen printed electrodes for biomedical applications

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We have studied electrochemical biosensors using screen printed electrodes which were available for different type of detection principle. Biomarkers like genes, proteins and cellular signals can be monitored by electrochemical biosensors. Printable electrodes have advantages in mass productive and disposable applications. Mobile electrochemical detector has been also developed and commercialized by Biodevice Tech. Ltd. Electrochemical DNA detection has been originally developed without immobilization of DNA onto electrodes (*Electrochemistry Commun. 6,337,2004*, *Electrochem.Acta, 82, 132, 2012*). PCR process can be monitored in real time and applied to detection of actual targets such as pathogens like Salmonella, O-157 and Flu virus, genetic modified organism (*Analyst 134,966,2009*), origin of meats (*Food Control, 21,599, 2010*) and so on. Microfluidic PCR and RT-PCR chips were useful for rapid detection with our electrochemical DNA sensor method. (*Analyst 136,5143, 2011*) Gold nanoparticle-antibody can be linked with new electrochemical immunoassay as GLEIA (gold linked electrochemical immunoassay). High sensitive detection of human chorionic gonadotropin (360 fg/mL) and insulin (100 pg/mL) were reported (*Electroanalysis, 20,14, 2008*). Antioxidative activity in food and amount of residual pesticides are also monitored by redox indicators and printable electrodes. Microbial respiration activity can be monitored by printable electrodes and mobile detector and applied to rapid measurement of microbial viable cells (*Electrochem.Acta,82,132, 2012*). Nanoparticle-antibody can be linked with an electrochemical immunoassay as Electrochemical Surface Enhanced Raman Scattering (EC-SERS) was also discussed with gold and silver nanoparticles interacting with bio-molecules. By several selected applied potentials, different adsorption mode of AGI (aminoglutethimide) interacting with the SERS-active substrate can be observed, such as monodentate interaction through aniline or glutarimide moiety and bidentate interaction through the both moieties （*Bull.Chem.Soc.Jpn 91,1579, 2018, Electroanalysis,30,1432,2018* ） We have also developed luminol-based electrochemiluminescence (ECL) biosensors that perform enzymatic reactions and bioanalysis using antioxidant molecules by controlling the spatiotemporal production of a luminescent substrate (*Electrochim.Acta,222,580,2016*), catalase activity (*Electrochim.Acta, 240, 447, 2017*) and glycated albumin (GA) (*Analytical Chemistry, 89, 5909, 2017). *Enzyme-free electrochemiluminescent (ECL) immunosensing scheme was developed utilizing the catalytic generation of reactive oxygen species (ROS) from gold nanoparticles.(*Analytical Chemistry, 90, 5773,2018*)

Ionic liquid electrolytes and ionogel composites that enable high capacity anodes for lithium and sodium batteries

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Traditional electrolytes currently used for Li-ion and Na-ion devices are not compatible with higher energy-density anodes required for next generation devices, such as Li metal and Na metal anodes. In addition, there is now a recognition that operation at elevated temperatures is desirable for some applications. Therefore, new electrolyte materials are currently actively being investigated for beyond Li-ion technologies. It has recently been shown that, by using an ultra-high concentration of lithium or sodium salt in an ionic liquid (or indeed some organic solvents),it is possible to achieve stable cycling of Li metal and Na metal anodes, often at high rates and current densities, and even in the presence of water. We will discuss the structure, transport and electrochemical properties in these electrolyte systems and their performance in full cells. The properties of iongels based on these electrolytes will also be presented.

It has also been demonstrated that polymerized ionic liquids, with either TFSI or FSI counterions, are capable of dissolving even higher concentrations of lithium salt leading to highly conductive solid electrolytes. These materials have high t_{Li+} and improved mechanical properties and also enable stable alkali metal cycling, thus offering exciting opportunities for all solid state lithium batteries. These materials will also be discussed in terms of their phase behavior, conductivity and electrochemical behavior.

Bio-inspired laser-induced electrochemical sensing strategies

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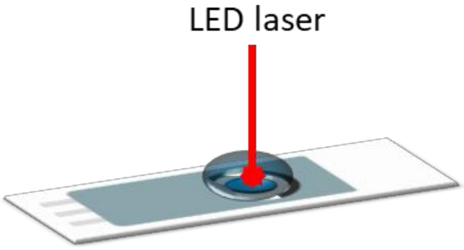
In my talk a sensing strategy inspired by the advantages of enzymes and photoelectrochemical sensing, namely the integration of aerobic photocatalysis and electrochemical analysis, will be presented. The photosensitizer, a bioinspired perfluorinated Zn phthalocyanine, generates singlet-oxygen from air under visible light illumination and oxidizes analytes, yielding electrochemically-detectable products while resisting the oxidizing species it produces. Compared with enzymatic detection methods, the proposed strategy uses air instead of internally added reactive reagents, features intrinsic baseline correction via on/off light switching and shows C-F bonds-type enhanced stability. It also affords selectivity imparted by the catalytic process and nano-level detection, such as 20nM amoxicillin in ml sample volumes. [1]

Additionally, this strategy can be applied to improve the sensitivity of assays by using magnetic beads in combination with an amperometric readout in a configuration so-called a electrochemical magnetosensor. The main difference between of a magnetosensor from a biosensor is that a biorecognition element is linked to magnetic beads and can be temporally dispersed in a sample for improving binding kinetics and, then, accumulated on an electrode by a magnet to register an analytical response. In comparison with conventional optical read-out systems, electrochemical sensors can register an analytical response almost immediately and without the need of developing the reaction in bulk volume, because the response of electrochemical sensors is determined by a thin layer of measuring solution near the electrode surface where the beads with immunoreagents are placed. This approach may improve sensitivity and decrease analysis time in comparison to conventional ELISA.



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Power Ultrasound for the Fabrication of Fuel Cell and Electrolyser Catalysts and Low PGM Loading Electrodes

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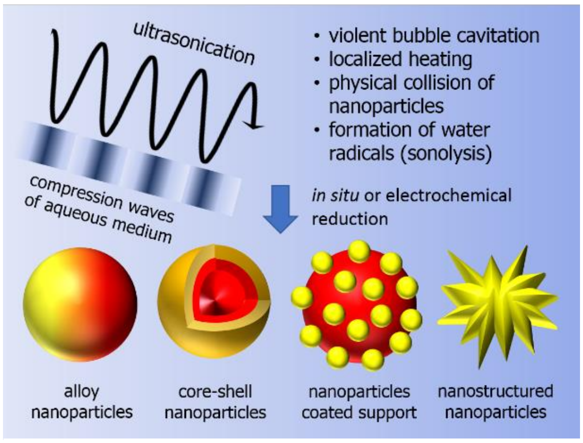

Figure 1. Sono(electro)chemical formation of fuel cell electrocatalyst nanoparticles [1,2].

This presentation highlights some of the research works undertaken over the years by the *Pollet's* groups in *Birmingham (UK)*, *Cape Town (RSA)* and *Trondheim (NO)* in the application of power ultrasound for the fabrication of hydrogen fuel cell catalysts and electrodes, and the generation of hydrogen [1-3]. Since the publication of 'the use of ultrasound for the fabrication of fuel cell materials' in 2010 [4] (Fig.1), there has been an upsurge of international interest in the use of ultrasound and sono(electro)chemistry for the production of hydrogen and fuel cell materials. The first paper describing the production of Pt nanoparticles from aqueous solutions (chloroplatinic acid) using sonoelectrochemistry [5] was in 2009. In these experiments, the fabrication of Pt NPs (≈15nm) was performed galvanostically at room temperature using a vibrating working electrode (*sonoelectrode*) producing short applied current pulses triggered and followed immediately by short ultrasonic pulses (20kHz) [5]. Later on, Pollet *et al.* [6] showed that power ultrasound can be used for the *in-situ* fabrication of PEMFC electrodes and Gas Diffusion Electrodes (GDEs). The electrodeposition of Pt on Gas Diffusion Layer (GDL) surfaces in dilute chloroplatinic acid solutions was performed potentiodynamically in the absence and presence of ultrasound (20kHz) at various ultrasonic powers. It was found that Pt electrodeposition required a substantial overpotential to drive the formation of Pt nuclei on GDL surfaces; however, under sonication, Pt electrodeposition became more facile due to lower concentration and nucleation overpotentials, and overall currents were significantly increased compared to *silent* conditions. It was also observed that the *ECSA* was improved for Pt/GDL electrodes prepared under sonication. In 2011, a research collaboration with *SonoTek Corporation (USA)* led to a novel ultrasonic-spray (US) method for preparing GDEs on various commercial woven and non-woven GDLs at several Pt loadings in the range of 0.40–0.05mg cm^{-2} [7]. It was found that the GDEs prepared by the US method exhibited better fuel cell performances compared to those prepared commercially, especially at low Pt loadings. More recently, it was successfully shown that simultaneous electrocatalytic Pt-NP synthesis and decoration of Vulcan XC-72 carbon black substrate was achieved in a novel one-step-process, combining galvanostatic pulsed electrodeposition and pulsed ultrasonication (20kHz) [8].

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Electro-Catalysis at the atomic scale

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The chemical industry should in the future be based on renewable energy. Therefore, material development for environmentally friendly, electrocatalytic production of valuable chemicals is needed.

Chemicals could be produced using safe, cheap, more environmentally friendly and more abundant reactants than today. The products could be provided on demand at the place where they are needed, reducing expensive and hazardous transport of chemicals. However, stable, efficient and selective catalysts have to be discovered. This requires insight into the surface chemistry at the atomic scale.

The challenge of discovering new catalyst materials is twofold: Firstly, the properties or descriptors of the wanted catalyst have to be identified. Secondly, real materials with the wanted properties should be found.

I will give examples of determining descriptors for different reactions and a method for identify promising catalyst materials based on high entropy alloy, which is a new class of materials with the promise to change the way we discover interesting catalyst materials.

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[3] Electrochemical CO2 Reduction: A Classification Problem, A Bagger, W Ju, AS Varela, P Strasser, J Rossmeisl, ChemPhysChem 18 (22), 3266-3273, 2017These instructions are an example of what a properly prepared meeting abstract should look like. Proper column and margin measurements are indicated.

Modeling of the Potential-Dependent Reactivity of Mg/Electrolyte Interfaces

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Understanding the electrochemical processes occurring at electrode/electrolyte interfaces in rechargeable batteries is crucial for optimization of the system's stability and electrochemical performance. However, due to the complex nature of the interfaces, very few theoretical approaches were proposed so far to tackle this challenge. A computationally affordable and suitable methodology was presented and successfully tested previously on lithium systems [1]. The system is modeled by explicit solvent molecules of the first solvation shell of the cation, while the rest of the electrolyte environment is described by the implicit solvent model implemented in some DFT codes [2, 3].

Herein we use the same methodological approach on two systems in the double-layer of the Mg^0/electrolyte interface: magnesium solvated in dimetoxyethane (DME), which works fairly well, and ethylene carbonate (EC), which fails completely. In both solvents we obtain the potential dependent free electrochemical energy and differential capacitance [4], as well as redox potentials. The fully unparameterized results are in excellent agreement with experimental data. We further develop the methodology to investigate the electrochemical stability and stability regions of the solvents at the interface. We find that the solvent stability is strongly modified in the presence of Mg^{2+} and the vicinity of the interface. This sheds light into why some solvents are not appropriate for Mg battery systems despite their stability in the bulk electrolyte. Furthermore, we use the methodology to study decomposition pathways. This information is crucial for understanding on the atomistic level why some systems work fairly well while others fail completely.

The obtained potential dependent results give new rational insights into the mechanisms controlling the reactivity and the degradation of electrolytes, and can prove valuable in the practical development of novel electrolytes with enhanced stability in a wider potential window.

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Li-insertion into Nanocrystalline $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC)

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While $LiCoO_2$, a commercial widely used cathode material, still raises some concerns about the cost, abundance of cobalt, and toxicity hazard, the layered $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC) is a promising cathode material from all points of view[1]. Its Co content is only 1/3 of that in $LiCoO_2$, it exhibits impressive stability upon cycling, reasonable specific capacity (150 mAh/g), good high rate capability, and good safety features. Due to relatively low Li^+ diffusion coefficients[2] NMC material consisting of nanocrystals with well-developed structure represents the best candidate for stable and fast Li-ion battery. Since commercially available NMC products are microcrystalline, development of nanoparticular product with excellent electrochemical performance represents the objective of our study.

Commercial $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ material was treated in appropriate way to provide cathode material with reasonable charge capacity and high cycling stability upon different charging/discharging rates. Electrochemical performance of the tested materials is studied by cyclic voltammetry of Li insertion and galvanostatic chronopotentiometry. An influence of calcination, surface area and particle size uniformity on the charge capacity and cycling stability is evaluated and the parameters of the optimized samples providing charge capacity of 141 mAh/g (cyclic voltammetry) and 144 and 135 mAh/g (galvanostatic chronopotentiometry) at 1 and 10C, respectively, represent a platform for scale up during the next period of the research[3].

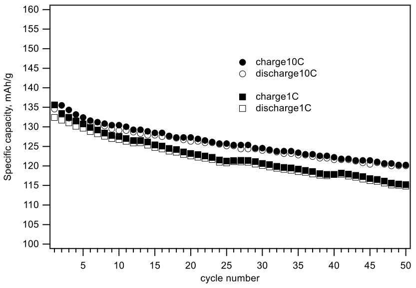

Figure 1. Galvanostatic cycling of the optimized NMC sample at 1 and 10C.

Acknowledgments
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Boosting Transport Properties of Phosphonium and Guanidinium Ionic Liquids

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Ionic liquids (ILs) are a very diverse and promising class of advances liquid materials with various applications. Among the most promising technical implementations is their incorporation as highly stable and safe electrolytes into electrochemical devices. ILs based on phosphonium cations are thereby of special interest for supercapacitors and batteries since they offer advantageous stabilities as well as good conductivities. ILs based on the tetramethylguanidinium (TMG) cation are promising candidates – in immobilized form - for High Temperature PEM Fuel Cells.

We have synthesised a variety of partly novel phosphonium ILs with different anions as well as with different compositions and lengths of the side chains of the cations. The phosphonium cations contain either 4 alkyl chains [1, 2], or 3 alkyl chains and 1 ether functionalized chain [1], or 1 alkyl chain and 3 ether functionalized chains [2]. The application of multiple ether functionalization has not been addressed before. In addition we have synthesized a series of mostly novel protic and aprotic ILs based on the tetramethylguanidinium (TMG) cation that is a derivative of the superbase guanidine; different substitution patterns and anions from acids with broadly varied pK_a values were investigated [3].

We have determined a variety of important transport properties such as viscosity, conductivity and diffusivity by means of stress-controlled rheology, impedance spectroscopy and PFGSTE NMR diffusometry.

For the ether-functionalized phosphonium ILs we found that the solidification temperatures of the ether-ILs were significantly lowered, while fluidity and conductivity were increased up to over an order of magnitude compared to the alkylated ones. At the same time the ionicity and thermal stability were not affected significantly. Overall the transport properties of the ether ILs were found to be comparable to the more widely applied (but less stable) imidazolium ILs; this makes ILs based on ether-functionalized phosphonium cations highly interesting candidates for electrochemical devices.

Both protic and aprotic TMG ILs show transport properties comparable to other ILs with similar molecular weight and high ionicity values especially in contrast to other protic ILs. Lowest ionicity values were found for the protic ILs with smallest ΔpK_a values between constituting acid and base. This can either be explained by stronger hydrogen bonding between cation and anion or lower anti-correlations between the oppositely charged ions.

Different models for the correlation of the transport properties, namely the Nernst–Einstein, Walden and Stokes–Einstein–Sutherland relations were applied. The deviation from ideal behaviour of fully dissociated electrolytes, often termed as ionicity, was quantified by the reciprocal Haven ratio, the fractional Walden rule and the ionicity obtained from the Walden plot. These models are well established in the literature and are herein applied to rarely studied but promising ILs. In comparison, the models show a qualitative correlation but distinct deviation in the quantification especially in the temperature dependent values. Velocity cross-correlation coefficients were calculated to gain further insight into the correlation between ion movements. Our studies contribute to a better understanding of the IL transport properties depending on the molecular composition and in this way help to choose the ILs with optimal properties for practical applications.

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Artificial Photosynthesis: Photocatalytic Conversion of CO_2 into Solar Fuels

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Photocatalytic reduction of CO_2 into hydrocarbon fuels, an artificial photosynthesis, is based on the simulation of natural photosynthesis in green plants that O_2 and carbohydrates are produced from H_2O and CO_2 using sunlight as energy source. It couples the reductive half-reaction of CO_2 fixation with a matched oxidative half-reaction such as water oxidation to achieve a carbon neutral cycle, which is like killing two birds with one stone in terms of saving our environment and supplying future energy.

This presentation will report the utilization of solar energy to highly efficient conversion of CO_2 into renewable hydrocarbon fuel over structured nanomaterials. The geometric shape and exposure of specific crystal planes of the nanostructures as well as combination of graphene as a good electron collector and transporter are a requisite for the high level of photocatalytic reduction of CO_2.

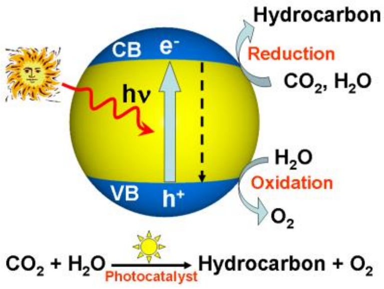

Fig. 1. Schematic illustration of photocatalytic reduction of CO_2.

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Using Voltammetry to Measure Hydrogen Bonding

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Hydrogen bonding is an essential and seemingly ubiquitous interaction in many biological and industrial processes. Examples include the directional interactions that control protein structure, protein folding and molecular recognition. Although the interactions are well known to occur, it is difficult to quantify the degree of the interactions experimentally. Voltammetry has been found to be extremely sensitive to hydrogen bonding interactions with the effects manifested in measurable and uniform shifts in the potentials of reduction/oxidation processes for certain compounds in the presence of hydrogen bond donors or acceptors. Notable examples include the large peak potential shifts of quinones [1,2] and phenylenediamines [2,3] observed in organic solvents in the presence of water and alcohols during the reduction or oxidation reactions. There are several criteria that must be satisfied in order for voltammetry to be used to study H-bonding: (*i*) the donor and/or acceptor must be electroactive, (*ii*) the H-bonding between the donor/acceptor must vary between the reduced and oxidized states, and (*iii*) the data must allow a differentiation between H-bonding and H-transfer. The primary reason why voltammetry is able to measure hydrogen bonding effects is because the redox state of the molecule changes during a measurement, thus one voltammetric scan involves a species in two or more oxidation states, with each redox state undergoing hydrogen bonding differently. An important feature of hydrogen bonding is that the effects can be modelled similarly to proton transfer, that is, the shift in redox potential can partially be understood based on the equilibrium expression in the Nernst equation. Therefore, there is often a log like dependence on the concentration of the donor/acceptor compounds and the formal potential or voltammetric peak potential. This means that the shift in potential due to hydrogen-bonding effects is often the largest at small changes in concentration. From a practical perspective, it means that the presence of small amounts of hydrogen bonding impurities (such as trace water) in organic solvents can greatly affect the redox response of the analyte.

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Application of Scanning Kelvin Probe for In-situ Studies of Hydrogen Permeation in Steel

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At present, the demand for ultra-high strength steels (HSS) is growing in many applications, particularly for the automotive industry. On the other hand, these materials with high hardness show increased sensitivity to stress corrosion cracking and hydrogen embrittlement. Even very small amount of hydrogen can lead to the embrittlement or cracking, and the evaluation of the susceptibility of material to hydrogen embrittlement becomes more important to ensure reliability and safety. Diffusible hydrogen absorbed by the specimen is considered to be responsible for hydrogen embrittlement of HSS angle. Scanning Kelvin probe is applied "in situ" to study the hydrogenation of high strength steel, with and without electrogalvanized zinc layer, and a foil of pure iron. SKP visualizes the hydrogen flux from corroding location at the reverse face in real time. Hydrogen is produced during atmospheric corrosion and decreases the Volta potential at the location of emerging due to the reduction of iron species in the oxide film. It is shown that the sources of hydrogen are anodic locations. Different SKP based setups are applied to determine the hydrogen diffusivity and distribution in the steel, in the vicinity to the corroding surface. The results are compared to classical permeation measurements.

Flexible Monolithic Electrocatalysts for Alkaline Electrolyzers

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Most electrocatalysts for oxygen and hydrogen evolution reactions (OER and HER) are usually prepared on conductive substrates such as glassy carbon, Nickel foam, carbon cloth and so on. Moreover, significant advancements have been made using some of these substrates. However, the major disadvantage of such electrocatalysts designed on substrates is that there is a tendency for the active catalytic layers to drop off the substrates in a situation where a large amount of oxygen is evolved, which will automatically reduce the catalytic efficiency and life span of the catalyst. [1] Thus, the durability of the catalysts should be further enhanced by developing self-supportive catalysts.

Herein, we present the use of commercial available substrates (such as carbon cloth, CC and 304-type stainless steel mesh, SS) as electrocatalysts for OER and HER. The commercial substrates were subjected to chemical different chemical treatment to enhance their electrochemical surface area and displayed excellent electrocatalytic properties than the untreated ones. After exfoliation of the CC and SS, their surfaces became rough and porous with increasing surface area increases. The modified CC exhibit enhanced alkaline electrolyzer performance with potential of 1.85 V at 10 mA cm^{-2} (Figure 1a and 1b) [2] and modified SS achieved excellent alkaline electrolyzer performance with potential of 1.74 V at current density of 10 mA cm^{-2} and outstanding stability without deterioration after 5.5 days (Figure 1c and 1d). [3] The remarkable electrocatalytic properties of the self-supportive catalysts can be attributed to the unique exfoliated-surface morphology, heteroatom doping, and synergistic effect from the uniform distribution of the interconnected elemental compositions. In conclusion, a simple and easily repeatable strategy was used to modify the ever-cheap SS and utilized as OER and HER electrocatalysts for achieving low-cost alkaline electrolyzers. This study creates prospects to the utilization of low-cost, highly active and ultra-durable electrocatalysts for electrochemical energy conversion.

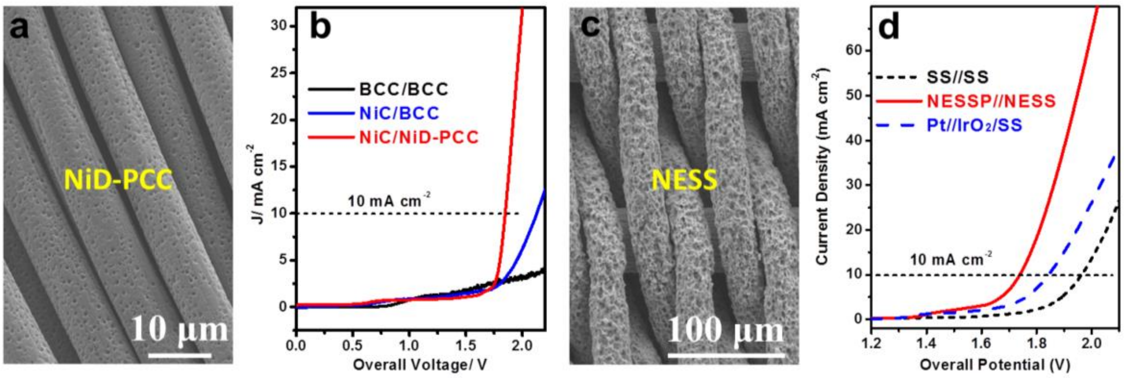

Figure 1. (a) SEM image of NiD-PCC and (b) electrolyzer LSV curves of NiD-PCC. (c) SEM image of NESS and (d) electrolyzer LSV curves based on NESS.

Note: BCC=bare carbon cloth, NiC=Nickel embedded porous carbon cloth and NiD-PCC= Nickel-free porous carbon cloth.

Note: SS=Stainless steel mesh, and NESS= N-doped exfoliated stainless steel mesh.

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Lubricin Modified Platinum Electrode: An Ultra-low Fouling Surface

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Surfaces with the capability to prevent nonspecific adsorption of proteins and cells, so called ultra-low fouling surfaces, are a crucial constituent in applications such as implantable biomedical devices, carriers for targeted drug delivery, and clinical diagnosis. Nonspecific adsorption of proteins can affect the performance of such surfaces in terms of reducing sensitivity (i.e. blocking the electron transfer pathway of redox reporters in the case of electrochemical interfaces) and selectivity (by interfering with the interaction of target species with the surface). Therefore, protein-resistant coatings are required when developing interfaces to deliver on the potential when it comes to biologically derived samples.[1, 2]

A promising electrode coating that has been used recently to address the issue of interface biofouling is lubricin (LUB), a large glycoprotein found in articular joints. LUB presents the ability of self-assembling on different types of surfaces, exhibiting great antiadhesive properties. In a work by Greene and co-workers it was shown that the LUB coatings were sufficiently low impedance that Faradaic electrochemistry could still happen at the underlying electrodes and effective in stopping biofouling by large molecules such as bovine serum albumin.[3]

Since it is unknown how LUB coatings on a platinum electrode behaves as an anti-biofouling layer, the purpose of this work was to evaluate the performance of LUB on platinum electrodes towards high-concentration nonspecific protein adsorption. The motivation of using platinum electrodes is its high importance to the biomedical applications as for example Cochlear implants. Three questions are addressed in this work: 1) can the LUB monolayer tethered to a platinum surface be quantified using an electrochemical approach? This question was investigated by using a similar approach used to quantify DNA probe density proposed by Tarlov. 2) How different LUB surface densities affect the ant-fouling properties of the interface? The differently prepared surfaces were challenged in high concentration protein solution and evaluated using impedance. And 3) can the LUB-Pt interface be challenged in an artificial perilymph solution over long period of time?

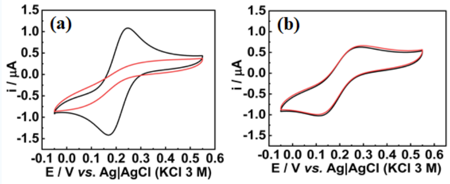

Figure 1 - Cyclic voltammograms recorded using (a) bare platinum electrode and (b) lubricin-platinum modified electrodes before (black lines) and after (red lines) incubation in a protein solution (HSA 5 mg mL^{-1}) for 1 hour. Experiments were measured in 1 mmol L^{-1} $K_3[Fe(CN)_6]$ solution prepared in PBS. Scan rate: 50 mV s^{-1}.

Accordingly, an easy to prepare anti-biofouling coating based on LUB is reported. It was possible to quantify the different amounts of LUB tethered to the platinum electrodes using chronocoulometry based on the electrostatic biding of $[Ru(NH_3)_6]^{3+}$ to mucin domain of LUB. Results obtained using cyclic voltammetry/electrochemical impedance spectroscopy and $K_3[Fe(CN)_6]$ as redox reporter suggested that, the LUB anti-biofouling capability is dependent on the LUB surface density. The optimized LUB coating retained its anti-biofouling and remained stable under passive and electrical stimulated conditions for a week in artificial perilymph media. These findings indicate the potential application of the LUB-Pt surface not only for Cochlear implants but also for broader range of bionic implants.

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A concept of double layer capacitance motivated by nanotechnology: Double layer impedance in mixture solutions

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The electric double layer (DL) is a layer in which nonuniformity of salt concentration and electric field orientation of dipoles are remarkable. The free energy gradient in the direction perpendicular to the electrode|solution interface is minimized by the formation of DL. From the previous experimental results, DL capacitance is made by the orientation of solvent dipoles, and it shows the relaxation of seconds required for orientation stabilization by dipole interaction. When mixing two kinds of solvents, we can compare the strength of the dipole interaction from the relationship between mixing ratio and electrostatic capacity. The interaction is discussed by measuring the electrostatic capacity in the polarization potential region in a mixed solution of water and acetonitrile.

DL impedances were evaluated in mixed solutions of water and acetonitrile (or ethanol) at various ratios in the polarized potential domain in order to find competitive orientation of the two solvent molecules on the platinum electrode. The DL capacitance at $0 < x < 0.2$ increases linearly with x from that in acetonitrile, and reaches the value for aqueous solution at $x = 0.2$, as shown in Fig.1. Field-oriented water dipoles are accumulated at the DL preferentially over dipoles of acetonitrile. The accumulation of water dipoles can be explained in terms of accumulation of water on the electrode excluding acetonitrile. The theory of the preferential accumulation is derived by use of statistical mechanics like Langmuir's method. It includes the difference in interaction energies of water-Pt from acetonitrile-Pt. The curve fitting assigned the energy difference to 6 kJ mol^{-1}. The accumulation of water generates an adsorbed film of ferrocene, which blocks diffusion from the bulk to the electrode. The inverse of the redox peak current has the linear relation with the inverse square-root of the scan rate, like Koutecky-Levich plots for mixed diffusion-kinetic control. This is the other demonstration of the accumulation of water at the DL.

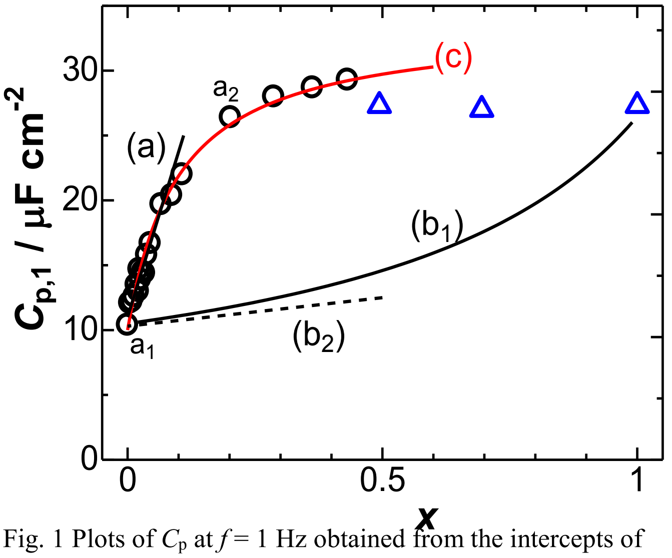

Fig. 1 Plots of C_p at $f = 1$ Hz obtained from the intercepts of Fig. 3 in the mixed solvent including (circles) 0.1 M TBAClO$_4$ and (triangle) 0.1 M KCl. Curve (b$_1$) was calculated from Eq. (7) on the assumption of bulk compositions at the interface against x. Line b$_2$ is the tangent of curve b$_1$ at $x = 0$. Curve (c) was calculated from Eq. (15) and (16).

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Surface Impurities on Layered Transition Metal Oxide Cathode Materials – Li_2CO_3 Decomposition in Li-Ion Battery Electrolytes

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Layered lithium transition metal oxides are state-of-the-art cathode materials for powering consumer electronics and battery electric vehicles. Especially for large scale manufacturing of batteries, the stability and robustness of the active materials is of great importance for cost efficient production.

The newest generation of layered transition metal oxides are very rich in nickel and suffer from high surface reactivity toward ambient air, leading to significant surface resistances[1] and severe gassing upon cycling. Besides hydroxides, carbonates (and hydrates of both) are known to be the major surface impurities formed. While the decomposition of Li_2CO_3 in a battery cell has been studied extensively, the mechanistic aspects of its decomposition during cell formation/cycling are still highly controversial.

In literature the decomposition mechanisms for Li_2CO_3 in an operating Li-ion battery include i) a chemical decomposition reaction,[2] (ii) its anodic oxidation concomitant with the electrolyte solvent,[3] and iii) the anodic oxidation of crystalline Li_2CO_3 upon singlet oxygen release.[4] All gassing analysis studies report the formation of CO_2 in the absence of O_2 gas, which was ascribed to the complete consumption of highly reactive "nascent" oxygen species by a chemical reaction with the organic solvent.[3-5]

In our study, the decomposition reaction of Li_2CO_3 in a standard Li-ion battery electrolyte (LP57; EC:EMC 3:7, 1M $LiPF_6$) is studied by on-line electrochemical mass spectrometry (OEMS) using our 1- and 2-compartment cells (in the latter, anode and cathode are separated by a Li^+-conducting glass).[6-7] The positive electrode stack consists of a working electrode made out of pure conductive carbon and an interlayer with carbon and small Li_2CO_3 particles (50-350 nm) coated on a porous separator. By modifying the electrode stack, we are able to show that the decomposition of Li_2CO_3 occurs as a chemical process without any anodic current flowing into the Li_2CO_3 particles. Nevertheless, CO_2 out of Li_2CO_3 is formed only after the carbon working electrode exceeds an anodic potential of roughly 4.2 V vs Li^+/Li. The decomposition must therefore occur via a chemical reaction that is initiated by anodically formed species within the cell. We show that these species are protons, formed upon anodic oxidation of the electrolyte solvent and trace impurities in alkyl carbonate based electrolytes. By adding ethanol or ethylene glycol (common impurity in EC), which form protons in significant amounts at lower anodic potentials, the onset of CO_2 evolution from Li_2CO_3 is accordingly shifted to lower potentials. Using ^{13}C-labeled Li_2CO_3 further allows a direct differentiation between Li_2CO_3 decomposition and electrolyte oxidation based on the amounts of $^{13}CO_2$ and $^{12}CO_2$ evolved upon charge. Tracing the $LiPF_6$ decomposition products PF_5/POF_3, the formation of protons can be followed quantitatively.[8] Thus, the "missing oxygen" upon Li_2CO_3 decomposition mentioned in the literature[4-5] is not related to the suggested rapid and complete reaction of a "nascent" oxygen species with the electrolyte solvent, but the reaction is simply the chemical reaction of Li_2CO_3 with protons, releasing CO_2 and H_2O. Implications of these findings for transition metal oxide based cathode materials in Li-ion batteries will be discussed based on our here found decomposition mechanism.

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Electrochemical Gas Phase Oxidation of Hydrogen Chloride to Chlorine: Model-based Analysis of Transport and Reaction Mechanisms

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Due to the steadily increasing production capacities of polycarbonates and polyurethanes, the volume of hydrogen chloride (HCl), which emerges as byproduct from these processes, is experiencing significant growth. Owing to the oversaturation of the market for HCl and hydrochloric acid, the question on how to utilize this byproduct in a sustainable and feasible manner is becoming increasingly important. Our recent studies showed that the direct electrolysis of gaseous HCl in combination with novel strategies for product purification leads to significant exergetic savings (36-38%) on the reactor as well as on the overall process level compared to the Bayer UHDENORA state-of-the art process, which employs aqueous hydrochloric acid as a feedstock [1]. Furthermore, we showed that despite of the improvements in the efficiency of the electrochemical reactor, it still has by far the greatest exergy demand of all the process units. For this reason the present work focuses on a more detailed understanding of the underlying physicochemical processes in the electrochemical gas phase reactor. While the ODC utilized in both process variants has been investigated in great detail in the scientific literature, the anodic oxidation reaction of gaseous HCl (HClOR) has not yet received much attention and is hence the major subject of this work. In earlier experimental investigations of the HClOR [2,3], a limiting current in the range of 400-900 mA cm^{-2}, depending on process conditions like temperature and reactant concentration, was observed. The origin of this limiting behavior is still not clear. In the past, membrane dehydration [3] and mass transfer resistances on the anode side were suggested as possible reasons [2]. In order to shed light on this phenomenon, a dynamic, one dimensional agglomerate model of the gas phase HCl oxidation half-cell, considering detailed micro kinetics, as well as the mass transfer of HCl in the different cell parts, is developed. Based on experiments of our group that yielded polarization data corrected for the ohmic resistance [2], the membrane dehydration effect can be presently ruled out. Moreover, the simulations of the present work show a sufficient membrane hydration due to the presence of liquid water in the cathode compartment of the cell. Furthermore, the modeling results suggest that the mass transfer of HCl in the gas diffusion media as well as within the agglomerates of the catalyst layer has only a very minor influence on the HClOR kinetics. Instead, the present work indicates that the observed limiting behavior is induced by the purely chemical Tafel step limiting the overall reaction rate at high overpotentials. These insights will have a significant impact on the strategy for further reactor optimizations. To give but one example, contrary to before, when mass transfer limitations were thought to be critical, thicker catalyst layers with an increased catalyst loading and hence also increased amount of active sites can now assumed to have a positive effect on the performance, which is also supported by experimental investigations [2]. Due to the great practical relevance of the HCl electrolysis, this is not only interesting from a purely scientific point of view, but harbors the potential of major energy savings in an industrial application of this process.

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Innovative Electrical Wiring of Enzymes via Non-covalent Binding of Redox Mediators on Buckypapers and Organic Nanoparticles

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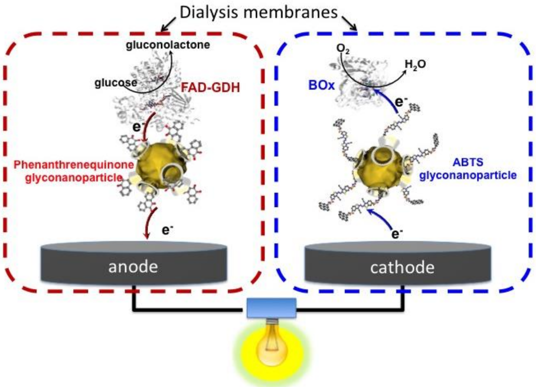
Fuel cells are one major alternative to replace power production from fossil fuels or nuclear energy. Enzymatic biofuel cells, a sub-class of fuel cells, rely on purified redox enzymes to achieve electrocatalytic reactions. Achieving a stable and efficient electrical contact between electrodes and the active site of enzymes remains one of the key challenges in the design of biofuel cells [1]. In this context, new processes implying electronic communication between enzyme and electrodes via organic or organometallic redox mediators in solution as electroactive organic nanoparticles or immobilized onto flexible buckypapers will be described.

The elaboration of glyconanoparticles exhibiting a shell of cyclodextrin as a versatile platform for the immobilization of redox mediators by host-guest interactions will be presented [2]. For instance, the electroactivity and stability of redox nanoparticles based on viologen derivatives, 9,10-phenanthrenequinone, anthraquinone sulfonate or (bis-pyrene-2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid were characterized in aqueous media. These organic redox nanoparticles were successfully applied to the electrical wiring of enzymes like bilirubin oxidase and FAD glucose dehydrogenase [3,4]. Furthermore, we will demonstrate the innovative elaboration of solubilized enzymatic fuel cell with permselective membranes to enable substrate and proton diffusion whilst trapping the enzymes and redox glyconanoparticles in separate compartments [4].



Recently, the use of buckypapers has led to more stable and flexible carbon nanotube electrodes. In particular, pi-stacking of pyrene derivatives was elegantly employed as a reliable and soft approach for the binding of redox mediators on carbon nanotube walls and the elaboration of redox buckypaper electrodes [5]. A new generation of buckypaper electrodes was produced by using linear bifunctionalized polynorbornenes containing multiple pyrene and NHS groups. Recent advances in the design of redox buckypapers based on the immobilization of thionin group or ruthenium complex bearing phenanthrolinequinone ligands and polyethyleneglycol-pyrene groups for the electrical wiring of immobilized enzymes will be presented [6]. In particular, excellent electrocatalytic NADH oxidation and electrical wiring of NAD- and FAD-dehydrogenases is demonstrated via the immobilized $Ru^{II/III}$ redox couple.

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Mining Nanopore Big Data to Reveal the Single Molecule Heterogeneity

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The recent development of nanopore techniques pushes the envelope in precision and complexity to maximize the information content. However, uncovering the interaction and kinetics of single molecules acquires statistical datasets by thousands of single molecule information. [1-2] The challenge still exists from effectively grouping the time-dependent ionic current trace into subpopulations. In this study, we applied the modified Hidden Markov Model to identify the ionic blockage merging inside current noise, which increase the temporal resolution and current resolution for nanopore techniques.[3-4] Then, we traced the multi-level current variations inside a blockade event by using Markov Chain Model, which reveals the dynamic kinetics for the conversion of multi-intermediates.[5] Since the ions migrate at different frequency inside nanopore, it acts as the smallest sensor to perceive and feedback the non-covalent interaction into the of ionic current frequency. We further employed Hilbert-Huang transform (HHT) to uncover these varied ionic frequencies which buried in the noise of the ionic current traces.[6] The HHT-based frequency analysis arises a two-dimension signal from time domain (time and current) into a three-dimension spectrum of energy-frequency-time distribution. The frequency-energy spectrum represents the fingerprint spectra for the characterization of non-covalent interaction due to the interaction between residues inside nanopore and the analyte. The very beginning frequency analysis let us mine more information from the data, which could help to unravel different hierarchical pathways and enables to discovery the subpopulations and hidden kinetic during the dynamic motion of single molecules.

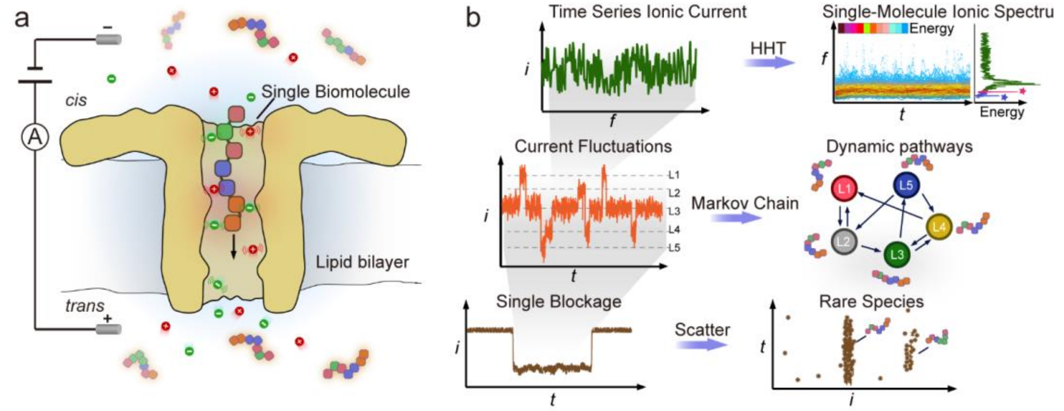

Figure 1. Nanopore-based single biomolecule interface for single molecule measurements. (a) a biological membrane protein molecule. (b) The obtained information from single blockade event.

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The origin for the instability of pyrolyzed Fe/N/C catalyst for oxygen reduction reaction

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The commercialization of proton exchange membrane fuel cells (PEMFCs), a clean and efficient energy, is severely hampered by the high cost of Pt catalysts. Due to the sluggish kinetics, cathodic oxygen reduction reaction (ORR) needs much more Pt catalyst than anodic hydrogen oxidation. Currently, pyrolyzed Fe/N/C catalyst has been considered as the most promising non-precious metal catalyst to replace Pt for ORR. However, the practical applications of Fe/N/C catalyst suffer from poor stability. Especially, the performance of Fe/N/C cathode will lose 20~50% within the initial a few hours.[1,2] Therefore, it is important to reveal the origin for the rapid initial performance decay.

Here, we will talk about the mechanism for the rapid initial performance decay of Fe/N/C cathode from the aspect of proton transport in micropores. We found that addition of trace amount of H_2SO_4 into Fe/N/C catalyst layer can greatly decrease the catalytic activity. This behavior was attributed to that H_2SO_4 can enter into the micropores of the Fe/N/C catalyst, and promote the protonation of pyridinic N located in micropores by Nafion, which decreases the proton transport rate. We further observed that the rapid initial performance decay of the Fe/N/C-based PEMFCs was accompanied by the protonation of pyridinic N and the increase of proton transport resistance. We then proposed that the protonation of pyridinic N in micropores to form pyridinium cation, which not only consumes the proton of Nafion, but also electrostatically impedes the proton transport to active sites, is the origin of the rapid initial performance decay of Fe/N/C catalysts.

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Photosystem 1 Monolayers with Controlled Orientation Enable Anisotropic Electron Flow for Photoelectrochemical H_2 Production

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The use of renewable sources for a sustainable molecular hydrogen production is of capital importance to ensure the availability of this promising fuel as energy carrier for current and future technologies. A particularly interesting approach in this regard constitutes the use of an efficient and ideally inexpensive photocatalyst enabling the use of solar energy for H_2 production from water as a vastly abundant resource. Through billions of years of evolution, Nature has developed a fully optimized machinery able to perform the photosynthetic process, allowing the conversion of solar energy and assimilation of organic matter. Photosystem 1 (PS1), one of the two key protein complexes involved in oxygenic photosynthesis, is able to act as a natural photodiode, delivering high-energy electrons upon absorption of visible light. Owing to the high quantum efficiency, abundance, and robustness of PS1, this biomolecule constitutes an attractive building block for the fabrication of semi-artificial photoelectrochemical assemblies and the development of energy conversion devices. Nevertheless, the considerably large voltage difference between the two opposite redox sites at PS1 obtained after light-induced charge separation translates directly into a substantial driving force for recombination processes and the re-oxidation of reduced charge carriers at the electrode surface, thus cancelling out part of the generated photocurrents and compromising the efficiency of the fabricated biophotovoltaic devices [1,2]. Therefore, one of the major challenges in the development of PS1-based devices constitutes the fabrication of well-defined structures able to provide a unidirectional electron flow.

An effective modification of electrode surfaces with a monolayer of biomolecules revealing a preferred orientation was envisioned. Taking advantage of the amphiphilic nature of PS1, the isolated protein complexes were spread onto a water-air interface were the hydrophilic ends at PS1 bearing the two terminal redox centers adopt a specific orientation either being solubilized in water or facing air, while the hydrophobic regions stack together enabling the formation of stable monolayers. The generated monolayer was then transferred to a gold surface serving as electrode substrate by Langmuir-Blodgett assisted deposition. PS1-based photocathodes assembled using this approach proved to be an effective means for the fabrication of functional devices enabling an anisotropic electron flow and consequently the efficient extraction of photoelectrons. The immobilized PS1 monolayer was further modified by deposition of a catalytic layer constituted by a [NiFeSe]-hydrogenase embedded in a viologen modified redox polymer [3]. In this way, the high-energy electrons generated at PS1 upon absorption of visible light are efficiently transferred to the highly active biocatalyst for the reduction of protons in solution and concomitant H_2 evolution.

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Superior Photocatalytic Activity of Anodic TiO_2 Nanotube Layers Coated with Secondary Materials using ALD

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The self-organized TiO_2 nanotube layers have attracted considerable scientific and technological interest over the past 15 years motivated for their wide range of applications including (photo-) catalysis, hydrogen generation and biomedical uses [1,2]. The synthesis of the 1D TiO_2 nanotube layers is carried out by a conventional electrochemical anodization of valve Ti metal sheets in various electrolytes. The main drawback of TiO_2 is its applicability in the UV light (wavelengths < 390 nm). In order to enhance the efficiency, TiO_2 has been doped by N [3] or C [4] to shift its absorption into the visible light.

Except doping, another intriguing approach to shift the light absorption to the visible light range is a homogeneous coating of the TiO_2 nanotube layers with thin layers of secondary materials. It has been shown that ultrathin layers of secondary materials can annihilate efficiently electron traps at the TiO_2 surface and, thus, increase the photo-generated concentration of charge carriers [5,6]. In the recent years, it has become clear that atomic layer deposition (ALD) is the only approach that enables the possibility of coating high aspect ratio structures homogeneously with thin and ultrathin layers of secondary materials [7,8].

In this presentation, the homogenous coating of high aspect ratio TiO_2 nanotube layers with different secondary materials, e.g. TiO_2 [9], MoO_xSe_y [10], or MoS_2, using ALD will be shown. The application of these coated TiO_2 nanotube layers for photocatalysis in the liquid as well as in the gas phase will be presented and discussed.

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Recent Advancements Towards Closing the Community Gap between Electrocatalysis and Battery Science: The Computational Lithium-Ion Electrode and Activity-Stability Volcano Plots

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Even though the underlying processes are of electrochemical nature, electrocatalysis and battery research are commonly perceived as two disjoint research fields. This finding might be traced to the fact that in electrocatalysis the reaction proceeds on the surface of the solid-state electrocatalyst, while in batteries metal-ions are intercalated into or out of the electrode material during charge and discharge. However, in both cases a two-phase boundary between the solid-state electrode surface and the surrounding liquid phase consisting of an aqueous electrolyte in electrocatalysis or dissolved salts in an organic solvent in batteries is present. The surrounding liquid phase may severely alter the surface structure of the electrode material depending on the respective environmental parameters, such as activities of reactants or the applied electrode potential in electrochemical applications.

The present lecture addresses the motivated aspect by summarizing recent advancements towards closing the apparent community gap between the research areas of electrocatalysis and battery science. Only recently the computational hydrogen electrode (CHE) approach of Nørskov and co-workers [1] was translated from electrocatalysis to electrode materials in lithium-ion batteries (LIBs).[2,3] In this context, the concept of a computational lithium electrode (CLiE) has been established that similarly to the CHE allows assessing the stability of surface phases as function of the applied electrode potential.

While for the investigation of battery materials by first-principles methods an expeditious tool with conceptual simplicity that enables *a priori* computational screening based on thermodynamics considerations is missing, the concept of Volcano curves serves this purpose in the field of electrocatalysis. This finding motivated to transmit the idea of Volcano curves from catalysis to electrode materials in LIBs.[4] These investigations result into the construction of activity-stability Volcano plots, which allow determining the performance of nano-sized LIB electrode materials within lithium intercalation and expand the concept of activity-based Volcano curves from electrocatalysis by including the stability as second performance parameter into the analysis. Consequently, exchange between the scientific communities of electrocatalysis and battery science should now take place in the opposite direction by incorporating the stability into the corresponding Volcano curves in catalysis.

In conclusion, an intimate interplay between the fields of electrocatalysis and battery science is suggested in order to develop novel approaches for an improved search of sustainable electrode materials in electrocatalysis as well as in battery science, summarized in **Figure 1**.[5]

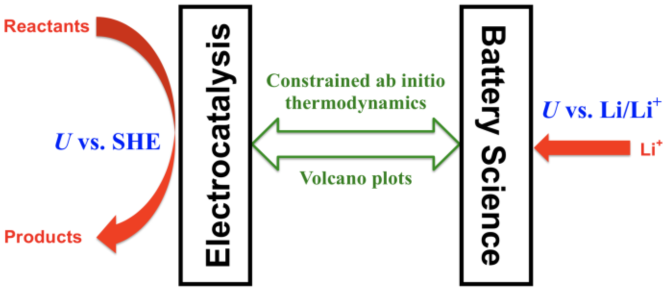

Figure 1: Creating synergies between the research areas of electrocatalysis and battery science, both driven by the applied electrode potential, may spur further progress towards improved theoretical models for the description of electrode surfaces.

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Ti Catalyst Biomimetic Sensor for the Detection of Nitroaromatic Pollutants

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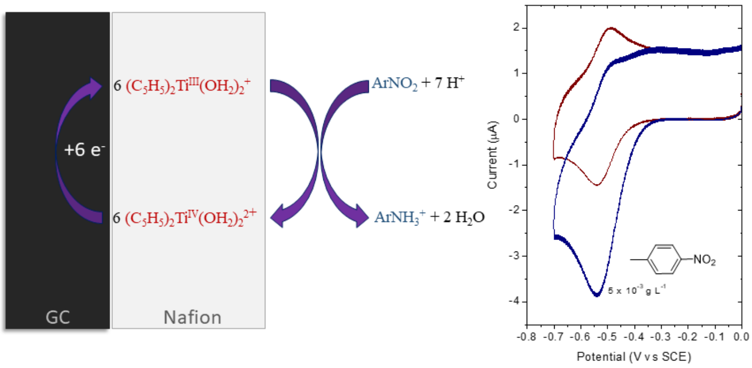
Nitroaromatic compounds (NACs) are unnatural species that came in the environment owing to anthropogenic activities such as manufacturing and use of dyes, pesticides, pharmaceuticals and explosives. The nitro group is well-known to reduce the biodegradability of molecules. NACs are biorecalcitrant molecules that could accumulate in soils and groundwater and that are often highly toxic and mutagenic.[1] Reliable and highly sensitive analytical methods are therefore necessary for controlling environmental pollution. The direct electrochemical reduction of nitroaromatic groups in aqueous medium gives hydroxylamine by a 4-electron process, the high stoichiometry being an advantage for the sensibility of the sensor. This interesting feature added to intrinsic properties of electrochemical sensors such as low-cost instrumentation, portability, simplicity to operate, short analysis time as well as high sensitivity and reliability makes those sensors promising analytical tools for NACs detection.

We have previously reported the interest of titanocene dichloride ($(C_5H_5)_2TiCl_2$) for the electrochemical reduction of biorecalcitrant pesticides containing a nitro group.[2] $(C_5H_5)_2Ti^{III}(OH_2)_2^+$ presents a high catalytic activity towards the reduction of nitroaromatic compounds with a 6-electron process and a high apparent chemical rate constant k_1 of 1.9×10^4 mol^{-1} L s^{-1}. We took advantage of this property allowing a constant potential measurement to achieve a sensor for NACs detection.[3]



Titanocene was immobilized in a Nafion® film on a glassy carbon electrode, as a first and simple method to highlight the performances of the sensor. Indeed, Nafion® allows a preconcentration of the nitro derivatives at the electrode surface during the analysis. A good stability and reproducibility for an electrode modified by drop-coating of a Nafion® solution are obtained. The modified electrode was able to detect several nitroaromatic pollutants at a fixed potential with a good linearity in the range of 5 to 500 $\times 10^{-4}$ g L^{-1} and a detection limit around 1-9 $\times 10^{-4}$ g L^{-1} (0.2-5.1 $\times 10^{-6}$ mol L^{-1}) depending on the nature of the analyte. Nitroaliphatic compounds are not detected, underlining the selectivity of the modified electrode for NACs. The sensor is therefore able to give quantitative information about the presence of nitroaromatic pollutants in aqueous solutions, giving rise to the NAC index, as referred to the phenol index used for the quantification of phenolic compounds in water quality monitoring. Since NACs are unnatural species that are often biorecalcitrant owing to the presence of the nitro group into their structure, a fast detection on pollution by NACs is required in water quality monitoring.

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Low Temperature Composite Sensors for Environmental and Medical Applications

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The sensing of gas molecules is of fundamental importance for environmental monitoring, control of chemical processes, medical applications, and so on [1]. In recent years, graphene-based gas sensors have attracted much attention due to enhanced graphene thermo-electric conductivity, surface area and mechanical strength. Thus, different structures have been developed and high sensing performances and room temperature working conditions were achieved [2]. However, they still suffer from several problems, which could be overcome by covering the graphene surface with metal oxide nanoparticles. Furthermore, studies regarding the detection of Volatile Organic Compounds (VOCs) are still at the beginning [3]. Hence, the present work will be aimed at: *i*) optimizing the synthetic routes of *ad hoc* composite VOCs sensing materials (based on graphene oxide/SnO_2 or ZnO hybrids); *ii)* engineering the gas sensor device; and *iii*) evaluating the sensing performances at both high and mild temperatures (also exploiting the UV light) towards gaseous ethanol, acetone and ethylbenzene.

Starting from pure graphite, graphene oxide (GO) powder was synthesized by adopting the Hummer's modified method. The synthetic route was deeply investigated by modulating both the starting carbon material (powder or flakes graphite) and the concentration of the H_2O_2 (*i.e.* the quenching/oxidizing agent), thus tailoring the final GO surface/structural properties. Once optimized this step, SnO_2 or ZnO were grown on its surface by hydrothermal method, varying the starting salt precursor/GO weight ratio between 4 and 32. For comparison, pure SnO_2 and ZnO (both commercial and home-made) were also tested. Several physico-chemical techniques have been used to characterize all the as-prepared nanopowders. Subsequently, a homogeneous layer was deposited by spraying technique onto Pt-Interdigitated Electrodes (Pt-IDEs) starting from an ethanol suspension of each sample (2.5 mg mL^{-1}, Figure 1). Then, gaseous ethanol, acetone and ethylbenzene were sensed, obtaining very promising results (in terms of both response/recovery time and sensibility down to ppb levels) for either pure and hybrid materials at 350°C, and at lower temperatures (150°C to 30°C) for the graphene-based samples.

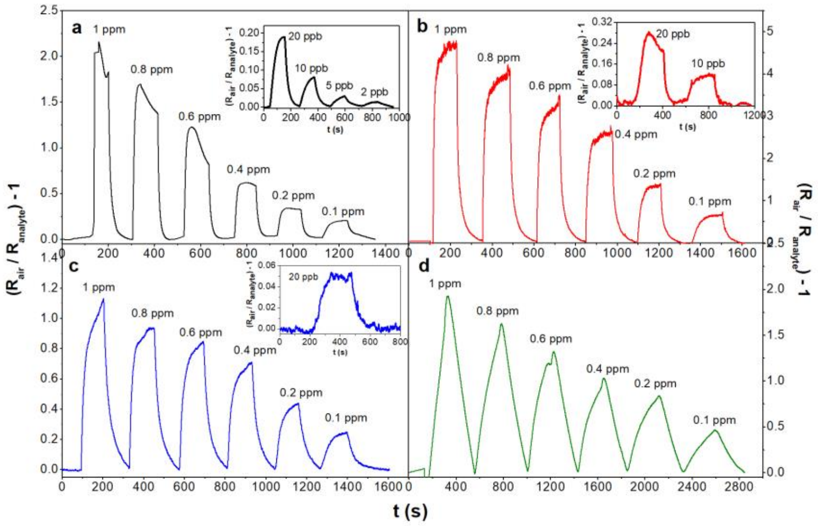

Figure 1. Ethanol sensor response obtained by **a)** pure home-made SnO_2 at 350°C (no UV), and SnO_2-GO 32:1 at **b)** 350°C (no UV), **c)** 150°C (with UV), and **d)** RT (with UV).

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Atomically Efficient HER Catalysts with Ultralow Precious Metal Loading

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Hydrogen is an ideal energy carrier with an energy density of 140 MJ kg^{-1} and water as its final product, which is considered as an ideal candidate for the replacement of fossil fuels.[1] To date, most H_2 is produced today through nickel-catalyzed conversion of CH_4 to H_2 and CO followed by a water gas shift reaction to yield H_2 and CO_2. However, this approach is based on unsustainable fossil energy and discharges greenhouse gas. Water is an ideal source for H_2 production as it is carbon-free, plentiful and almost costless. Water electrolysis, with only H_2 and O_2 as the final product, is a highly promising route in environmental benign H_2 generation.[2, 3] Although the ultimate goal is to couple hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) to an integrated efficient device for whole water electrolysis, one of the most crucial issues that must be solved is the development of highly efficient and durable catalysts for water oxidation and reduction.[3]

Herein, we report a highly efficient molybdenum disulfide (MoS_2) based HER catalyst, where doping a low content of atomic palladium using a spontaneous interfacial redox technique causes enormous boost in HER performance. This is the first report to unveil the MoS_2 redox feature and use it to induce interfacial heteroatom doping. We found that Pd replaces Mo at the surface, bonds covalently with S atoms at a coordination number of 4.3, causes SVs formation and phase conversion, and strongly activates the neighboring S sites for HER. The Pd–MoS_2 catalyst exhibits the highest activity towards the HER among phase-pure MoS_2 based materials in acid media. The overpotential for 1%Pd–MoS_2 at 10 mA cm^{-2} is only 78 mV cm^{-2}. More attractively, the more defective Pd–MoS_2 demonstrates better matrix stability than the pristine MoS_2. Therefore, the catalytic efficiency and stability problems for MoS_2 are addressed at the same time, leading to a promising future in replacing Pt based electrocatalysts for the HER.

Acknowledgments

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Highly Efficient ORR Electro-catalysts with Finite Number of Metal Atoms as Active Center

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Developing highly efficient, earth-abundant and stable materials for oxygen reduction reaction (ORR) in acidic electrolyte is extremely desirable but still challenging, which largely determines the prospect for industrial applications of proton exchange membrane fuel cell (PEMFC) technique. Pyrolyzed M-Nx/C catalysts (M=Fe, Co) are recognized as the most promising candidates to replace platinum towards the oxygen reduction reaction (ORR), according to the tremendous progress made in catalytic performance in the past years. However, further advance is hindered due to the unsatisfied intrinsic activity of the single-atom metallic center M-N_4 sites, which is far away from meeting the requirements to replace Pt-based catalysts for ORR in real applications.

Enlightened by the binuclear characteristic of the porphyrin catalyst site for ORR widely in biological respiratory systems, it is reasonable to predict the multi-metal-atom site structure for the pyrolyzed M-Nx/C catalysts can outperform the single-atom metallic center M-N_4 sites to catalyze ORR, which was proposed by previous theoretical calculations. Herein, we designed and successfully fabricated a series of novel binuclear active site structure as ORR catalyst site (Co-Co, Co-Cu, Fe-Cu, Fe-Ni, etc), which was achieved by precisely controlling precursor's structure at atomic level. Two-atom sites with atomic distance at approximately 2.15±0.1 Å were directly observed in the catalyst from aberration-corrected scanning transmission electron microscopy (STEM), which was also confirmed by the EXAFS with the observation of novel metal-metal coordination path. The further confirmation of the detailed coordination structure was assisted by density functional theory (DFT) calculation. Excitingly, dramatic enhancement on the ORR activity was obtained on the dual atom site, the highest activity of the dual metal sites exhibit on ORR on set potential at 1.02 V and half wave potential at 0.86V.The site activity is more than 1 magnitude higher than that of the single atom sites (CoN_4, FeN_4). Theoretical density functional theory calculations were applied to reveal the mechanism of ORR on the novel binuclear site, on which thermodynamic barrier towards ORR was considerably reduced, thus contributing to the much higher intrinsic activity of the dual atom center site. Our finding is of significance for rational designing non-noble metal catalysts to completely replace Pt for ORR in the future.

Acknowledgments

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Flexible nanoporous gold film based enzymatic biofuel cells for wearable biopower sources

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Enzymes are natural catalysts that harness metabolic reactions with high activities and selectivity. Oxidoreductase that are redox active can be immobilized onto inorganic electrodes and studied by electrochemistry, which is the basis for electrochemical biosensors and enzymatic biofuel cells (EBFCs). There is growing interest in fabrication of wearable biosensors for personal healthcare. Wearable EBFCs using sugars in tears or sweat are potential, miniaturized power sources for wearable microelectronics. Those applications require flexible, biocompatible and high-surface-area electrodes. Dealloyed nanoporous gold (NPG), which has 3D porous structure, can be an excellent candidate meeting all the requirements[1]. Our previous work verifies that NPG is promising as the supporting electrode of EBFCs with enhanced performance[2, 3]. Very recently, we have fabricated mechanically stable and flexible NPG electrodes by electrochemically dealloying Au/Ag alloy films that had been sputtered on plastic membranes[4]. Enzymes are then immobilized on the NPG electrodes and characterized for EBFC applications. Flexible NPG based lactate/O_2 EBFCs on commercial contact lenses give a power density of 1.7 ± 0.1 μW cm^{-2} in air-equilibrated artificial tear solutions, which is slightly lower than that obtained in phosphate buffer solution (PBS) (2.4 ± 0.2 μW cm^{-2})[4]. A quasi-solid-state and flexible EBFC can be worn on skin, consuming the reservoir of fuel stored in a hydrogel electrolyte, eliminating the need for sugar from sweat[5]. Such a device can also function as a self-powered biosupercapacitor, delivering pulses for over 600 cycles.

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Cu-based Electrocatalytic Reduction of CO_2 to Hydrocarbons

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The rise in CO_2 emissions caused by burning fossil fuels poses considerable risks to the environment and climate as well as all living creatures on the earth. Electrochemical conversion of CO_2 using electricity generated from renewable energy sources could provide viable solutions to the development of carbon-neutral fuels. However, CO_2 electroreduction is a kinetically slow and diverging reaction that requires a significant magnitude of overpotential and generates a myriad of products. Many electrocatalysts including solid-state materials and molecular complexes have been extensively investigated for CO_2 reduction reactions. Among all the materials studied, Cu metal has received substantial attention due to its distinct ability to generate reasonable amounts of hydrocarbon products, which requires addition of multiple electrons and protons to a CO_2 molecule and C-C bond formation. In the past several decades, a number of strategies have been developed to increase the performance of Cu based catalysts, including shape control, alloying, surface modification and oxidative treatment. However, the low catalytic durability, selectivity and activity remain as three major problems that have not been solved. In this presentation, I will show some of our original ideas and related progresses in solution to those troubles: 1) utilization of foreign metal atoms to induce surface restructuring for realizing self-cleaning metallic Cu catalysts against deactivation; 2) coordination of Cu atoms with molecular ligands to form heterogeneous molecular Cu catalysts for increasing the slectivity and activity towards hydrocarbons. Employing *in-situ* and *operando* X-ray absorption spectroscopy measurements, we found a reversible restructuring phenomenon for molecular Cu catalysts, and elucidated their real active sites.

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Studying Extreme Fast Charging of Li-ion Batteries Using a Reference Electrode

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Li-ion batteries (LIBs) permeate the modern world, powering from portable electronics to electric vehicles (EVs). While there exist compelling environmental arguments favoring mass adoption of EVs, the very long recharging times required by current battery technologies does not appeal to the majority of consumers. There is clearly a need for creating LIBs capable of extreme fast charging (rates >4C, or recharge times <15 minutes), which is made difficult by fundamental problems on both electrodes. The particles of layered oxide cathodes (as $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$, or NCM523), for example, may undergo fracturing during these high charging rates, due to strain gradients created by slow Li^+ diffusion.[1] Such fractures increase electrode impedance, further decreasing the power capability of the cell. On the other end of the battery, graphite anodes (Gr) become dangerously susceptible to the deposition of metallic lithium. As Gr operates at potentials close to 0 V vs Li/Li^+, polarization at high currents can render this Li plating favorable, creating reactive metallic domains that greatly accelerate cell failure.[2] Due to the diverse nature of these problems, a complete grasp of the causes and consequences of extreme fast charging can only be acquired if both electrodes are *individually* monitored as the battery operates. The electrochemical tool that provides such level of information is a reference electrode (RE). Here, we demonstrate how a Li micro-RE can report accurate potentials even during the passage of high currents in the battery, and how the experiment design affects the accuracy of such measurements (Figures 1a-b). We also use REs to discuss the effect of fast charge on electrode impedances, and of impedances on fast charge. Finally, we show how the thresholds for Li plating can be detected (Figure 1c), and how this information can be used to learn about the mechanisms of Li nucleation on the anode surface. The knowledge acquired from REs can benefit both applied and fundamental investigations, inspiring the design of experiments, materials, and methods to improve cell performance.

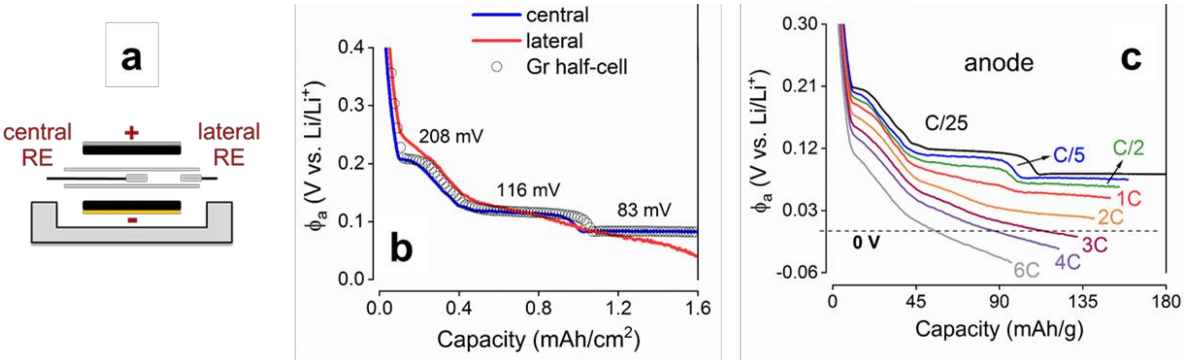

Figure 1. RE measurements in a NCM523//Gr cell: (a) schematic illustration of two configurations for 3-electrode tests, differing only by the positioning of the RE with respect to the cathode and anode. (b) Gr profiles during charging at C/25 as sensed by REs in the configurations shown in panel a. Data from a Li//Gr half-cell cycled at C/100 is also shown for comparison, and demonstrates how a *central* RE allows accurate measurements of electrode potentials. (c) Gr profiles recorded by a *central* RE while charging the cell to 4.39 V at the indicated rates. The dashed line indicates the threshold where Li plating becomes favorable.

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Remediation of soil polluted with hydrocarbons using reactive barrier and electrokinetic remediation

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In this work, a novel, original and ecological alternative to treat soils contaminated with diesel was proposed. Coupling two well-known technologies, electrokinetic remediation and permeable reactive barriers (PRBs), the depollution efficiency was evaluated; however, the originality of PRBs concept is the use, for first time, of cork as the main barrier were composition. The barrier was placed into the soil in different sections anode, central and cathodic compartments to favor the retention and adsorption of hydrocarbon due to the migration/diffusion effects promoted from soil to the anode during the electrokinetic remediation (ER). For this reason, SDS and Tween 80 were used as supporting electrolytes in cathodic reservoirs, in order to promote the mobility of organic compounds through the soil and consequently, decreasing the treatment time and costs. Additionally, the influence of direct current (DC) and reverse polarity (RP) approaches for applying electrical fields were evaluated for removing hydrocarbon from the soil. Results clearly indicated that, the novel PRBs concept was efficient when coupled with ER because higher hydrocarbons removals were achieved. During ER coupled to cork barriers, it was observed that the use of SDS and RP contributed positively to the transport of total petroleum hydrocarbons. At the end of the 20 days of depollution treatment, the cork contributed to increase the removal efficiency of hydrocarbon due to adsorption phenomena. Therefore, this technology provided a global treatment to soil without following treatments of the contaminated effluents.

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The Unusual Electron/Proton Coupling Behavior of Ultra-Reduced Polyoxometalate Clusters and Its Application for Flexible Energy Storage

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As our reliance on renewable energy sources grows, so too does our need to store this energy to mitigate against troughs in supply. Energy storage in batteries or by conversion to chemical fuels are the two most flexible and scalable options, but are normally considered mutually exclusive. Energy storage solutions that can act as both batteries and fuel generation devices (depending on the requirements of the user) could therefore revolutionize the up-take and use of renewably-generated energy.

POMs have already shown the promising application as proton/electron buffer for water splitting and some redox flow batteries.[1-3] However, the electron storage density in those systems are usually only around 1 or 2 electrons, thus results in low energy densities. Meanwhile, the physical and chemical properties behind the electron/proton coupling behaviours are rarely explored. Herein, we present a polyoxoanion, $[P_2W_{18}O_{62}]^{6-}$, that can be reversibly reduced and protonated by 18 electrons/H^+ per anion in aqueous solution, and which can act either as a high-performance redox flow battery electrolyte (giving a practical discharged energy density of 225 Wh L^{-1}), or as a mediator in an electrolytic cell for the on-demand generation of hydrogen.[4] Furthermore, it also shows some usual photophysical and magnetochemical properties of the ultra-reduced cluster.

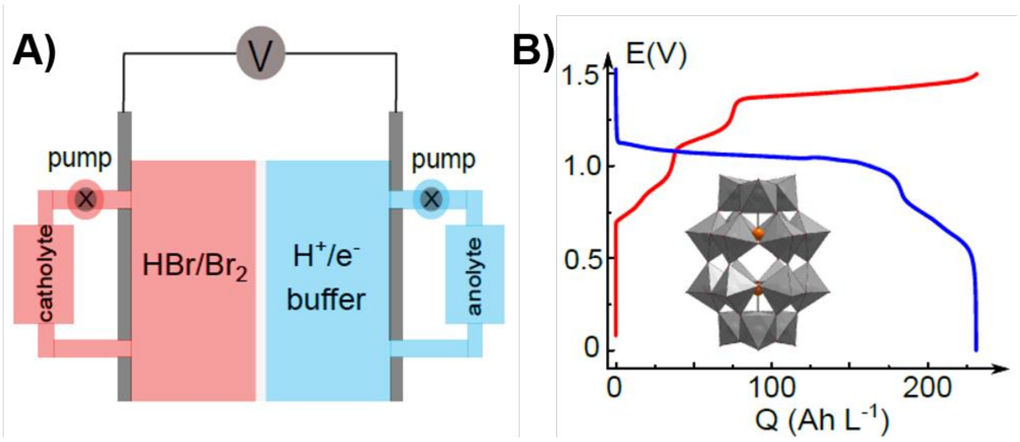

Figure 1. (A) The schematic of Li-Dawson cluster based redox flow battery and (B) the charging-discharging curves of 0.5 M Li-Dawson cluster in H_2O.

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Screening of Structured 3D Electrode Geometries to Overcome Mass Transfer Limitation Problems in Electrochemical Reactors

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In the next decades the chemical industry is facing a paradigm shift regarding its industrial production methods as government regulations will demand greener technologies. Electrochemistry is promising in this regard as electrons are used as driving force for the chemical reaction, omitting the need for expensive and polluting oxidizing or reducing chemicals. Moreover, the combination of an electron transfer with a chemical reaction allows to operate at ambient conditions. Electrochemistry, however, is inherent a surface process and as a result reagents have to be transported towards the electrode surface. If not mended, mass transfer will be limiting in electrochemical reactors, severely lowering the efficiency. Current strategies to increase mass transfer in electrochemical reactors exist in reducing the diffusion boundary layer at the electrode surface by incorporating turbulence promotors or via flow channels in the current collector plate. The adverse effects of the diffusion boundary layer are however primarily caused due to the fact that the electrode is planar. Using 3D electrodes fluid control can be achieved by the electrode geometry itself, no longer requiring external features [1].

In this work structured 3D electrodes were examined as a solution to overcome mass transfer limitation in electrochemical reactors, such as redox flow batteries. To enhance mass transfer while at the same time keeping pressure losses to a minimum, regularly structured electrodes were superior over disordered structures such as foams and felts. Through combination of experimental work and multiphysics computational simulations were the mass transport properties of varying 3D electrode geometries studied. To minimize pressure drop and inhomogeneous current distribution electrode geometries derived from static mixers were examined. Likewise, static mixers try to maximize rotational flow and enhance mass transfer at minimal pressure loss.

Through in-house developed additive manufacturing (i.e. indirect 3D printing) were structured all metal 3D electrodes fabricated in a low cost and rapid-prototyping manner [2], allowing on the one hand to experimentally study its mass transport properties but on the other hand also allowing to validate the computational model, setting-up a powerful tool to screen different geometries (Fig. 1). Using the limiting current technique mass transport properties were quantified, showing an increase in mass transport properties of 47% compared to flat electrodes. Hence, these electrodes showed severely improved mass transport properties, demonstrating the efficiency gain that can be achieved with structured 3D electrodes.

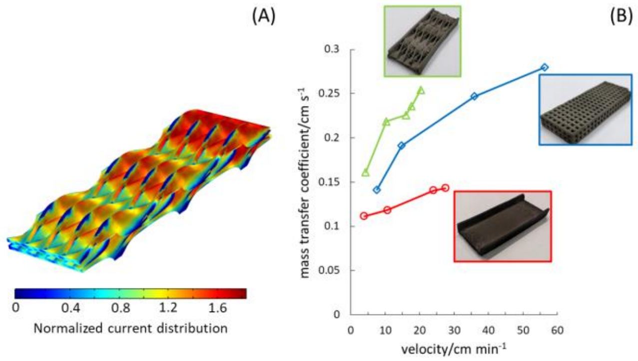

Figure 1: (A) Computational simulation of a helical 3D electrode. (B) Experimental limiting mass transfer coefficient as function of the velocity for a flat (red), cubic (blue) and helical (green) electrode.

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New Advances in Buckypaper Bioelectrodes: From Single Layers to Multilayer Structures for Energy In Vivo

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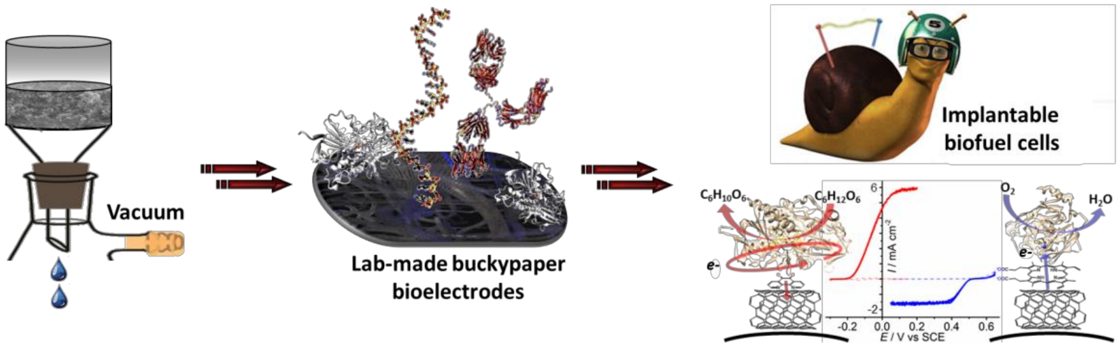
Buckypapers are self-supporting thin films of entangled carbon nantubes (CNTs), resembling an electronic paper, with excellent prospects for the construction of implantable and wearable catalytic interfaces for use in biological fuel cells (microbial and enzymatic), biosensors, and bioreactors [1-3]. Until now, the vast majority of reported buckypaper bioelectrodes have been prepared from a commercial source owing to its easy availability and properties including high conductivity and porosity, mechanical strength and flexibility, and lightweight [4,5]. This talk will present our latest developments and advances in buckypaper in the context of enzymatic biofuel cells for in-vivo applications. Our recent work on the fabrication, characterization and bioelectrocatalysis of lab-made and commercial buckypapers prepared with functional 'precision' polynorbornene polymers, redox molecules and enzymes (FAD-dependant glucose dehydrogenase and bilirubin oxidase) will be discussed [1,5,6]. New advances in the development of multilayer compression "mille-feuille" (custard slice) and biocompatible alginate electrodes will be presented, and the first in-vivo experiments with lab-made buckypapers in rats will be revealed.



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Extending the operating temperature range of ionic liquid-based EDLCs down to -50 °C by implementing binary mixtures and carbons with optimised porous texture

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Ionic liquids (ILs) are a solvent-free perspective class of electrolytes for high voltage electrical double-layer capacitors (EDLCs). They are characterized by high electrochemical stability, as well as they are neither volatile nor flammable. Therefore, ILs are superior to conventional organic electrolytes, e.g., 1 mol L^{-1} $TEABF_4$ in acetonitrile, which pose safety and toxicity concerns. However, the relatively high melting point of ILs restricts the scope of their applicability at low temperature compared to traditional EDLCs performing from -40 °C up to +70 °C. To overcome these limitations and to extend the operating range of EDLCs with ILs to sub-ambient temperature, their binary mixtures have been proposed as electrolytes [1]. Recently, a graphite oxide-based EDLC incorporating a binary mixture (1:1 by molar ratio) of 1-butyl-4-methyl-pyridinium tetrafluoroborate ($BMPBF_4$) and 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIBF_4$) could perform even down to -50 °C [2]. Nevertheless, as graphite oxide has a relatively low density, the resulting volumetric capacitance of such EDLC is very low.

The present study is focused on the use of imidazolium-based ILs, due to their relatively low viscosity and relatively high conductivity in contrast to their piperidinium or pyrrolidinium counterparts. Binary mixtures with various molar ratios were formulated using two ILs with 1-ethyl-3-methylimidazolium cation, $[EMIm]^+$, coupled with bis(trifluosulfonyl)imide $[FSI]^-$ or tetrafluoroborate $[BF_4]^-$ anions. Some mixtures did not show any first order transition unlike the parent ILs, and remained liquid below -90 ºC, where they underwent devitrification. The temperature dependence of the dynamic viscosity and ionic conductivity of the pure ILs and their mixtures followed the Vogel-Tamman-Fulcher equation, while the corresponding Walden plot revealed a high degree of ionicity classifying them as “good ILs”. Accordingly, we selected the $EMImFSI/EMImBF_4$ (1:1 molar ratio) mixture, as it exhibited only a glass transition at -97°C (Fig 1a), relatively low viscosity of 33.0 mP s and relatively good conductivity of 12.1 mS cm^{-1} (at 20 °C).

To uphold the low-temperature performance of carbon-based EDLCs in the $EMImFSI/EMIMBF_4$ (1:1 molar ratio) electrolyte, we applied electrodes made of mesoporous materials: SC2A carbon black (by Cabot, $S_{DFT} = 1502$ m^2 g^{-1}; $V_{meso} = 1.05$ cm^3 g^{-1}) and an home-made carbon [3] MP98B ($S_{DFT} = 1556$ m^2 g^{-1}; $V_{meso} = 1.30$ cm^3 g^{-1}) having well-defined mesopores with average size of 3.5 nm. Both EDLCs operated down to -50 ºC (Fig 1b, c), while at this temperature the cell based on MP98B exhibited lower resistance and higher gravimetric capacitance (106 F g^{-1*} vs 73 F g^{-1*}).

* the capacitance values are expressed per average active mass in one electrode.

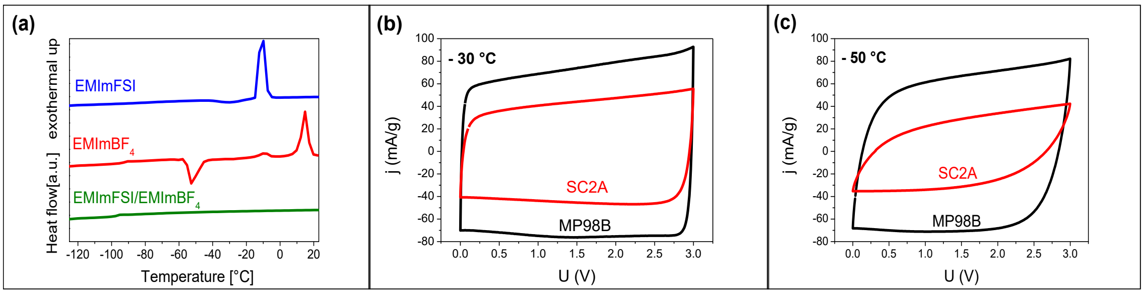

Figure 1: *(a) DSC thermograms of neat ILs and $EMImFSI/EMIMBF_4$ upon heating at 10 K min^{-1}; Cyclic voltammograms ($v = 1$ mV s^{-1}) of EDLCs based on SC2A and MP98B electrodes in $EMImFSI/EMIMBF_4$ (1:1 molar ratio) mixture at (b) -30 °C and (c) -50 °C.*

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Early stage detection of cancer biomarkers using Nano-materials based sensors

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Abstract:

Electrochemical sensors based on Nano-materials modified electrodes hold a great promise to serve as suitable devices for point-of-care diagnostics. They can allow for a simple, rapid, and inexpensive multiplexed analysis with remarkable reproducibility and ease of miniaturization. Moreover, the use of nanostructured surfaces, offer new opportunities for highly sensitive cancer biomarkers detection. In fact, the unique electronic and optical properties of nano-materials, in conjunction with their size and robust nature, make them crucial to the development of bio-sensing platforms[1].

Cancer is the leading cause of death in developed countries and the second leading cause of death in developing countries, after heart disease. In 2008, 7.6 million people died of cancer globally, which equates to 21,000 cancer deaths a day. By 2030, 21.4 million new cancer cases are expected to occur globally with 13.2 million cancer deaths [2]. A serious limitation involved in several types of cancer is the absence of non-invasive and early stage warning procedures. Therefore, there is an urgent need for uniform, early stage screening methods[3]. In this context, we have been interested in the development of electrochemical sensors for the detection of cancer biomarkers as early stage, which is very important for successful diagnostic of the disease, patient survival and makes a challenge and critical step for cancer therapy. The different experimental measurement conditions have been optimised and the biosensors response has been checked using different techniques such as cyclic voltammetric (CV), stripping square wave voltammetry (SSWV), differential pulse voltammetry (DPV) and impedance spectroscopy (EIS). The obtained promising performances, in addition to their good selectivity and stability, has allowed to test their response in real samples such as urine and serum demonstrating the potential of the developed biosensors for the point of care clinical applications.

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Improving the durability of membrane electrode assemblies during voltage reversal

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During the operation of proton exchange membrane fuel cells (PEMFCs) instances occur in which the cell may be starved of fuel, especially during start up and shut down processes. During these occurrences, while the cathode potential would decrease, a significant increase in anode potential occurs, resulting in cell voltage reversal. The anode potential increases to >> 1.2 V in which the terminal cell voltage can go from 1.0 V to -2.0 V in seconds. The cell will consume energy instead of supplying it, resulting in accelerated electrode degradation. There are two primary mitigation strategies for cell reversal: systems management and materials modification. Auxiliary systems parasitic loads and can be complex, bulky and difficult to install. In this study, materials modification was made to the anode catalyst layer of a standard commercial membrane electrode assembly (MEA). The most common methods generally include the addition of additives or an oxygen evolution reaction (OER) catalyst to promote water electrolysis over catalyst corrosion in the catalyst layer. An in-house MEA was made using unique combinations of additives and catalysts, while optimizing the electrode design which improved the durability of the MEA during cell reversal events.

The MEAs were tested using simulated fuel starvation induced voltage reversal events. Herein, the anode gas was switched from H_2 to N_2, while asking a current of 200 mA.cm^2. The event, or test, stops when the cell reached critical failure at -1.5V. The reversal tolerance of the anode was determined by how long the cell could remain in cell reversal, before reaching critical fail. This work presents a MEA with an anode design which could remain in cell reversal for up to 90 minutes, meeting international fuel cell manufacturer specifications. The in-house MEA increased the anode reversal tolerance by close to 200%, compared to an unmodified standard commercial MEA, which failed after 5 minutes. The designed reversal tolerant MEA, could also maintain 95% of its original performance before and after cell reversal testing. The integrity of the MEAs was monitored using X-ray photoelectron spectroscopy, X-ray fluorescence as well as electrochemical evaluations, including Electrochemical Impedance Studies and Cyclic Voltammetry, to determine the impact of the events on the catalyst layer. The physical and electrochemical evaluation of the MEAs showed that the reversal tolerant events impacted on both the catalyst support as well as the ionomer in the catalyst layer.

Treatment of wastewater with electrochemical methods: Opportunities and side reactions that should be considered

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The treatment of wastewater by electrochemical methods offers the opportunity to oxidize organic matter. By this approach, harmful and unwanted substances can be reduced, contributing to less contaminated water with lower impact on our aquatic environment. One method well known is the use of boron doped diamond (BDD) anodes enabling use of the high oxidation potential of OH-radicals for the mineralization of organic matter. In most examples reported in literature, the cathode does not contribute to the purification process. However, if the cathode is a gas diffusion electrode (GDE) it can be designed to produce hydrogen peroxide (H_2O_2). As a result, both electrodes can act simultaneously to lower organic matter contamination and the applied electric current causes electrochemical oxidation in both half-cells of the electrolyzer, which can improve current efficiency theoretically up to 200 %.

BDD electrodes are available in technical dimensions, but the GDEs for the cathode compartment are not. Therefore, within the radar project (https://machwas-material.de/) a carbon-based GDE was developed in cooperation with Covestro AG, which can be manufactured in technically relevant dimensions.

The activity of carbon materials for the 2-electron step of H_2O_2 formation is been known for a long time and most electrodes for electrochemical H_2O_2 synthesis are based on carbon. On the one hand, they enable the two-electron reaction step on the other hand, they offer large BET surface areas and thus excellent electro catalyst support qualities. Moreover, they are inexpensive and offer sufficient chemical and thermal stability.

In addition to the technical electrode design, the operation mode has a great influence on hydrogen peroxide production. During the electrolysis process the pH-value at the cathode shifts to higher values and the conditions for H_2O_2 formation shift as well. Without controlling the pH at the cathode it is not clear which pH value is the best for optimal H_2O_2 formation. [1] In our investigation, the pH value was kept at constant levels by balancing the pH shift with controlled dosing of water whereas the pH at the acidifying anode is kept constant by dosing sodium hydroxide. The current density was at least 0.5 kA/m^2, important for the design of compact technical reactors. By this approach stationary operation was reached, allowing to identify the best conditions for H_2O_2 formation.

The composition of the treated water also has great influence on the treatment process. As mentioned above the cathode shifts into alkaline pH-values during operation. This can cause precipitation reactions on the cathode. Generally, this is not desired, since the cathode can get covered by deposits, lowering efficiency and lifetime. [2] Nevertheless, this offers the opportunity to remove water hardness components [3] and this aspect was also investigated during our work. For this approach, another cathodic concept was invented and evaluated, which is based on in-situ moving cathodes.

Our H_2O_2–GDE investigations show that varying temperatures between 15 °C and 50 °C influence the H_2O_2 yield. Increasing the temperature from 15 °C to 20 °C, H_2O_2 production changed only slightly, but with further temperature increase from 25 °C to 60 °C, H_2O_2 current efficiency decreased significantly due to H_2O_2 self-decomposition. Furthermore, the present carbon-based GDE produces H_2O_2 with current yields greater than 90 % at 15 °C electrolyte temperature at a current density of 0.5 kA/m^2, but also up to 2 kA/m^2. In addition, the choice of the pH value is critical with respect to attainable H_2O_2 concentration.

The application of the cathodic pH shift for the decalcification of wastewater was also studied and is working, but the precipitation of carbonaceous matter or phosphates on the cathode as a side reaction depends strongly on the buffer capacity of the treated water, requiring a profound adaption of the water treatment process.

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Structure dependent electrocatalytic properties of nanoporous gold: A mechanistic study of ascorbic acid and dopamine electrode reactions kinetics

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Understanding of electrode reactions kinetics of electroactive compounds on porous nanomaterials like nanoporous gold (NPG) is very important to design an electrocatalysts for specific applications. In this aspect, NPG materials were electrosynthesized through Dynamic Hydrogen Bubble Template [1] approach from 5 mM gold chloride in 0.5 M H_2SO_4 precursor solutions and the optimized platform was employed to investigate electrode processes of Dopamine (DA) and Ascorbic Acid (AA). Comparison of anodic oxidation of DA and AA on NPG through cyclic voltammetry (CV) revealed that DA oxidation proceeded through 3-fold enhancement in anodic current, but no change in overpotential, whereas AA oxidation followed a 350 mV cathodic shift in overpotential but no change in current (Fig. 1a and 1b) compared to bare gold electrodes. Such voltammetric responses confirmed that DA and AA oxidation on NPG surfaces takes place through different mechanism and each of the compounds might have affinity towards particular structural features (porosity, surface area, crystalline facets and defects) of NPG. A comprehensive reaction kinetics study by Electrochemical Impedance Spectra (EIS) using NPG and bare gold electrodes further revealed 10 times smaller R_{CT} of AA than DA on NPG surfaces, which corresponds to faster heterogeneous electron transfer (HET) rate for AA oxidation than DA. Moreover, HET rate of AA oxidation was faster on NPG than gold electrode in contrast to DA, in which they were similar on both surfaces. These kinetic parameters were correlated with the structure of NPG and a possible interaction of AA and DA with the electrode has been presented (Fig. 1e). Because of relatively slower HET rates, DA resides longer time close to NPG film before getting oxidized, thus penetrates deeper within the NPG volume. Hence, a higher proportion of the active area is used, in contrast to AA oxidation which remains confined closed to surface of the NPG owing to the faster HET rate. This also explains the 3-fold enhancement in oxidation current in CV of DA, but no change for AA. The faster HET rate of AA is justified by its specific affinity with crystalline defects in NPG, which reduces the activation energy of the oxidation process as demonstrated by the cathodic shift in the oxidation overpotential in Fig. 1b. Such reaction kinetics study can be extremely useful in designing a selective NPG electrocatalysts for either AA or DA sensors.

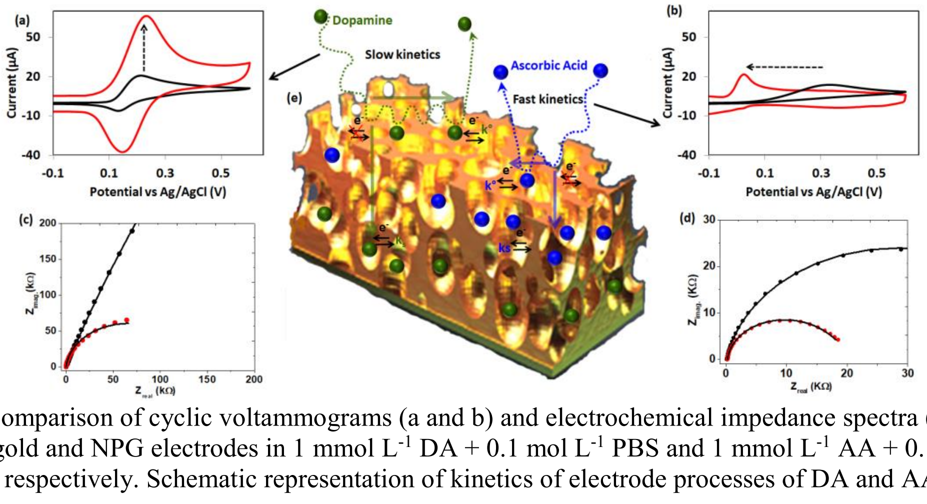

Fig 1: Comparison of cyclic voltammograms (a and b) and electrochemical impedance spectra (c and d) of bare gold and NPG electrodes in 1 mmol L^{-1} DA + 0.1 mol L^{-1} PBS and 1 mmol L^{-1} AA + 0.1 mol L^{-1} PBS respectively. Schematic representation of kinetics of electrode processes of DA and AA (e).

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Nucleic acid hybridization-induced electrically reconfigurable network of gold-coated magnetic nanoparticles enables ultrasensitive microRNA detection in blood

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The intense interest in quantifying levels of microRNA is because of its importance as a blood-borne biomarker. The challenge has been to develop methods that can monitor microRNA expression both over broad concentration ranges and ultralow amounts directly in a patient's blood. Here, we show using gold-coated magnetic nanoparticles modified by probe DNA (DNA-Au@MNPs) that possess a redox label. The DNA-Au@MNPs diffuse through the sample for analysis and collect the majority of miRNA in a sample before being brought back to the electrode. The resultant microRNA sensor is able to detect concentrations of microRNA from as low as 10 aM to 1 nM in unprocessed blood samples. The exceptionally low detection limits are a result of an unexpected amplification process where hybridisation of a single DNA-microRNA duplex switches off the electrochemistry from hundreds of DNA-Au@MNPs. This amplification system appears to be *via* an electric-field-induced reconfiguration of a network of DNA-Au@MNPs. The highly-sensitive biosensor is capable of direct analysis of nucleic acids in samples as complex as whole blood. It can distinguish small variations in microRNA concentrations in blood samples of animal models that occur due to the presence of a tumour with changes in miRNA levels detected by the biosensor correlated with real-time polymerase chain reaction (qRT-PCR) analysis of the same blood samples. The ultrasensitive and direct detection of microRNA using electrically-reconfigurable DNA-Au@MNPs network makes the reported device a promising tool for cancer diagnostics.

An extended homogenized FEM model for Li-ion Batteries

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Future expectations on lithium-ion batteries (LiB) are increasing energy density, power density and lifetime. Computational models are essential for performance analysis and prediction. Constant current measurement methods are limited for model parameterization, whereas electrochemical impedance spectroscopy evaluates the cell impedance over a wide frequency range (μHz ... MHz).

In this work an extended homogenized FEM model is introduced, experimentally parameterised and validated. The model is based on the Newman model published in 1975 [1, 2], and extended to a particle size distribution instead of a single particle diameter [3]. Thus, the electrochemical coupling between particles of different particle size can be studied. The extended homogenized FEM model is validated with a parameter set derived from a commercial high power cell (KOKAM SLPB 283452H pouch cell). The microstructure parameters (volume fractions, tortuosity, particle size distribution, active surface area) are determined by microstructure reconstruction (focused ion beam/scanning electron microscopy and high-resolution Xray tomography [4, 5]), the open circuit potentials of the electrodes are measured by constant current discharge and charge with C/40 and the reaction rate as well as the SEI-resistance are obtained by fitting of physically based equivalent circuit models to measured impedance spectra of cathode and anode characterized in experimental cells [6]. In order to enable a detailed validation of the implemented processes, the model was extended for simulations in the frequency domain and simulated spectra were compared to measured ones. This approach enables the deconvolution of the individual loss processes of each electrode by their relaxation times. Deviations between the model and measurements will be discussed and approaches to calculate not directly measurable parameters will be presented.

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Catalysts for Electrochemical Hydrogen Purification and Compression

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As the rate of commercialization of water electrolysers and hydrogen fuel cells continues to grow, the drive towards more sustainable, energy efficient and competitive hydrogen processing technologies increases. The Electrochemical Hydrogen Pump (EHP) is an isothermal process which, theoretically, allows for compression of hydrogen with higher efficiencies than conventional mechanical compression[1]. This electrochemical compression of hydrogen utilises the hydrogen oxidation reaction (HOR) and hydrogen evolution reduction (HER) to pressurise hydrogen for PEM Fuel Cells and other applications.

In addition to compression, the EHP allows for purification of hydrogen due to the proton selective proton electrolyte membrane (PEM) (Figure 1), however, the Pt catalysts used on the anode are poisoned by the contaminants in the hydrogen feed. This talk will discuss the MEMbrane based Purification of HYdrogen System (MEMPHYS) project which investigated active Pt/C and PtNi/C catalysts for the anode and cathode reactions, as well as poison tolerant PtRu/C catalysts for the anode of EHP systems. Moreover, poison mitigation strategies, such as an oxygen bleed and ozone bleed, were also investigated in order to assist in the oxidation of contaminants from the catalyst surface.

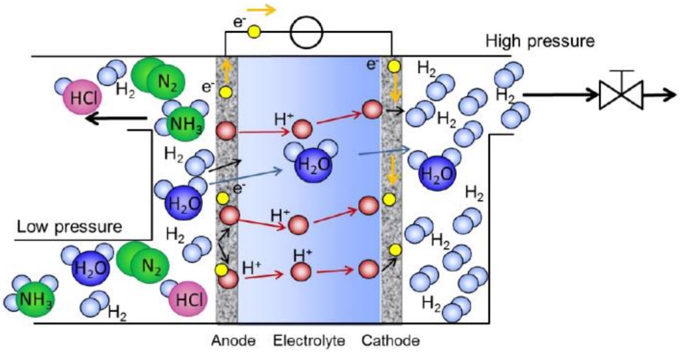

Figure 1: Schematic of the Electrochemical Hydrogen Compression (EHC) setup[2], showing the HOR in the presence of contaminants at low pressure on the anode and HER at high pressure on the cathode.

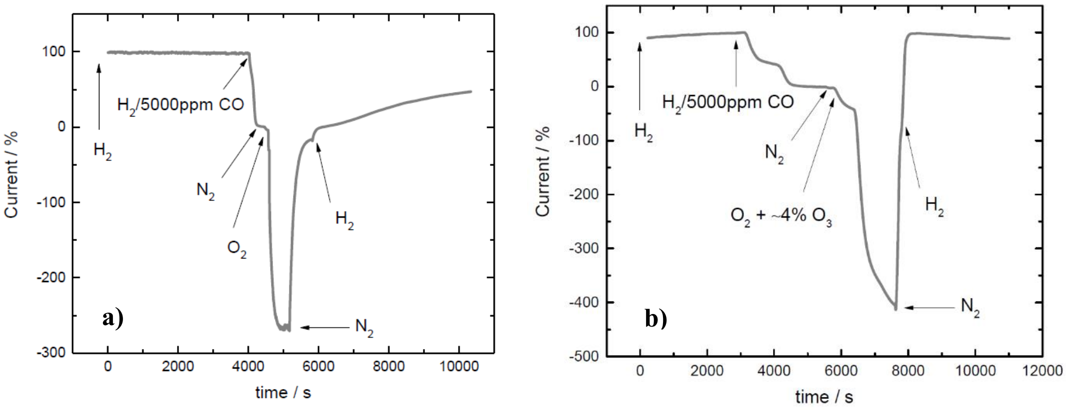

Figure 2: The effect of a) oxygen and b) ozone/oxygen regeneration on the catalyst performance for HOR after poisoning with 5000 ppm CO, measured using the rotating disc electrode with a rotation rate of 1600 rpm in 0.1 M $HClO_4$ at room temperature and pressure.

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Experimental and Model-Based Characterization of Gas-Diffusion Electrodes for Oxygen Reduction

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In gas diffusion electrodes (GDE), electrocatalysts are in contact with gas and electrolyte ensuring a large active three-phase boundary. GDE are used for important technical applications in energy transformation and chemical synthesis such as fuel cells and modern electrolysis processes. Silver-based GDE have been commercialized for a new energy-efficient chlor-alkali process [1] and are presently also under investigation for CO_2 electrolysis [2]. Our research unit studies the interplay of reaction and transport processes in silver-based GDE during oxygen reduction in alkaline electrolyte with a variety of modern methods. Specifically, it is aimed to analyse the local distribution of pore sizes and surface properties in GDE, to carry out *in situ* analysis of electrolyte distribution and local measurement of activities, and to develop mathematical models for the electrode performance during steady-state and transient operation.

GDE with different properties are prepared from Ag powders and PTFE suspensions via spraying on nickel nets. Electrodes with low overvoltage during oxygen reduction at typical chlor-alkali conditions (80 °C, 30 wt.% NaOH) contain 2 – 5 wt.% PTFE and have average pore sizes of 1 – 3 µm. GDE with even lower PTFE content suffer from electrolyte flooding whereas higher PTFE contents lead to insufficient liquid penetration. Figure 1 (left) shows the result of a tomographic analysis revealing intimate contact between silver electrocatalyst and PTFE binder. The intrusion of liquid electrolyte in the pores is mathematically modelled (Fig. 1 middle) while first results of in situ measurements of a working GDE depicted in Fig. 1 (right) provide insight into the electrolyte transport under reaction conditions.

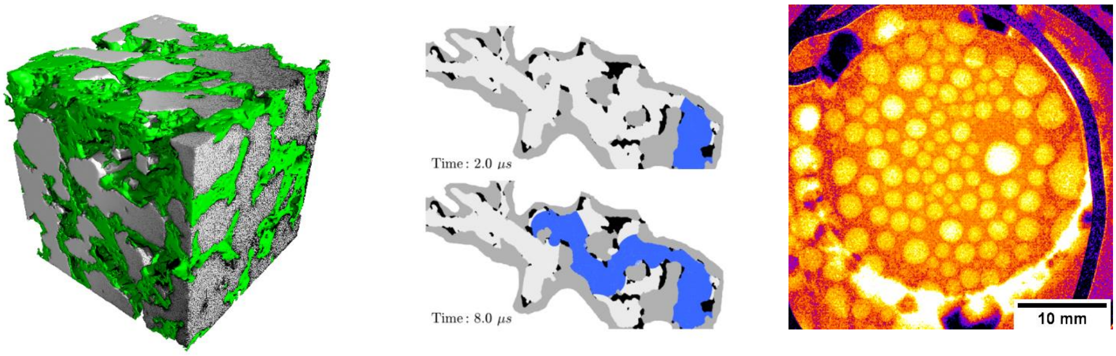

Fig. 1. Distribution of Ag (grey) and PTFE (green) in a GDE (left), simulated intrusion of electrolyte in pore structure (middle), measured liquid distribution in working GDE (right).

The measurements of the electrolyte distribution are supported by calculations of the contact angles during fluid-solid interactions in the GDE [3]. Electrode structure and electrolyte distribution are used together with the oxygen reduction kinetics to develop a mathematical model for the description of the overvoltage. In contrast to earlier assumptions that only the low oxygen solubility and diffusivity limits the achievable GDE performance at higher current densities [4], recent findings indicate that local changes in the activity of OH^- ions and H_2O must be also taken into account [5].

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Development of Electrochemical Sensors Based on Molecularly Imprinted Polymers for Emerging Pollutants Determination

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Molecularly imprinted polymers (MIPs) are considered as stable polymers with molecular recognition abilities, provided by the presence of a template during their synthesis. They are generally used to mimic the natural biological receptors. MIPs offered various advantages over antibodies such as robustness, with high stability and required low-cost preparation towards the targeted analyte. Recently, we reported various applications of MIPs based electrochemical sensors for the determination of different emerging pollutants and contaminants such as sulfonamides, 17-β-Estradiol, Bisphenol A (BPA) as well as bacterial spores.

Regarding the sensitive and selective sulfonamide determination, we have developed an impedimetric sensor based on hybrid nanomaterial based on decorated magnetite nanoparticles by the MIPs. This novel sensing strategy allowed detecting sulfonamide at very low concentrations with a LOD of 10^{-12} mol.L^{-1} and its application to screen sulfonamide in seawater samples showed the applicability of this promising analytical method [1]. Concerning the 17-β-Estradiol selective detection, we recently reported a novel biomimetic sensor based on the modification of screen-printed electrodes by a nanocomposite of magnetic MIPs (Fe_3O_4-MIP) that amplifies the oxidation current of 17-β-Estradiol allowing a LOD of 20 nM. Furthermore, the Fe_3O_4-MIP sensing system exhibits a high selectivity towards 17-β-Estradiol and was applied successfully for its determination in river water samples [2].

Our research group has developed recently another application for the use of MIPs to detect BPA. This analytical strategy consists on a new mode of adsorption and separation methods using the magnetic molecularly imprinted solid phase extraction technique combined with a nanocomposite carbon black and gold nanoparticles sensor for BPA detection. The sensing approach exhibits a high sensitivity in the concentration range of 0.07 µM to 10 µM with a LOD of 8.8 nM. The combination of the developed sensor with the ultrasound-assisted magnetic molecularly imprinted polymers allowed a high affinity towards BPA compared to other interfering species [3].

Recently, we reported the first spore-imprinted polymer (SIP) based sensor for the detection of bacterial spores. Indeed, a simple, low cost and selective electrochemical sensor for *Bacillus Cereus* spores detection was developed. The proposed method is based on SIP, exhibits a high selectivity to *Bacillus Cereus* spores, and allowed the detection of 10^2CFU/mL of *Bacillus cereus* spores.

Since MIPs synthesis time is one of the drawbacks of the use of MIPs, we have introduced recently for the first time a developed fast method for MIPs synthesis based on High-energy ultrasound assisted probe. The novel synthesis strategy allowed a reduction of MIPs synthesis time from several hours to a few minutes. The synthesized MIPs exhibits good adsorption properties towards sulfonamide detection [5].

A general overview on the electrochemical methods based on MIPs will be presented and discussed.

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Electrochemical Machining on Semiconductor by Photocorrosion

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In the past several decades, electrochemical machining (ECM) has enjoyed the reputation of a powerful technique in the manufacturing industry. Conventional ECM methods can be classified as electrolytic machining and electroforming: the former is based on anodic dissolution and the latter is based on cathodic deposition of metallic materials. Strikingly, ECM possesses several advantages over mechanical machining, such as high removal rate, the capability of making complex three-dimensional structures, and the practicability for difficult-to-cut materials. Additionally, ECM avoids tool wear and thermal or mechanical stress on machining surfaces. Thus, ECM is widely used for various industrial applications in the fields of aerospace, automobiles, electronics, etc.

However, with the rapid industrial development of microelectromechanical systems (MEMS), ultralarge scale integration circuits (ULSI) and miniaturized total analysis systems (μ-TAS), the machining demands on semiconductor wafers are becoming more and more urgent. The challenges for the traditional wet chemical etching are the controllability and accuracy of the machining processes. Here we present the ECM on semiconductor wafers based on a controllable photocorrosion.

The principle of photocorrosion is actually the photoelectric effect. When semiconductor is illuminated, charge separation will occur and result in the localized potential distribution across the semiconductor-solution interface. If the photogenerated electrons are transferred to the electron acceptors in the solution, the illuminated area of the semiconductor wafer will be polarized anodically. This phenomenon can be controlled well by the illumination intensity and the redox couple used in the electrolyte solution.

The machining method can be either the direct writing or template forming. In this talk, we will give a fast glance of our previous work and then focus on our newest progresses in this domain.

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Highly Selective Pt/TiO$_x$ Catalysts for the Hydrogen Oxidation Reaction

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A major durability issue of fuel cells is the long-term stability of the cathode, especially during start-up and shut-down (SUSD) events, when a H_2/air gas front passes through the anode.[1] In the air-filled segment of the anode, the oxygen reduction reaction (ORR) takes place, while carbon oxidation as well as H_2O oxidation take place at the adjacent segment of the cathode, leading to its degradation. Several mitigation strategies have been explored, including reduced residence times of the H_2/air front and/or using corrosion resistant graphitized carbon or conductive oxide supports for the cathode catalyst.[1-2] However, retarding/preventing the ORR of the anode catalyst without compromising its activity towards the hydrogen oxidation reaction (HOR) would significantly reduce the degradation of the cathode during SUSD.

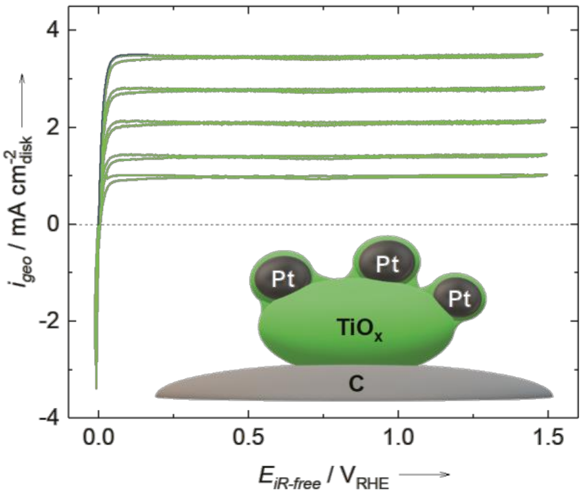

Figure 1: HER/HOR polarization curves recorded in H_2-saturated 0.1 M $HClO_4$ showing the high potential HOR-performance of the Pt/TiO$_x$/C catalysts.

Here we report on a novel anode catalyst which is selective for the HOR, i.e., which exhibits poor ORR activity while retaining high HOR activity.[3] The catalyst consisting of platinum nanoparticles (≈2.8 nm diameter) supported on titania nanoparticles (TiO$_x$ with ≈10 nm diameter) which in turn are attached to a carbon-support (Pt/TiO$_x$/C) was synthesized as follows: i) preparation of TiO$_x$ nanoparticles via hydrolysis of a titania precursor; ii) synthesis of Pt nanoparticles using a polyol process; iii) adsorption of the Pt particles onto the TiO$_x$ particles; and, iv) adsorption of Pt/TiO$_x$ onto a Vulcan carbon support. Finally, the as-produced Pt/TiO$_x$/C material was heat-treated in reductive atmosphere (5% H_2/Ar) to yield the final catalyst. The formation of a strong metal-support interaction (SMSI) resulting in the encapsulation of the Pt particles by a layer of TiO$_x$ is evidenced by high resolution transmission electron microscopy (HR-TEM). This SMSI effect is ascribed to cause the very high HOR selectivity of these Pt/TiO$_x$/C catalysts which is desired to mitigate SUSD in fuel cells. Rotating disk electrode (RDE) experiments were performed to demonstrate the uncompromised HOR and the reduced ORR activity of the catalysts compared to a Pt/C catalyst synthesized from the same batch of Pt nanoparticles. This results in the superior HOR selectivity of these Pt/TiO$_x$/C catalysts, defined as the ratio of the HOR over the ORR activity. Furthermore, catalysts with an optimized heat treatment exhibit a high resistivity towards Pt oxidation, thus being capable of oxidizing hydrogen at potentials as high as 1.5 V vs. the reversible hydrogen electrode (RHE) potential, so that it could be used as a co-catalyst in water electrolyzer anodes which would eliminate crossover H_2.

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Enhancing photoelectrochemical redox batteries by depositing gold nanoclusters on TiO_2 films.

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Photoelectrochemical processes have been widely studied for water splitting [1] and for the dye-sensitized solar cell [2]. Lately a new concept has emerged: the photoelectrochemical redox flow battery [3]. In a photoelectrochemical redox flow battery, the adsorption of a photon by the photoanode generates an electron-hole pair, with this hole oxidizing the positive electrolyte redox couple at the photoanode and the electron reducing the negative electrode redox couple at the cathode. In these systems, the obvious choice of the semiconductor as the photoanode is TiO_2 due to its band-gap, compatibility of its energy levels with the majority of the redox flow battery systems [4] and stability under photoanodic conditions. Unfortunately, in these systems, the photocurrents achieved are not high enough for a commercial device. As an example, the best photocurrent reported is around 0.25 mA cm^{-2} when using a WO_3/TiO_2 photoanode in an all-vanadium solar redox battery illuminated by AM 1.5 light [5]. This photocurrent is equivalent to an external quantum efficiency of 0.8 %. The major issues with this system is that the band-gap of TiO_2 means that this only adsorbs UV light (wavelengths < 390 nm) and is characterized by a high recombination rate of the electron-hole pair. To reduce the band-gap, the TiO_2 can be doped [6] or improved through the deposition of metallic nanoparticles [7]. Gold nanoparticles are particularly useful due to their surface plasmon resonance in the visible light region and their ability enhance photocatalytic reactions. In our work, we have studied the possibility of using gold nanoparticles and atomically precise gold nanoclusters to enhance the photoanodic currents in a vanadium photoelectrochemical redox battery. We find that small gold clusters can significantly enhance photoanodic currents compared to bare TiO_2 surfaces, especially when these clusters are sintered to promote surface plasmon resonance.

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Advanced Electrocatalysts Based on Metal Nanoclusters

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Due to the size-dependent unique physical and chemical properties resulting from the discrete energy levels and band-gap energy structures, metal nanoclusters consisting of several to hundreds of atoms have attracted intensive attention and show promising application in catalysis. We report here the synthesis of metal nanoclusters with controlled composition and size through chemical reduction processes by using porous nanostructures as templates. After loading the as-synthesized metal clusters on different substrates, the nanoclusters were successfully applied to the electrocatalysis. Compared to large metal nanoparticles, the nanoclusters exhibited higher electrocatalytic activities for oxygen reduction reaction and hydrogen evolution reaction etc. [1-6]

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Ruthenium – Cobalt Phosphide Hybrid Clusters with Superior Electrochemical Hydrogen Evolution Performance

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RuCoP (**Figure 1a**) are prepared and show superior electrocatalytic performance for the hydrogen evolution reaction (HER), with overpotentials of merely 11 and 23 mV to deliver a cathodic current density of 10 mA cm^{-2} in 0.5 H_2SO_4 and 1.0 M KOH, respectively (**Figures 1b and 1c**).[1] Their turnover frequencies (TOFs) are as high as 10.95 and 7.26 s^{-1} at 100 mV in 0.5 H_2SO_4 and 1.0 M KOH (**Figures 1d and 1e**). Density functional theory calculations indicate that the RuCoP hybrid exhibits a hydrogen adsorption energy very close to that of platinum and water and –OH adsorption energies distinct from pristine Ru, which reasonably explain the experimentally observed excellent HER activities (**Figures 1f, 1g and 1h**).

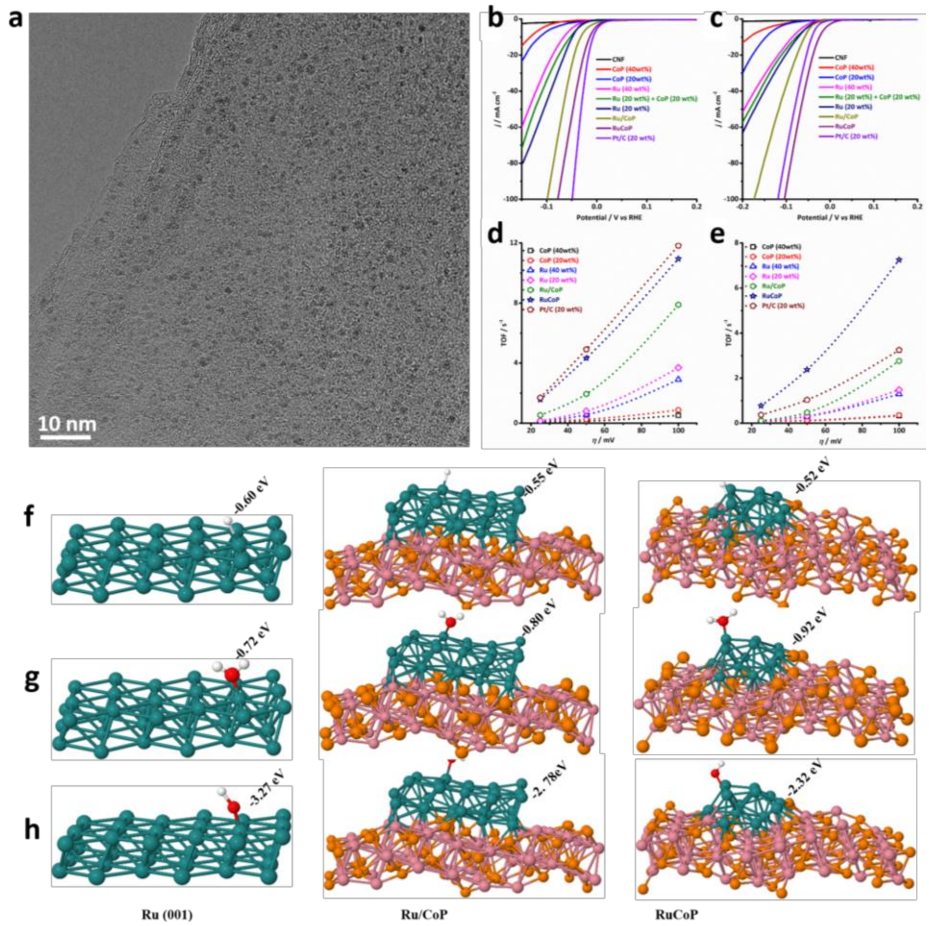

Figure 1. (a) TEM of RuCoP catalyst. *iR*-corrected polarization curves of RuCoP and reference catalysts with the loading of 0.30 mg cm^{-2} in 0.5 M H_2SO_4 (b) and 1.0 M KOH (c). TOF Comparison in 0.5 M H_2SO_4 (d) and 1.0 M KOH (e). The adsorption energies of (F) H, (c) H_2O and (d) –OH on RuCoP and other Ru-based catalysts.

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Glucose Oxidation on Carbon Supported Electrode Materials in Alkaline Medium

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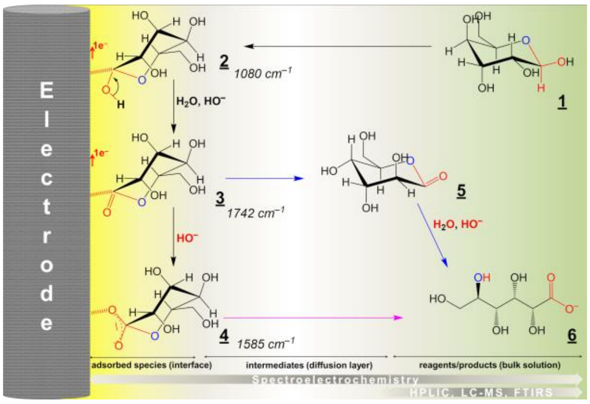
The development of organic molecule-based fuel cells mostly relies on designing efficient anode materials capable of withstanding the poisoning effect of strongly adsorbed species at lower potentials, which prolongs the durability of the catalytic process. So as to obtain catalysts with excellent ability towards organic fuel oxidation, electrode materials were synthesized from a surfactant-less method, to single out different promotional effects in the activation and removal of adsorbed species from the electrode surface.

In this work, glucose was used as an organic fuel for its direct conversion to electricity and value-added chemicals. Physical characterizations of the anode catalysts permitted to correlate their elemental composition and structure to their electrochemical activity towards glucose electro-oxidation. Carbon monoxide (CO) considered as the main poisoning species in organic oxidation was utilized in a CO-stripping method to probe the electrode surface. An unprecedented potential shift of its removal toward lower values allowed the comprehension of the CO-to-CO_2 reaction mechanism and the re-design of the catalyst composition in accordance with a selective glucose electro-conversion. It was thus observed that the glucose oxidation strongly depends on the nature of the catalysts, the metallic composition and the carbon substrate (Vulcan, reduced graphene oxide...). Complementary analytical techniques were employed to probe the glucose oxidation process, which enables to determine the resulting reaction compounds and thereby, to understand reaction mechanisms of their formation over the studied electrode materials (Scheme 1). Gluconate was found to be the main reaction product that showed a selective 2-electron conversion of glucose (Figure 1).

This multivariate study coupling electrochemical techniques with spectroscopic and chromatographic methods decisively advances the research towards more effective electrochemical cogeneration devices wherein bio-resources such as (oligo)saccharides are selectively oxidized towards high value chemicals.



Scheme 1. Glucose electro-oxidation to gluconate on gold electrode deposited onto carbon substrate.

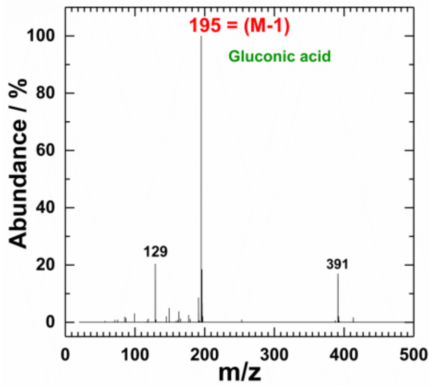


Figure 1. LC-MS negative ionization mode of mass spectrum (M-1) for the main reaction product resulting from glucose oxidation

Acknowledgements
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Catalytic Cascades in Fuel Cell Applications

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Deep or complete oxidation of complex fuels is challenging in fuel cells, because different catalysts are needed to catalyze different steps of the oxidative process. In biology, this is done via enzyme cascades, such as the glycolytic pathway, the pentose phosphate pathway, and the Krebs cycle. This talk will discuss the design issues of working with enzymatic cascades for fuel cell applications and then move on to working with hybrid catalytic cascades combining enzymatic catalysts with other catalytic moieties. The talk will discuss the role of the chemical microenvironment on catalytic rates and the need for substrate channeling of intermediate between catalytic active sites, as well as a discussion of the materials design aspects of catalytic cascades. The presentation will show biofuel cells utilizing a variety of fuel options from alcohols to lactate to pyruvate, to glycerol and sugars.

Single-Molecule Nanocatalysis Reveals In-situ Deactivation of Pt/C Electrocatalyst for Hydrogen Oxidation Reaction

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In fuel cells, carbon-supported platinum (Pt/C) has been extensively used as anode electrocatalyst for hydrogen oxidation reaction (HOR) or cathode for oxygen reduction reaction (ORR) [1]. However, due to the complexity of porous electrode used in traditional ensemble experiments, the variation or deactivation process of Pt/C catalysts in the working condition is still not clearly understood. For instance, one of the most significant problems hindering the large-scale application of proton exchange membrane fuel cells is the performance decay of fuel cells induced by the gradual loss of catalytic activity of Pt/C[2]. Developing an electro-catalyst with long-term operation stability requires a deep understanding to the deactivation mechanism during the long-term operation process at microscale (such as single-molecule single-nanoparticle) level.

Here, by coupling a Pt-catalyzed fluorogenic reaction with Pt-electrocatalyzed hydrogen oxidation reaction (HOR), we combine single-molecule fluorescence microscopy with traditional electrochemical method to "see" and then study the HOR-induced real-time deactivation kinetics of Pt/C electrocatalyst at single particle level (Fig.1) [3]. It was revealed that the decay of catalytic performance of Pt/C could be mainly attributed to the electrocatalysis-induced etching or dissolution of Pt nanoparticles. Spontaneous regeneration of activity and incubation period of Pt electrocatalyst were also observed at single particle level. All these new insights are practically useful for the understanding and rational design of high efficient electrocatalysts for fuel cells.

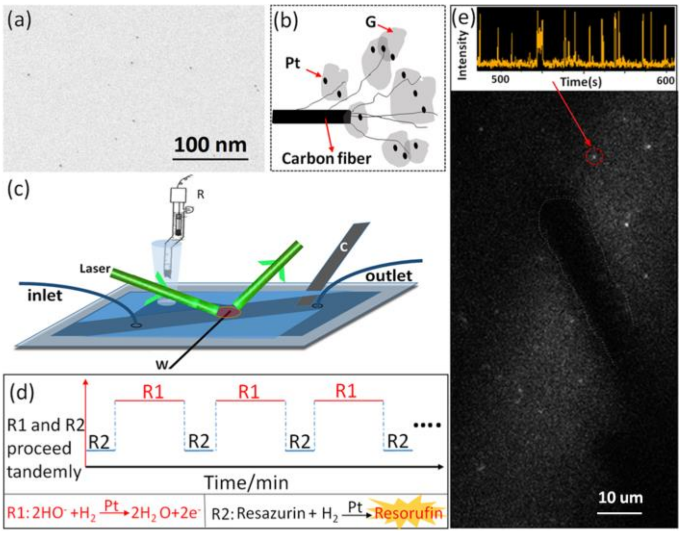

Fig. 1. (a) Typical TEM image of Pt/G (Pt 0.1 wt. %). (b) Scheme for the dispersion of Pt/G on carbon fiber microelectrode. (c) Combination of microflow cell with electrochemical system; W: working electrode, C: counter electrode, R: reference electrode. (d) Scheme for the coupling of Pt-catalyzed **R1** and **R2** tandemly. (e) Typical optical image (45×88 um^2) for single-molecule nanocatalysis. The carbon fiber microelectrode was marked with dotted white line. The top inset shows typical fluorescence intensity versus time trajectory for **R2** obtained from a location indicated by a red circle on the optical image.

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A 0-dimensional stationary performance model for PEM single cells

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In this work, we present a zero-dimensional, stationary model which precisely predicts the current-voltage-characteristics of a polymer electrolyte membrane fuel cell over a wide range of operating conditions (temperature, humidity, gas composition).

The model was parametrized by means of impedance measurements on incremental cells, which allow the investigation of parameter influences independently of each other [1]. Different kinds of electrode polarization resistances are determined from the recorded spectra by the distribution of relaxation times (DRT) [2,3] and fitted to a physicochemically meaningful, equivalent circuit model (ECM). Such linearized model only reflects the small signal ac behavior of the cell in a given operating point.

To model the cell performance over a wide range of technically relevant current densities, a DC performance model considering nonlinear effects was set up. In this model ohmic losses are modeled by Ohm's law, whereas activation losses at cathode and anode are modeled by distinct Butler-Volmer equations. Loss contributions from gas diffusion polarizations are calculated applying Fick's law. The different model parameters required in this approach were extracted from impedance spectra using an approach formerly applied to solid oxide fuel cells [4,5]. The partial pressure and humidity dependency of the anodic and cathodic exchange current density as well as the humidity dependency of the membrane conductivity could be determined by a fit of semi empirical power law equations. An Arrhenius approach is used to consider the temperature dependency of exchange current densities and membrane conductivity.

Simulations performed with the DC performance model showed an excellent agreement with experimental results over a wide range of operating conditions (Figure 1). Deviations for high current densities ($j > 0.6\ \mathrm{Acm^{-2}}$) and low cell voltages ($U < 0.6$ V) will be discussed. The model is not only able to predict the CV-behavior of the cell but furthermore provides quantitative information about the different losses (ohmic, activation and gas diffusion polarization in anode and cathode) in the cell.

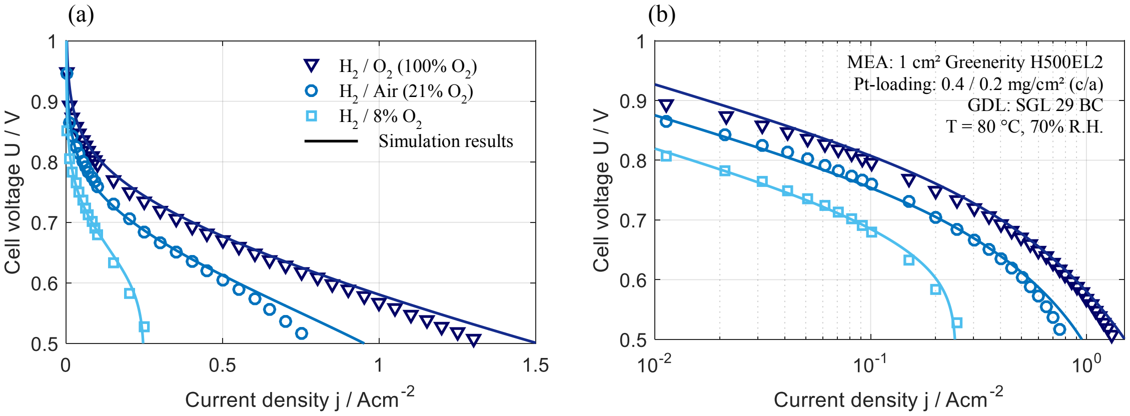

Figure 1. *Polarization curves and simulation results of a commercial 1 cm² MEA (Greenerity H500EL2) at T = 80 °C and 70% R.H. operated with oxygen (100% O_2), air (21% O_2) and low oxygen partial pressure (8% O_2). (a) Linear scale, (b) logarithmic scale.*

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Electrochemical Investigation of Tertbutylphenoxy Phthalocyanine Complexes towards Oxidation of 4-Chlorophenol.

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Screen printing techniques have attracted a lot of attention recently especially in the field of electrochemistry, these techniques seems to be one of the most promising approaches which allows for simple, versatile, rapid, and low cost sensor production. In addition, screen printed electrode (SPE) **(Scheme 1)** allows for the production of modern sensors, which can be incorporated in portable systems, an important requirement of detection methods for the direct on-field analysis of a sample without changing of the natural environmental conditions. Modified screen-printed carbon electrodes (SPCEs) are known to lower the oxidation overpotential and improve the peak current of phenols. In this paper, the screen printed electrodes are modified with tertbutylphenoxy phthalocyanine with varying the metal centers **(figure 1)**. The study investigates the effect of the metal center on the oxidation of chlorophenols. Phthalocyanines are used as the electrode modifier because of their high catalytic activity and their ability to prevent electrode fouling due to passivation by chlorophenols. Self-assembled monolayer technique is employed for the immobilization of the synthesized phthalocyanine complexes onto the electrode. The study compares the modified electrode and the bare unmodified electrode.

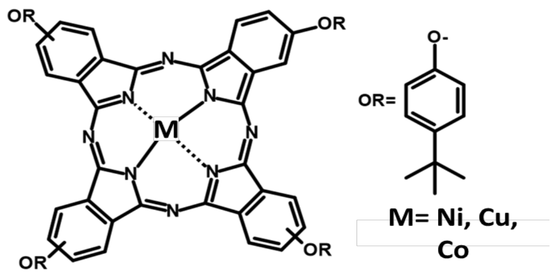
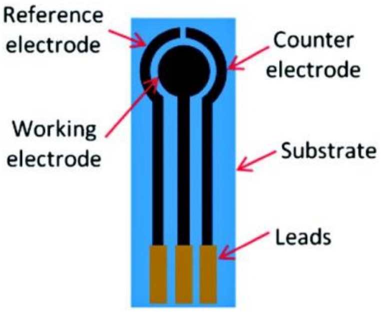


Figure 1: structure of the phthalocyanine complex



Scheme 1: an example of the screen printed electrode

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Investigation on the oxide-oxide galvanic displacement reactions employed in the preparation of electrocatalytic layers

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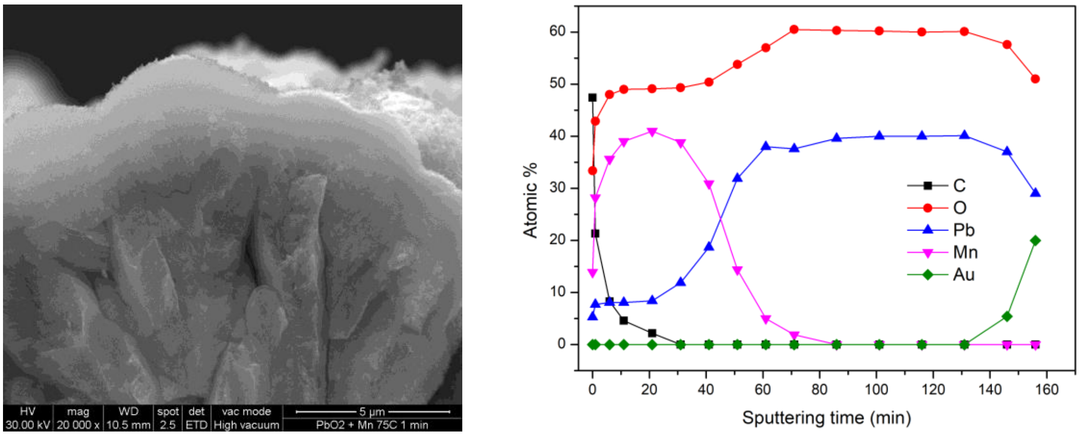
Porous electrodes active in the OER have been prepared by combining oxygen bubble templated electrodeposition of PbO_2 [1] and galvanic displacement of this oxide by low valent cations. The first step provides a porous sacrificial substrate, the second causes the formation of a secondary oxide on top of PbO_2. When the exchanging cation is Co^{2+}, the secondary oxide consists of Co_3O_4, the electrocatalytic material [2]. An alternative approach involved the preparation of the porous sacrificial lead oxide by hydrogen bubble templated electrodeposition of metallic Pb and its electrochemical oxidation, in the first step, and galvanic exchange, in the second. Electrodes thus prepared stably sustained the OER (in 1.0 M NaOH) at 10 mA cm^{-2} with an overpotential below 300 mV, with a 60 mV Tafel slope [3].

Oxide-oxide galvanic displacement is a little investigated process for which fundamental understanding is still missing. To achieve basic information, various combinations of sacrificial oxide and exchanging cations have been investigated. Growth rates of the coatings have been estimated by electrochemical methods and compared with SEM and XPS data. For both SEM and XPS studies, compact samples of the sacrificial oxides have been deposited and exchanged with low-valent cations. Then, fracture sections have been investigated by SEM and XPS has been used to obtain depth profiles, measuring the surface composition of the samples after increasingly long periods of Ar sputtering.

These investigations have shown that the growth rates of the secondary oxides cannot be rationalized in terms of thermodynamic driving force (defined as the difference between the reduction potential of the sacrificial oxide and that of the secondary oxide) [2]. XPS profiling has shown that significant amounts of the sacrificial oxide cation are found throughout the secondary oxide, whereas no penetration of the exchanging cation occurs in the sacrificial oxide. While a complete explanation of the experimental observations still requires additional work, the presently available data suggest that diffusion of the sacrificial oxide cation through the growing secondary oxide may be the rate limiting factor.



Left. Cross-sectional SEM image of a sample consisting of sacrificial porous PbO_2 and secondary MnO_2 layers.
Right. XPS depth profile of a sample consisting of sacrificial compact PbO_2 and secondary MnO_2 layers. Deposits were formed onto Au. C is due to surface contamination

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Methods of electrode surface modification using porphyrin-type molecules combined with nanomaterials

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Porphyrin-type molecules such as phthalocyanines (Pcs) are employed as electrode modifiers in order to enhance electrode activity [1]. Nanomaterials such carbon nanotubes (CNTs), quantum dots and metal nanoparticles are employed together with Pcs to further enhance electrode activity due to the synergistic effect of these nanomaterials with Pc molecules. Methods of electrode modifications using Pcs alone or the nanocomposites include self-assembled monolayer formation, polymerization, adsorption, grafting or click chemistry. Characterization of the conjugates or surfaces modified by conjugates will be discussed. Methods of characterization include voltammetry, X-ray photoelectron spectroscopy, scanning electrochemical microscopy and other microscopic techniques. The applications of the nanocomposites as electrocatalysts will be discussed.

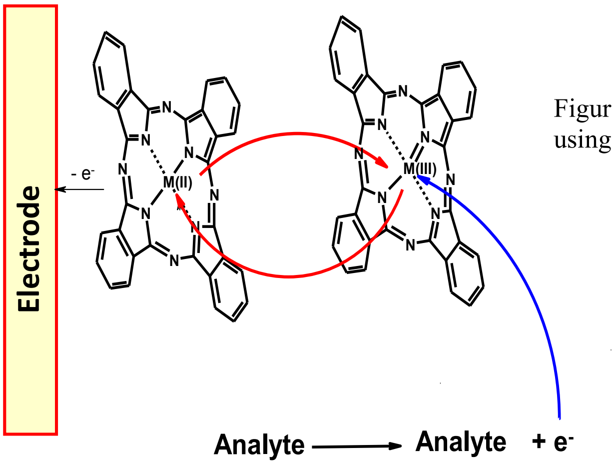

Figure 1. Electrode modification using metallophthalocyanines

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From bioelectrocatalysis to electrocatalysis. A contribution to sustainability of energy provision

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The provision of sustainably generated energy is of utmost importance for the future of our planet. Without any doubt, electrochemistry in general and especially the elucidation of fundamentals of (bio)electrocatalysis will be on the forefront to preserve a planet providing suitable living conditions for a growing population. Evidently, the access to energy may mean completely different things in a mega-city, in rural areas in Europe, or in growing arid areas in the sub-Sahara or villages in central Africa. However, in the one or the other way, provision of energy today has a substantial environmental impact by e.g. cutting the last trees leading to even more erosion or by emitting exceeding amounts of CO_2 for setting the air condition system to very low temperatures.

Despite big political decisions are urgently needed, electrochemists need to contribute to the scientific basis to make sustainable energy provision possible at each level. And it is probably even more important, that the next generation of electrochemists gets aware and contributes to this endeavor.

This presentation will make a journey from bioelectrocatalysis to electrocatalysis, seeking for similarities and differences and will present tools which are providing a better insight into fundamental features being the basis for highly selective reactions. This journey will show possibilities to use highly oxygen-unstable biocatalysts in biofuel cells and biosupercapacitors as well as to use gas-diffusion electrodes to increase the local availability of low soluble gaseous substrates. It will continue to locally arranged catalytic sites looking at similarities between enzymes and nanoparticles following the "nanozyme" concept and further to nanoelectrochemical tools for elucidating the electrocatalytic activity of single nanoparticles under conditions where mass transfer is not limiting. Finally, it will arrive at new noble-metal free catalyst materials for energy conversion reactions.

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Photoelectrochemical Activity and Selectivity of Alkaline Earth Nanocubes

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The n semiconducting oxides make important class of materials for solar fuel generation as well as for waste water treatment applications. The materials for these applications combine a multiple functionality since they act simultaneously as the energy harvesters as well as actual catalysts in complex charge transfer reactions.

While the optimization of the semiconductor oxides has focused mainly on the band gap optimization to improve the energy harvesting capabilities; the optimization of the catalytic activity progressed so far mainly by extensive approaches (i.e. by increasing the total electrode area by employing the nano-particulate forms of the catalysts) rather than by optimizing the intrinsic catalytic activity of the oxide surfaces which remains poorly understood. Also the effects of low dimensionality sites (crystal edges, vertices) have yet to be addressed in depth.

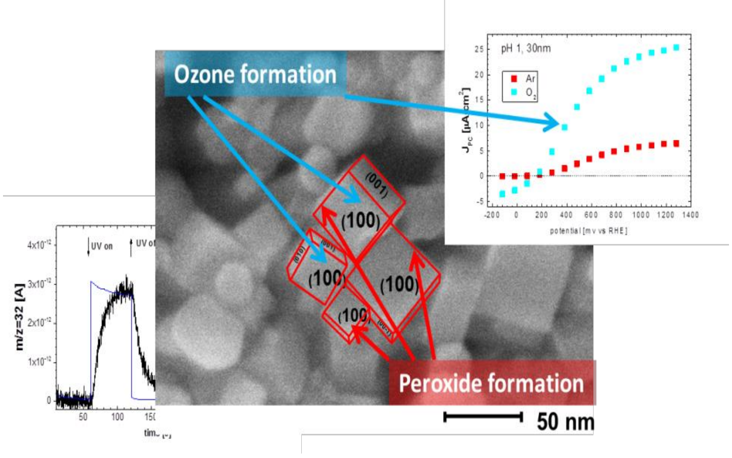

Figure 1 SEM image of nanocube $SrTiO_3$ electrode tested in water oxidation. The arrows mark the sites for corresponding ozone and hydrogen peroxide formation. The insets show a comparison of the photocurrent behavior in presence and absence of oxygen (right) as well as a comparison of the measured photocurrent along with MS detected oxygen produced in photoelectrochemical water splitting. Data were gathered in 0.1M $HClO_4$ upon illumination with monochromatic light of λ=365 nm.

This paper attempts to describe synthesis, characterization and particle size role in the photo-electrochemical behavior of alkaline earth titanates. Nano-cubes of $SrTiO_3$, $BaTiO_3$ and $CaTiO_3$ are compared with respect to their activity in the photo-electrocatalytic oxidation of water and with respect to their selectivity toward ozone formation. All included materials are crystalline and conform to the perovskite structural type. The prepared materials also feature only {100} oriented faces at the surface avoiding the ambiguity possibly connected with different surface orientation. The activity of the alkaline earth titanate perovskites in water oxidation decreases with decreasing particle size clearly showing the overall activity of the perovskites is controlled by charge transfer at the surface namely by the local structure. The sites at the crystal faces are active in conventional oxygen evolution and in ozone formation. The low dimensionality sites, on the other hand, act as trap states for reductive production of hydrogen peroxide.

Stability of Nanosize Ni-Based Hydrogen Oxidation Reaction Electrocatalysts in Alkaline Media

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The latest progress in the development of platinum group metal (PGM)-free electrocatalysts for the hydrogen oxidation reaction (HOR) [1-5] has opened up new horizons for H_2-O_2 (air) anion exchange membrane fuel cells (AEMFC). *However, until now the durability of PGM-free HOR electrocatalysts is barely addressed* for the operating conditions close to those in AEMFCs.

In this work, a series of carbon supported nanoparticles of monometallic Ni and bimetallic Ni_3M_1 electrocatalysts (M=Co, Fe, Cu, Mo) were synthesized using sodium borohydride reduction method. The in situ electrochemical stability of the catalysts was studied using on-line ICP-MS in 0.05 M KOH at 25 °C. Cu undergoes noticeable electrochemical dissolution at the electrode overpotential value of 0.3 V, whereas Ni, Co and Fe showed no electrochemical leaching in the overpotential range of 0−0.7 V. The cycling stability of the catalysts was characterized using RDE and CV methods at the same conditions as ICP-MS tests. Auxiliary to on-line ICP-MS experiments, potential cycling tests allowed revealing the changes of the electrocatalytic activity in HOR while scanning in the same overpotential range. All the electrocatalysts were shown to retain their electrochemical surface area and catalytic activity after 1000 cycles in the range of 0−0.3 V, whereas cyclic polarization up to 0.7 V led to the full oxidation of the surface and loss of the catalytic activity. Chemical corrosion of the catalysts was tested in aerated 1 M KOH at 60 °C. Drastic changes in the electrocatalysts morphology and the full oxidation of Ni with the formation of $Ni(OH)_2$ were observed which resulted in the loss of the catalytic properties (**Table 1**).

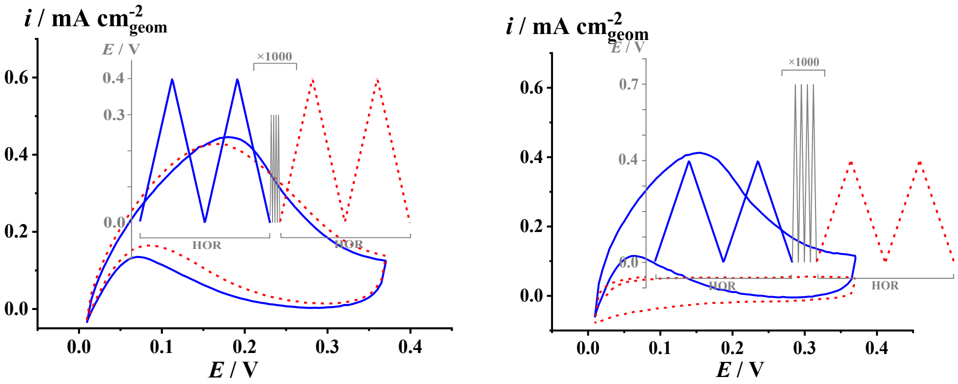

Figure 1. Hydrogen oxidation polarization curves for Ni_3Fe_1/C before (solid) and after (dash) 1000 cycles in the potential window of 0−0.3 V (a) and 0−0.7 V (b). 0.05 M KOH, 25 °C, 1 mV s^{-1}, 1600 rpm.

Table 1. Resume on the electrochemical and chemical stability of the Ni_3M_1/C electrocatalysts.

Catalyst	Initial		ICP-MS / ng cm^{-2}		Cycling stability test				Chemical corrosion	
	i_0 / mA cm$^{-2}_{Ni}$	S / m$^2_{Ni}$ g$^{-1}_{Ni}$	η=0.3 V	η=0.7 V	η=0.3 V		η=0.7 V			
Ni/C	0.064	3.10	negl.	negl.	negl.	negl.	loss	loss	loss	loss
Ni_3Co_1/C	0.058	1.93	negl.	negl.	negl.	negl.	loss	loss	loss	loss
Ni_3Cu_1/C	0.065	4.40	2.91	265.1	negl.	negl.	loss	loss	loss	loss
Ni_3Fe_1/C	0.089	1.89	negl.	negl.	negl.	negl.	loss	loss	loss	loss

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A photobioelectrochemical cell based on the combination of two light-sensitive entities: quantum dots and photosystem II

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The coupling of photoactive proteins with electrodes has developed to a recent research trend based on the progress in understanding and handling of these complex bioentities and the developments in materials sciences. The focus is mainly on the application of these systems for light-to-current and light-to-chemicals conversions [1,2]. Here we introduce a new system by combining the photophysical properties of the biological photosystem II with a second light-sensitive entity – PbS quantum dots. This is inspired by the natural photosynthesis since also here two photoactive molecules are combined for the whole process of water splitting and usage of electrons for energetic (chemical) purpose.

The combination of quantum dots and PSII (from *T. elongatus*) is realized in a 3D electrode structure in order to ensure a proper protein loading and a large interface for hosting QDs and PSII. As basic electrode material TiO_2 is chosen since it provides advantageous properties for charge carrier separation at the interface to PbS QDs which are directly synthetized on the TiO_2 surface [3]. PbS is used as QD material since it allows excitation in the visible wavelength range. In order to connect the PSII efficiently with the TiO_2/PbS electrode an osmium-based redox polymer has been used (poly(1-vinylimidazole- co-allylamine) - $Os(bipy)_2Cl$). The electrode structure is prepared by a template-based approach employing a simple spin coating procedure to adjust the thickness of the 3D structure [4].

These electrode architectures have been characterized by scanning electron microscopy, wavelength dependent measurements and photochronoamperometric experiments. They show that the photocurrent magnitude can be well correlated to the amount of PSII integrated within the 3D electrode architecture. Interestingly the electrons from water oxidation can be collected at very low potential starting from -550mV vs Ag/AgCl. This is about 200mV below the redox potential of the acceptor site in PSII and illustrates one beneficial feature of the new developed system.

This photobioanode has been coupled with a bilirubin oxidase (BOD) based cathode. Here, a transparent electrode has been developed which allows also the illumination of the whole cell through the cathode. For this purpose 3D electrodes based on the same template procedure have been prepared with antimony tin oxide as material (ATO). A high transparency can be ensured even when 8 layers of inverse-opal ATO are deposited on FTO electrodes (Fluor-doped tin oxide). The ATO surface has to be modified with pyrenecarboxylic acid in order to provide a suitable surface for the direct electron transfer of BOD. Here current densities of about 135 $\mu A/cm^2$ have been obtained in air-saturated solution for the oxygen reduction process. The process is rather effective since these current values are limited by mass transport. By combing both electrodes, a photobioelectrochemical cell (PBC) can be fabricated, which does not need any fuel to be supplied, but allows the light-driven generation of electricity by regeneration of O_2 and H_2O at the photobioanode and biocathode, respectively. The PBC gives a rather high open cell voltage of about 1V under illumination and a maximum power density of about $50\mu W/cm^2$.

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Spectroelectrochemical Investigation of Flavoproteins

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In our group we work on the spectroelectrochemical investigation of flavoproteins. The reduction of a flavin cofactor follows an *ece*(*c*)-mechanism, *i.e.* **e**lectron transfer to the flavoquinione leads to the flavosemiquinone radical anion, which gets protonated (a **c**hemical reaction step resulting in the neutral semiquinone radical) before a second **e**lectron transfer step follows leading to the flavohydroquinone anion. Depending on the pH and the pK_a of the flavohydroquinone a second protonation may follow. For free flavins in solution the redox potential of the second electron transfer step is more positive (or less negative) than that of the first. Therefore the reduction of free flavins in solution occurs as an overlapping two electron, one or two proton reduction leading from the quinone directly to the hydroquinone without formation of a stable semiquinone radical anion or a neutral radical state. In contrast, in some flavoproteins the radical anion or the neutral radical may be stabilized due to interaction of the flavin with the apoprotein. Flavin radical states can also be observed when they are thermodynamically not favored in case the flavin reduction is carried out at non-equilibrium conditions. As the different flavin redox states can be distinguished by their absorption spectra, the redox chemistry of individual flavoenzymes can be unraveled by pH dependent spectroelectrochemical measurements.[1]

As an example for the different flavin redox states I will first discuss the absorption spectra of glucose oxidase, which does not form stable semiquinone radicals, when its reduction is carried out at equilibrium conditions.[2] When in contrast the reduction is carried out at non-equilibrium conditions, *e.g.* by photochemical reduction (*via* irradiation with blue-light in the presence of EDTA), a stable semiquinone radical anion or a neutral radical has been observed depending on the pH.[1, 3] From pH dependent spectroelectrochemical measurements also the pK_a of the flavohydroquinone can be determined.[2]

Next I will discuss the redox chemistry of flavodoxins, for which a neutral semiquinone has been observed. For flavodoxins the redox potential of the first reduction exhibits a pH dependency of -60 mV per pH unit over a broad pH range whereas the second redox step is pH independent above pH 7.

Thereafter I will discuss the redox chemistry of flavoenzymes such as D-amino acid oxidases or cholesterol oxidases which comprise a stable semiquinone radical anion state.[4-6] For these enzymes the first redox potential is expected to be pH independent, whereas the second redox potential should comprise a pH dependency of -60 mV per pH unit as long as the resulting hydroquinone anion is not protonated.

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Kinetic study of oxygen reduction reaction over nitrogen-doped and iron-nitrogen-doped carbon catalysts

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Abstract: Oxygen reduction reaction (ORR) plays an important role in proton exchange membrane fuel cell [1, 2] and electrochemical synthesis of hydrogen peroxide based on fuel cell setup [3]. Recently, much attention was focused on develop new ORR non-precious-metal catalysts, nitrogen doped carbon (N/C) and Fe-containing nitrogen doped carbon (Fe/N/C) catalysts [4-6]. Over these catalysts, there are maybe different pathways for ORR. (1) Oxygen could be directly reduced to water by 4-electron-reduction pathway and the corresponding active sites or catalyst is desirable for PEMFC application; (2) oxygen is reduced to hydrogen peroxide by 2-electron-reduction pathway and the corresponding active sites or catalyst is expected for electrochemical synthesis of hydrogen peroxide; (3) And the produced hydrogen peroxide could be further reduced to water by (2+2)-electron-reduction pathway. Therefore, it is of great significance to clarify the real ORR pathway over Fe/N/C and N/C catalysts. In the present study, we tried to investigate the mechanistic pathway of the ORR over Fe/N/C and N/C catalysts prepared from the pyrolysis of polyimide particles at high temperatures in the presence and the absence of $Fe(acac)_3$, in acidic media based on the model with loading correction which, in order for concision, was denoted as Nabae model [7] (Figure 1(a)). It demonstrated that Fe/N/C catalyst facilitates the oxygen reduction to water (dominant 4-electron-pathway) for PEMFC generating power, and N/C catalyst is promising to the selective electrochemical production of hydrogen peroxide (dominant 2-electron-reduction pathway) based on fuel cell setup (Figure 1(b)).

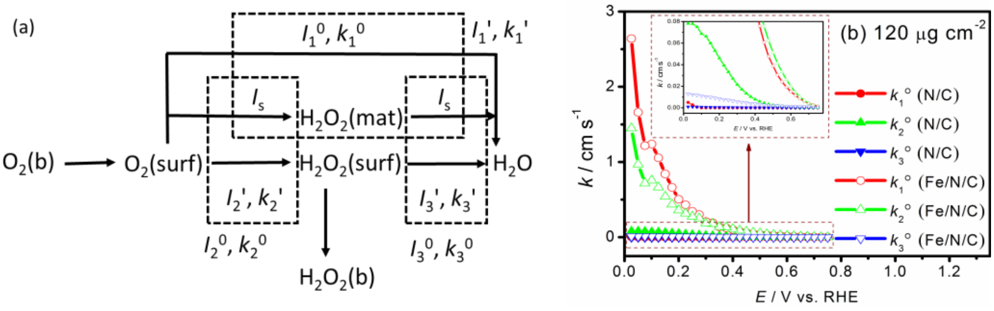

Figure 1. (a) Nabae model, which consider H_2O_2 to be further reduced to H_2O in the catalyst layer matrix, H_2O_2 (mat). I_1', I_2', I_3', k_1', k_2' and k_3' are the individual currents and kinetic constants based on the Damjanovic model with a modified mathematical approach. I_1^0, I_2^0, I_3^0, k_1^0, k_2^0 and k_3^0 are those based on the correction for the quasi-four-electron reduction. I_s is the current via the series reaction in the catalyst layer matrix. (b) Comparison of individual rate constants based on Nabae model for 120 g cm^{-2} of the N/C and Fe/N/C catalysts.

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Electrochemically Oxidative C-H Functionalization of Quinoxalin-2(1*H*)-ones: An effective Synthesis of 3-substituted Quinoxalin-2(1*H*)-ones through Direct Electrolysis

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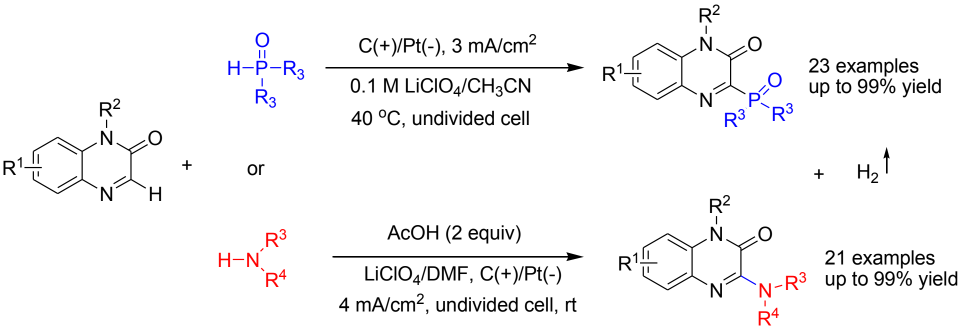
Direct electrochemical dehydrogenative cross-coupling of C-H bonds have emerged as sustainable and atom economy methodology for the formation of C-C or C-Het bonds. Efficient synthesis of quinoxaline-2(1*H*)-ones has attracted much attention due to their diverse biological properties and pharmacological properties. Herein, we reported an efficient protocol for the synthesis of 3-substituted quinoxalinones via the electrochemical dehydrogenative cross coupling of quinoxalin-2(1*H*)-ones with aliphatic amines and azoles as the nitrogen sources, or H-phosphonates and H-phosphine oxides as the phosphorus sources. The chemistry was performed in an undivided cell and the corresponding products were afforded in up to 99% yield. This direct electrolytic method avoids the use of transition metals and external oxidants, and it represents an appealing alternative to the synthesis of 3-substituted quinoxalinones.



Scheme 1. Electrochemical C-H phosphonation or amination of quinoxalin-2(1*H*)-ones

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Novel polymer-graphene nanocomposite multi-layered coatings for improved anticorrosion and antifouling performance

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There is huge economic demand for coatings that would allow the extension of the 5-year dry docking cycle of ocean going vessels, which will require improvements in both the anticorrosion and antifouling properties of proactive coatings. To this end, the finding on a new class of novel polymer-graphene nanocomposite multi-layered coatings will be presented.

Positively charged nanodiamond (ND) is used to decorate negatively charged graphene oxide (GO) to form a GO-ND hybrid nanomaterial by electrostatic force. Structural studies results showed that after the decoration, the aggregation of GO sheets is extensively hindered in both at the powder and dispersion states, with a clear reduction in the layer numbers in the latter. The mechanical properties of epoxy/GO, epoxy/ND and epoxy/GO-ND were investigated and compared. The results showed that the GO increased the ductility of epoxy, while the ND increased the rigidity. The best mechanical performance was found for the epoxy/GO-ND nanocomposites, at a GO:ND ratio of 1:5. The reinforcement mechanism of the nanophases was further illustrated by the fracture surface of SEM/optical images and TGA analysis. The superior anti-corrosion properties of the epoxy/GO-ND coatings were revealed by electrochemical impedance spectroscopy.

A similar approach improved the hardness of a commercial antifouling polydimethylsiloxane coating, the major drawback of these systems, without any deterioration in its non-stick performance. If time permits, improvements in the efficiency of the cathodic protection offered by zinc based primers by the careful incorporation of graphene based fillers will also be presented and discussed.

Studying Pt Nanoparticle Dissolution on Carbon Surfaces using the Electrochemical Quartz Crystal Nanobalance

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With renewed interest in polymer electrolyte fuel cells (PEFCs) as an alternative energy technology, a drive towards improving catalyst stability under load cycling conditions has become paramount. The conventional Pt/C electrocatalyst has been studied in detail, however the exact degradation mechanism of the catalyst under standard operating conditions has been debated for years. Works by Mayrhofer *et al.* [1, 2] have focused on better understanding Pt dissolution mechanisms both *in-situ* and *ex-situ*, with various mechanisms explained in detail by Meier *et al.* [3] and Jerkiewicz *et al.*[4].

Many degradation studies make use of the protocols as described in Ohma *et al.* [5], with the addition of *in operando* inductively coupled plasma mass spectroscopy (ICP-MS) [2] or electrochemical quartz crystal nanobalance (EQCN) [6] to further elucidate the degradation mechanisms. While these studies have been relatively successful, probing the carbon support structure has not been instituted in detail.

In this work, Pt was deposited onto partially oxidised graphitic substrates. The graphite was oxidised either by Fenton's reagent ($H_2O_2/FeSO_4$) or a 5 N equal mixture of HNO_3 and H_2SO_4 under reflux for 24 hours at 80 °C or 120 °C respectively [7]. This treatment served to create vacancies within the sp^2 carbon structure and to terminate with various functional groups. A loading of 20 and 50 $\mu g.cm^{-2}$ Pt was deposited onto the graphite substrates by DC magnetron sputtering.

Samples were characterised electrochemically by cycling potential between 0.6 V and 1.0 V vs RHE using a square wave-form with a period of 3 s. Current responses from cyclic voltammograms at a scan rate of 50 $mV.s^{-1}$, in 0.5 M H_2SO_4 and under an inert room temperature environment, were taken in logarithmic intervals to account for the transient behaviour of the degradation mechanisms. *In operando* EQCN frequency responses were monitored and used to qualitatively show the non-monotonic nature of the electrocatalyst surface charge. Further to this, the frequency response was used to track Pt dissolution with time. This study shows that Pt dissolution across an oxidised carbon surface is lowest on the acid treated surface, followed by un-treated and that treated with Fenton's reagent.

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Carbon-based electrodes for metal deposition and electrocatalysis

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Carbon plays a particular important role in electrochemistry, not only as support for electrocatalysts, but also as model electrode with well-defined structure and properties. Due to its various structural variations (*e.g.* graphene, graphite, HOPG, CNT, MWCNT, etc.), which also comes with unique electronic properties, a wide range of applications have already been realized and are still explored.

In this talk we will combine experiment and theory in order to understand the role of carbon-based materials as templates for metal electro-deposition and dissolution. Besides deposition of Pt and Ir nanoparticles [1], we will in particular concentrate on chromium, which is necessary for various industrial applications. So far, the most common sources for chromium electrodeposition are hexavalent chromium baths, especially for hard chromium deposits. However, the use of Cr(VI) solutions is coupled with a huge health risk related to the toxic and carcinogenic nature of such baths. Consequently, the use of these salts has already been (or will be soon) banned by most countries, making the search for alternatives most important. Hence, trivalent baths have gained an increased interest, as it might be the most viable substitute. Motivated by this, we have used carbon-based electrodes to develop a functional Cr(III) electrolyte to replace toxic Cr(VI) electroplating baths [2]. For this the initial stages of deposition have been investigated on glassy carbon electrodes, which allowed us to better understand the deposition mechanism. Based on this knowledge an improved trivalent chromium system could be developed, which lead to the formation of micrometer-sized hexagonal chromium hydride crystals, whose structural changes upon extended deposition times could be monitored by scanning electron microscopy and electrochemical characterizations.

In the second part of this talk we will concentrate on the electrochemistry of graphene oxides (GO). Graphene oxides is a particular interesting system for electrochemistry due to the individual contributions to the voltammetry arising from edges, the basal planes or defects as well as from the high proportion and diversity of oxygenated species on this system. The advantage of GO over other carbon-based systems (*e.g.* graphite, fullerenes, etc.) includes its facile synthesis, tunable conductivity, biocompatibility, high surface are, electronic structure, and so on. Here we will discuss the synthesis of different GO materials as well as their electrochemical characterizations [3]. Afterwards, these systems were used as electrocatalysts for different electrochemical reactions, including the ORR, which already shows the wide variety of applications, for instance as metal-free catalysts in fuel cells.

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Role of exogenous Cu^{2+} in the catalytic properties of *Thermus thermophilus* Laccase

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Blue multicopper oxidases have received considerable attention because of their ability to oxidize a large variety of organic substrates while reducing O_2 into water with efficiency comparable to platinum catalyst. Bilirubin oxidases (BOD), laccases (Lac) and copper efflux oxidases (CueO) belong to this family. They share different copper sites: one type 1 copper, the entry site of electrons where the substrate binds, one trinuclear active site where O_2 reduction takes place and which is composed of one type 2 copper and a binuclear type 3 copper (1). In addition to these four Cu sites, CueO is able to weakly bind additional Cu atoms at a methionine-rich helix positioned as a lid over the binding site cavity. Hence, depending on the environmental condition, CueO is involved either in organic substrate oxidation (phenol oxidase activity for example) or in Cu^+ oxidation, acting then as a copper detoxifier (2).

As a thermostable enzyme, Lac from *Thermus thermophilus* HB27 (*Tt* Lac) may be coupled with thermophilic hydrogenases in H_2/O_2 enzymatic fuel cells. Enzymatic activity in solution using classical Lac substrates is however very low, only enhanced by exogenous Cu^{2+}. As *Tt* Lac possesses a Met-rich hairpin, Cu binding to this domain was proposed to be involved in the activity. Little is known however about electrocatalysis using *Tt* Lac (3), and the effect of copper salt addition has never been studied at electrochemical interfaces.

In this work, we discuss the electrochemical behavior and enzymatic properties of *Tt* Lac immobilized on different electrodes. Based on a careful examination of the enzyme structure, we demonstrate that the direct wiring of the enzyme is driven by strong repulsive electrostatic interactions between the Met-rich hairpin domain and the electrode. We then highlight an additional electroenzymatic process in the presence of exogenous Cu^{2+}, and we discuss its link with the Met-rich hairpin. Finally, mutant studies allow to give new insight in the electron transfer pathways.

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Cyclic voltammetry of carbon-felt electrodes for application in all-vanadium redox flow batteries: Theory and experiment

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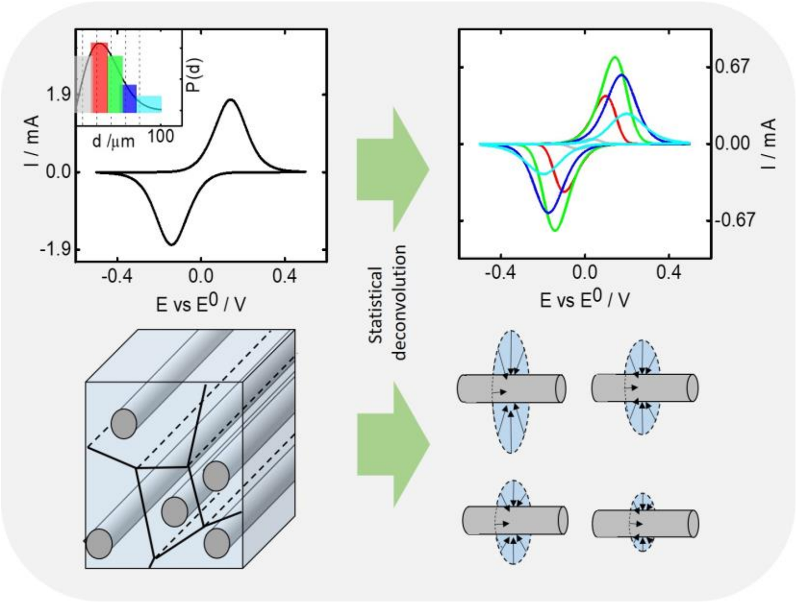
Cyclic voltammetry (CV) has been used extensively in the electrochemical characterization of various electrode materials for application in all-vanadium redox flow batteries. Especially carbon felt electrodes functionalized with oxygen surface groups by heat or acid treatment have been studied manifold in the literature, and their kinetic performance is either qualitatively investigated by comparing the separation of the redox peaks or quantitatively by applying the irreversible Randles-Ševčík relation. However, the Randles-Ševčík relation derived for a planar semi-infinite electrode geometry can hardly be applied to a felt electrode for the following two reasons: 1) diffusion domains inside a felt electrode are finite, 2) diffusion towards the fibres of a felt takes place in an external cylindrical geometry.

In this paper, we present a way to approximate the diffusion phenomena inside a felt electrode by extending the theory of CV to a finite external cylindrical diffusion space. The CV response of a felt electrode is calculated by statistically weighting individual CV responses for diffusion layers with variable finiteness following a nearest-neighbour Poisson distribution, describing the fibre distance distribution in the felt. Butler-Volmer electrode kinetics, preceding and succeeding homogenous first order chemical kinetics and electroactive species with non-equal diffusion coefficients were implemented in the calculations as well. In the experimental part, CV data of pristine, functionalized and aged carbon felts were recorded.

Finally, simulated CV responses were fitted to the experimental data. The simulated data is in good agreement with the experimental results, providing a suitable toolbox for quantitatively investigating the kinetics of felt electrodes using CV.



Influence of microstructure of zinc-aluminium-magnesium alloyed coated steel on the corrosion behaviour in laboratory tests and outdoor marine atmosphere

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Zinc coatings alloyed with aluminium such as Galfan (Zn-5Al) and Galvalume (Zn-55Al) have been proved to provide better corrosion performance than conventional hot dip galvanised zinc coating steel (HDG) in various atmospheric environments. The improvement on long term exposure usually ranges between 1.5-2 to 2-4 for Zn-5Al and Zn-55Al respectively. While Zn-5Al and Zn-55Al are mostly used in the building industry as prepainted systems, zinc coatings alloyed with low amount of aluminium and magnesium show interesting properties for being used in the automotive industry. Due to their superior corrosion properties compared to HDG, it may indeed be possible to lower the thickness of the metallic coating and to avoid any other additional corrosion protection in confined areas such as hem-flanges. Typical microstructures of Zn-Al-Mg coatings include three main phases e.g. primary zinc with small amount of aluminium, binary eutectic MgZn2-Zn and ternary eutectic aluminium. It is believed that microstructure induced by the alloying might play a key role in the formation of the protective layers. While coarse microstructures are favorable to the formation of areas with extreme pH at anodic and cathodic sites, a finer microstructure may indeed avoid such situations by averaging the surface pH, resulting in the creation of layers of improved protective quality.

The effect of microstructure modifications of line hot-dip model Zn-Al-Mg coatings was investigated in outdoor marine atmosphere and laboratory tests. Weight loss measurements and cross section observations revealed a tendency for fine microstructures enriched in eutectic phases to be the most corrosion resistant. This was connected to a lower size of cathodic areas at the surface (zinc dentrites), the preferential dissolution of Mg-rich phase (eutectic) and the formation of a stable layer double hydroxide on the surface as detected by FTIR spectroscopy.

Modelling Reactive Electrified Interfaces:
From DFT to Force Fields

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Electrocatalysis is at the heart of energy conversion devices such as fuel cells and solar cells or electrolyzers powered by "excess" electricity. A third field of application is electrochemical synthesis, where, for example, the electrochemical potential can be used to activate inert molecules such as the largely available C1 building block CO_2. All these applications have in common that they take place a highly complex interface between the (metal) electrode and a solution that contains a high-dielectric solvent with a high concentration of ions. Furthermore, the surface charge is tuned in order to impose the electrochemical potential. When modelling such systems from first principles in periodic systems, a neutralizing counter charge needs to be introduced, which physically represents the electrical double layer. An attractive solution is the Poisson-Boltzmann (PB) equation, which reduces the environment (solvent and electrolyte) to an easily computable mean-field which can be included in the DFT computations. Alternatively, the electrolyte can be described by molecular mechanics in order to obtain a molecular description of the solvent (see Figure 1,left). However, an accurate force field is a prerequisite for such investigations.
In this contribution I will present results illustrating the importance of accounting for the polarization of the electrode, for instance to qualitatively reproduce the preferential binding mode of pyridine on Au(111).[1] Additionally, I will discuss our efforts to develop accurate force fields for the interaction between water an metal surfaces,[2] assisted by our recently developed energy decomposition analysis tool for metallic surfaces, which allows to gain insight into the underlying physics of the interaction between the solvent and the metal surface (see Figure 1,right).[3]

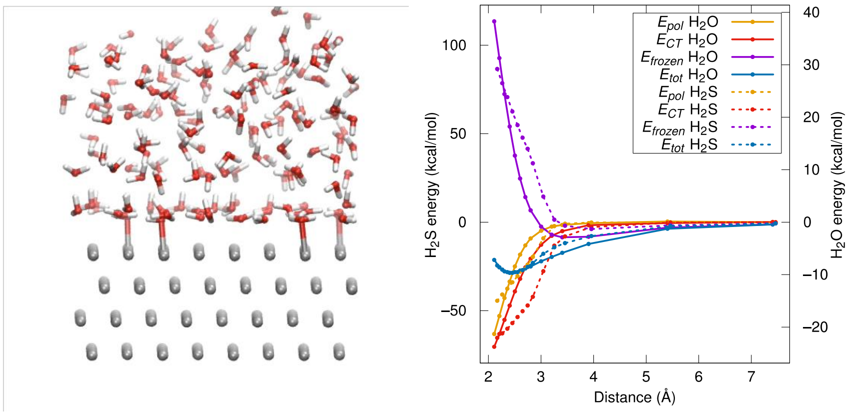

Figure 1. Left: Snapshot of a 1 ns molecular dynamics simulation of the Pt(111)/H_2O interface performed with GAL17[cite]. Right: Decomposition of the interaction energy of H_2O and H_2S on Pt(111) to assess the importance of the polarization (Epol) and charge transfer (CT) energy.

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Electrodes Two-phase boundary layers multiphysics modelling in a hydrodynamic alkaline water electrolyzer

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The presented work is a multiphysics calculation using Ansys-Fluent® CFD modelling of a hydrodynamic alkaline water electrolyzer. This work will start with an exhaustive review of the transport properties necessary for the multiphysics modelling of alkaline water electrolyzer. A recently published article provides experimental data and the correlations needed to calculate thermo-physical properties such as electrical conductivity, density, viscosity, heat capacity, heat and mass transfer diffusion coefficients as a function of temperature and electrolyte mass fraction for two classical alkaline electrolytes (KOH, NaOH). Different interpolation models from various authors are compared to raw experimental data. The goal of this work was to give to the modeler the correlations needed for the simulation of alkaline water electrolysis.

Thus, the two electrodes two-phase boundary layers can be calculated with precision. Calculations under discrete phase modelling (DPM) and Euler-Euler hypothesis have been performed and are presented.

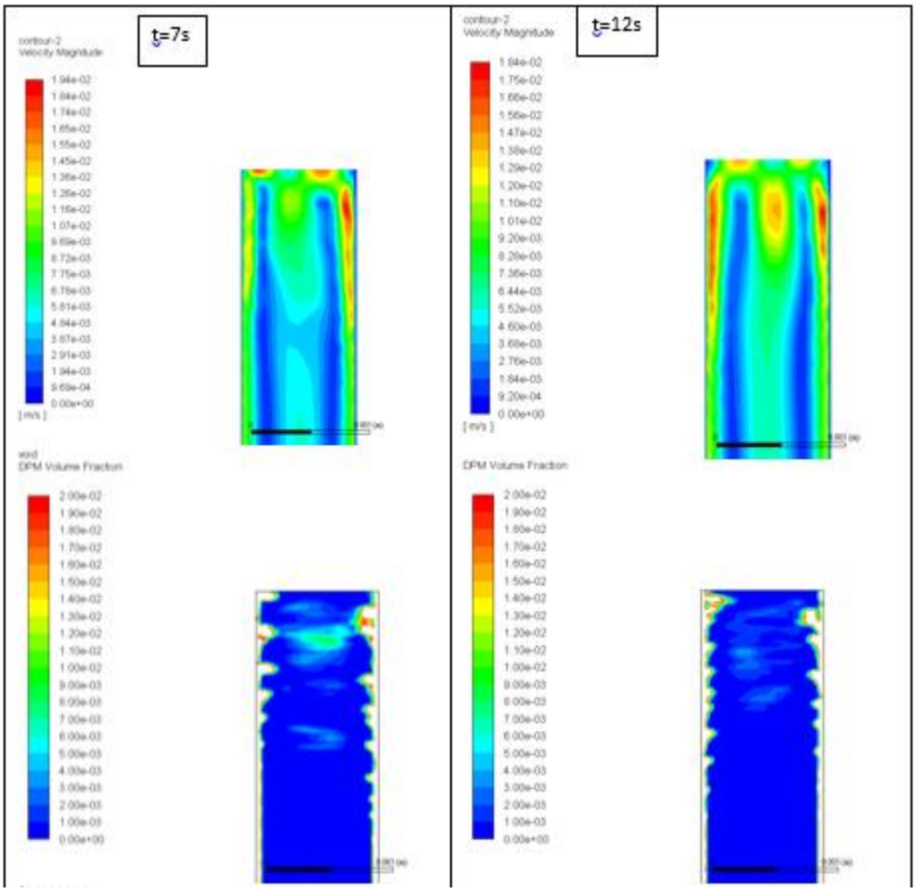

Figure-Countour of velocity magnitude and gas volume fraction at both electrodes

Machine Learning Integrated Electrical Biomedical Sensors for Neuron Biomarkers Analysis: from Single Neuron to Brain Slice

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Direct detection and analysis of biomolecules and cells in physiological microenvironment is urgently needed for fast evaluation of biology and pharmacy. The past several years has witnessed remarkable development opportunities in vitro models from single cell to 3D tissue with multiple functions based on microfluidic devices, termed as “cell/organ-on-a-chip”. By recapitulating the multicellular architectures, cell-cell interfaces and physicochemical microenvironments, these devices enable high-resolution, real time sensing and in vitro analysis of biochemical, genetic and metabolic activities of living cells/tissues in a functional tissue and organ context. This lecture will outline our recent research activities for the fundamental study of physical and electrical properties of cells, as well as the development of a new generation of cell/organ on chips that combine aspects of “top-down” nanofabrication approach with a “bottom-up” self-assembly method for cell and tissue measurements. The biosensors can monitor crucial cell signaling networks cell metabolic pathways, as well as detecting diseases such as Alzheimer’s disease in their earliest stage, titrating drug effects and enabling worldwide remote diagnosis. Further, we will report a chip based neuron mapping devices composited by several hundreds of microelectrodes for throughput neurotransmitters mapping by integrating machine learning technology.

Electrochemical Behaviors of B(III) and its Co-reduction with Mg(II) in molten chloride salts

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Molten salts electrolysis is still the main method for industrial production of pure Mg metals. Impurity oxides in raw materials commonly caused the cathode passivation and high energy consumption. The aim of this study is to deterimine the behaviors of B(III) in $MgCl_2$-KCl-NaCl molten salt system in the temperature range 973-1053 K. Because of the low solubility and high melting point of boron oxide, B(III) ions were introduced into the melt in the form of magnesium borate. The cathodic reduction mechanism of B(III) under different concentrations and electrochemical windows were investigated on tungsten electrodes using voltammetry, chronopotentiometry and open circuit chronopotentiometry methods. The results show that the cathodic reduction of B(III) was a one-step quasi-reversible process followed by three-electron transfer; which was controlled by both diffusion and electron transfer step. And the cathode passivation in the $MgCl_2$ electrolysis caused by B(III) was characterized by SEM. When the concentration of B(III) is 1.01×10^{-4} mol cm^{-3}, a new substance was observed, which was inferred to be the co-deposition of Mg and B. And the co-reduction of B(III) with Mg(II) were performed by potentiostatic electrolysis on tungsten electrode. The deposit was analyzed by X-ray diffraction(XRD), which showed that B_2Mg, and B_4Mg phase were formed in the B-Mg alloy.

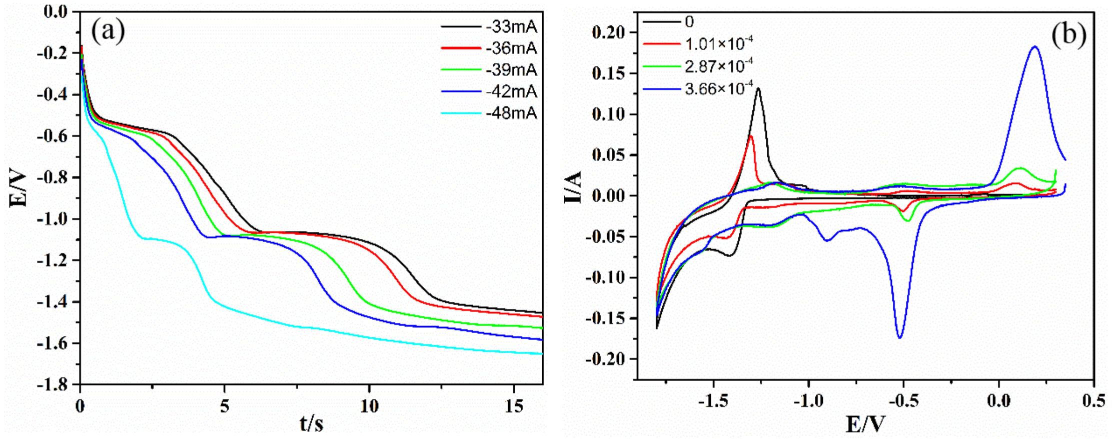

Fig1 (a) CPs of B(III) at 1.01×10^{-4} mol cm^{-3} (b) CVs at different B(III) concentrations(mol cm^{-3}) Scan rates: 0.1 V/s. W electrode (A = 0.283 cm^2) T= 973 K

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Water at electrode-ionic liquid interfaces: a combined study using AFM force curve and electrochemistry

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Ionic liquids have received increased attention in recent years in the field of electrochemistry due to their properties of a wide electrochemical window, low vapor pressure, and moderate solubility. This has stimulated study to understand the structure of electrode/ionic liquid interfaces, where electron transfer reactions occur.[1, 2] Both theoretical and experimental studies show that ionic liquids can form layering structures near the electrode surfaces.[3, 4]

When ionic liquids are used as electrolyte for electrochemical research, the water content exists as an impurity and can reduce or oxidize on electrode surfaces, which possibly decreases electrochemical windows. Some measures are usually taken to remove the absorbed water from ionic liquids before experiments are conducted to eliminate the influence of water on the properties of the ionic liquids. However, both homemade and commercially available ionic liquids still contain a small amount of water. Therefore, studies on the effect of water on the properties of ionic liquids are crucial to the applications of ionic liquids.[5]

In this talk, we present results on the structure of the electric double layer of ionic liquid interfaces with small amounts of water molecules, which was revealed by using electrochemical techniques and AFM-based force curve measurements under potential control. By analyzing the potential-dependent layering structure including the number, thickness, and stability of the layers at different water concentrations, a better understanding of the role of small amounts of water in the structure of the electric double layer of the electrode/ ionic liquid interface is achieved.

We also present results about the effect of hydrophobicity/hydrophilicity of ionic liquids and electrodes on interfacial distribution of ions and electrosorbed water. The results demonstrate that using hydrophilic ionic liquids would help to keep water molecules away from the negatively charged electrodes, even at large electrode polarizations, which is very important for selecting appropriate ionic liquids to avoid the influence of water.

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Fast Production of a Low-Cost SERS Platform by Gold Electrodeposition on Porous Polymeric Templates

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Among common methods for SERS substrates preparation, those with greater reproducibility usually rellies on lithography, etching and ion-beam, leading to good control on surface morphology but at the expense of high-priced equipment and often extensive multi-step procedures[1].

Here, we present a 90-second two-step procedure focusing in the spatial delimitation of electrode's submicrometric domains by breath-figure method (BFM) with poly(methyl methacrylate) (PMMA) spin-coating, forming a thin porous film onto the ITO electrode[2], Figure 1.

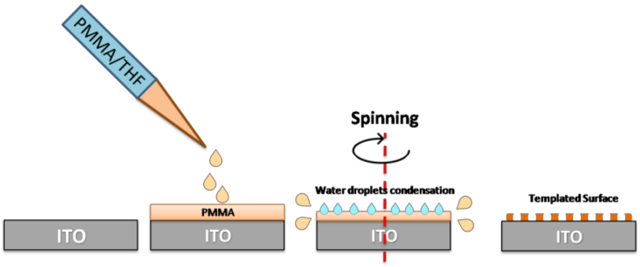

Figure 1. Scheme of the BFM for porous PMMA film formation, comprising PMMA in THF casting, spinning for solvent evaporation and water droplets condensation and the solid honeycomb pattern.

In order to obtain confined gold nanostructures inside the pores, electrochemistry emerged as an important tool to have precise control on the amount and shape of deposits, Figure 2a.

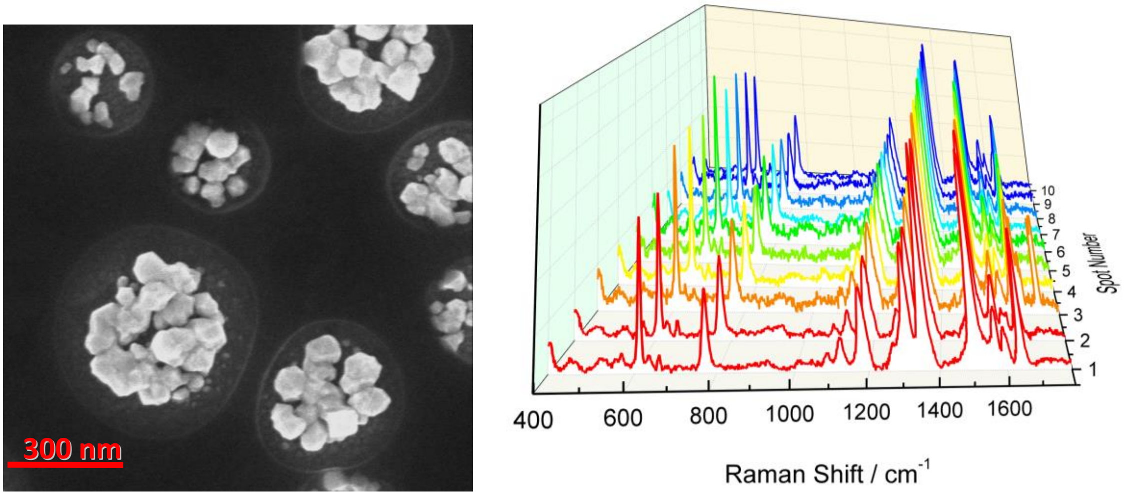

Figure 2. (Left) Micrograph of gold nanoparticles deposited in PMMA pores; (right) normalized Raman spectra of Rhodamine 6G in different surface spots, baseline-corrected, 633 nm excitation wavelength.

The quickly-produced SERS substrates were active showing good reproducibility in both 633 nm, Figure 2b, and 785 nm excitation sources, with average enhancement factor in the order of 10^7, detection limit in the nanomolar range and stability for at least 30 days.

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The function mechanism of a novel quasi-solid-state Li-S battery

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We propose a $[Li(triglyme)]^+[TFSI]^-$ solvent-salt complex with excellent stability towards $Li_{10}GeP_2S_{12}$ electrolyte and demonstrate its application in the high-performance quasi-solid-state lithium-sulfur battery. A spot of LiG3 addition into cathode dramatically facilitates the Li^+ ionic transfer and the transition of a solid-solid redox reaction for sulfur species to solid-liquid dual-phase redox reaction. And LiG3 addition accelerates the kinetic process at the beginning of discharge, and LGPS powders scattered in cathode could greatly strengthen the solid-phase redox reaction process, promoting the excellent electrochemical performance of the solid-state Li-S battery.

Experimental methods. The composite cathode powders were prepared by a two-step mechanical milling method. Firstly, 0.2 g LGPS electrolyte, 0.05 g VGCFs and 0.2 g sulfur were mixed with a rotate speed of 250 rpm and 10 h in a 60 mL zirconia jar with 5 mL mineral spirit solution, ratio of grinding media to material was controlled at 20:1, solid content was controlled at 40%. Subsequently, 0.05 g VGCFs was added into the mixture and remixed with a rotate speed of 100 rpm and 10 h. Then, the mixture was dried at 60℃ for 24 h, and the obtained pristine composite cathode powders were denoted as S-0 powder. Finally, 0.25 g LiG3 complex and 5.0 g the obtained S-0 were mixed in an agate mortar and formed the optimized composite cathode powders, denoted as S-5, the weight ratio of sulfur, LGPS electrolyte, VGCFs and LiG3 complex in the composite is 4: 4: 2: 0.5.

Results. Fig.1(a) presents the typical charge-discharge curves of the Li-S cells used in this work. The S-5 cells exhibit two discharge voltage plateaus, while there is only one reductive peaks at 1.5 V for the S-0 system. Fig.1(b) shows the surface morphology changes of S-0 and S-5 cells changes after cycling, and it suggests that the reaction mechanisms between S-0 and S-5 cells are different. Moreover, the XPS results (fig.1(c)) directly prove that S-0 cells perform a totally different reaction route with conventional Li-S battery, which is no polysulfide lithium intermediates generation. Nevertheless, with the LiG3 addition, the S-5 cells generate lithium polysulfide (Li_2S_n) and follow an apparent solid-liquid dual-phase redox reaction. In addition, we attempt to replace LGPS within the S-5 cathode with the Li^+ insulated SiO_2 nano-filler, to deeply elucidate the role of LGPS electrolyte in the cathode, and cells present inferior solid-phase redox reaction with poor capacity and cycling stability. Therefore, it can be believed that LiG3 addition accelerates the kinetic process at the beginning of discharge, and LGPS powders scattered in cathode could greatly strengthen the solid-phase redox reaction process, promoting the excellent electrochemical performance of the solid-state Li-S battery.

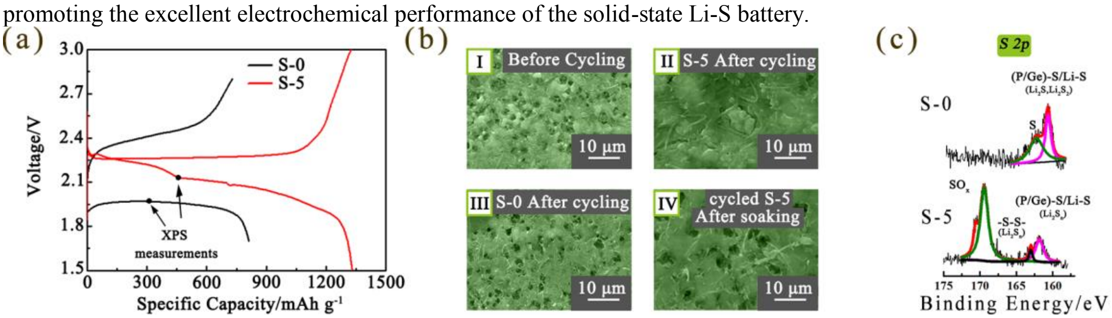

Figure 1 (a) Charge-discharge curves of S-0 and S-5 cells at 50 μA/cm^2, RT.; (b) SEM morphology of S-0 and S-5 cells before and after cycling tests and cycled S-5 after soaking by LiG3 for 5d; (c) XPS spectrum of the surface of discharged composite cathode S-0 and S-5.

Conclusions. The addition of LiG3 facilitates the Li^+ ionic transport kinetics at the cathode/electrolyte interfaces, and changes the reaction mechanism from solid-state Li-S battery to solid-liquid dual-phase redox reaction without sacrificing the ability to inhibit shuttle effect. And it can be believed that LiG3 addition accelerates the kinetic process at the beginning of discharge, and LGPS powders scattered in cathode could greatly strengthen the solid-phase redox reaction process, promoting the excellent electrochemical performance of the solid-state Li-S battery.

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Electrografting Organic Amines on Indium Tin Oxide of 3D Interdigitated Electrode Array for Immunosensing

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Three-dimensional (3D) interdigitated electrode array (IDA) on a microfluidic chip can offer great opportunity for multiplex electrochemical biosensors with high sensitivity requiring extremely small amount of sample. Indium tin oxide (ITO) as an electrode material can make 3D IDA much more attractive because limit of detection goes down owing to substantially low background current. Additionally, this transparent electrode allows simultaneous optical detection that could widen the range of options for electrochemical biosensing chip. ITO based IDA can be easily and precisely patterned using conventional etching process to be integrated in a single microchannel which very small volume of liquid sample is enough to fill in. Therefore, ITO is an ideal electrode material for electrochemical 3D IDA system. There are two key issues toward practical uses. One is reference electrode that needs to lie as closely as possible to working electrodes for precise control of electrochemical potential. It is problematic because reference electrode can be hardly miniaturized to be integrated inside the microchannel without loss of its own performance. The other issue is exclusive immobilization of functional materials on ITO surface. ITO is chemically inert, thus few organic molecules can be anchored and any functional layer on it is readily detached to go away. With regard to immunosensing with 3D IDA, antibodies should be immobilized on glass surface between neighboring microband electrodes to which mediators are firmly bound. In this presentation, we propose two-electrode (2E) system that has appropriate mediator layer on ITO IDA. 2E system consists of only two complementary IDA demanding no reference electrodes while electrochemical potential can be tuned due to the mediators lying on the ITO electrodes. For instance, poly(methylene green), a redox polymer formed by electropolymerization of methylene green monomers, on ITO IDA makes electrochemical potential of electrodes keep under control of its own redox potential. Moreover, this mundane redox layer serves as a successful mediator for redox cycling among the microband electrodes upon relatively low overpotential, leading to effective signal amplification without aid of chemical or biological reducing (or oxidizing) reagents deliberately added. Experimental evidences support this strategy works well. The remaining task to be addressed is the reliability of the proposed system as electrochemical biosensors, which depend on adhesion between ITO surface and mediators. We suggest two solutions, i.e. utilizing dopamine when electropolymerizing redox polymer and utilizing electrografted organic molecules to link ITO electrode to mediators. The former indeed improves the adhesion, thus we can reproducibly fabricate immunosensors based on 3D ITO IDA to see the results corresponding with the proposed concept. Since it relies on adsorptive property of dopamine and entanglement between polydopamine and poly(methylene green), its application should be limited in terms of stability and diversity of mediators to be immobilized. In this sense, the latter can be a remedy. It has been reported that oxidative electrografting of amines is possible in aprotic media on glassy carbon, Au and Pt. Although electrografting on ITO surface has been published as well, the functional materials immobilized in such a way are unstable for fabrication. We will present a more reliable way of electrografting to firmly bind various mediators, and experimental aspects that originate from the resulting structure.

Designer Electroactive Bacteria

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One of the research questions that we have found most fascinating in bioelectrochemistry is, what makes electrogenic bacteria, electrogenic? And more importantly, can we turn turn non-electrogenic bacteria to electrogenic bacteria? Using the tools of synthetic biology, synthetic chemistry and standard as well as new genetic engineering tools, we have replaced the pili of *pseudomonas aeruginosa* with pili of electrogenic bacteria using CRISPR/Cas 9 technology and studied the new bacteria properties. We have genetically expanded the genetic code of *pseudomonas aeruginosa* and modified its flagellin peptides using an unnatural amino acid (UAA) in order to site-specifically attach to it electro-transferring enabling moieties (such as gold nanoparticles). We have studied single pilin electron transferring properties and their directionality, in different peptide orientation on electrodes. Using these novel technologies, we could successfully confirm some of the suggested mechanisms of electron transfer in such electron transferring microorganisms, furthermore we could successfully demonstrate that if specific molecular components are correctly identified as electron transferring components, transplantation of these proteins into non-electron transferring microorganisms, greatly enhances their electron transferring properties.

Catalytically Synthesized Prussian Blue Nanoparticles Defeating Peroxidase: Application for Electroanalysis

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There is an increasing interest in mimicking peroxidase activity. However, real analytical applications became possible only after the discovery of nanoparticles with peroxidase-like activity (catalysis of hydrogen peroxide reduction), later referred to as nanozymes. The main disadvantages of the reported metal oxide and noble metal based nanozymes are their low specificity in addition to their oxidase-like and catalase-like activities. Moreover, in physiological solutions (pH 7.0 – 7.5) commonly used for bioanalytical applications such nanozymes are catalytically inactive.

Prussian Blue (PB) is recognized as the most advantageous electrocatalyst for hydrogen peroxide reduction in neutral media over all known systems [1, 2] and, thus, is favorable for bioanalytical applications. In the present study we synthesized Prussian Blue nanoparticles in course of reduction of ferricyanide, $[Fe(CN)_6]^{3-}$, and ferric ions, Fe^{3+} mixture either by hydrogen peroxide, or by conducting polymer forming organic molecules. In this case the precipitation is caused by the same reaction that occurs upon electrocatalysis, which results in formation of Prussian Blue nanoparticles with the highest catalytic activity [3].

Kinetic properties of the catalytically synthesized PB nanoparticles allow to conclude that they defeat natural enzyme peroxidase. Peroxidase activity of nanoparticles and the enzyme has been investigated oxidizing 3,3',5,5'-tetramethylbenzidine (TMB), apparently the fastest substrate of the enzyme peroxidase. The initial reaction rate of hydrogen peroxide reduction, catalyzed by PB nanoparticles, is linearly dependent on H_2O_2 concentration, which has never been observed either for peroxidase-like nanozymes, or for natural peroxidase. This indicates that substrate (H_2O_2) activation by PB nanoparticles occurs much faster even compared to the natural enzyme. Moreover, importantly, in the absence of hydrogen peroxide no oxidation of TMB has been registered in its entire concentration range. Hence, the obtained PB nanoparticles do not display oxidase-like activity (reduction of molecular oxygen).

Catalytic constants in H_2O_2 reduction for catalytically synthesized PB nanoparticles are nearly volume dependent (the slope of size dependence in double logarithmic plots exceeds 2.5) indicating that hydrogen peroxide penetrates the bulk of nanoparticles. Most importantly, for all sizes of PB nanoparticles the catalytic rate constants are higher, than for natural peroxidase (for PB nanoparticles 200 nm in diameter the turnover number is 300 times higher).

Except for the activity defeating even the natural enzyme catalytically synthesized PB nanoparticles are highly active even at pH 7.4, and k_{cat} evaluated for TMB as a substrate at pH 7.4 is less than 1.5 times lower than in pH 5.0 used for kinetic investigations.

Drop-casting of the nanoparticles suspension with subsequent drying allows to modify the electrodes. The latter, similarly to conventional Prussian Blue film modified electrodes, display the two sets of peaks corresponding to Prussian Blue|Prusssian White and Berlin Green|Prussian Blue redox transitions in their cyclic voltammograms. Analytical properties of PB nanoparticles modified electrodes were investigated at constant potential (E = 0.00 V) providing hydrogen peroxide reduction. Linear calibration range is prolonged over more than 3 orders of magnitude of H_2O_2 concentrations. Sensitivity evaluated as a slope of the calibration graph is of 0.85 $A \cdot M \cdot cm^{-2}$ (30% higher compared to it for similar three-electrode structure modified with PB film). The improved analytical performance characteristics of the PB nanoparticles modified electrodes are most probably due to their increased roughness providing more efficient mass transfer compared to conventional PB films.

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Operando Raman Nanoscopy:
Watching Electrochemical Surface Reactivity with EC-TERS

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Understanding the correlation between structure and reactivity of electrified interfaces under *operando* conditions is essential for the development of improved electrocatalytic or -synthetic platforms or energy conversion devices *(1,2)*. For example, adsorbate geometry and orientation relative to an electrode surface strongly influence the interfacial charge transfer properties. The nanoscale chemical composition and topography at active sites plays a fundamental role for preferential reaction intermediate formation or pathways. However, quasi-atomistic insight into such surface reactivity parameters is challenging to obtain under operating conditions.

In my talk, I will present how electrochemical tip-enhanced Raman scattering (EC-TERS) can provide unique nanoscale insights into electrochemical interfaces, particular with respect to redox activity and orientation of molecular adsorbates and mapping of chemical conversion at active electrode sites *(3,4)*.

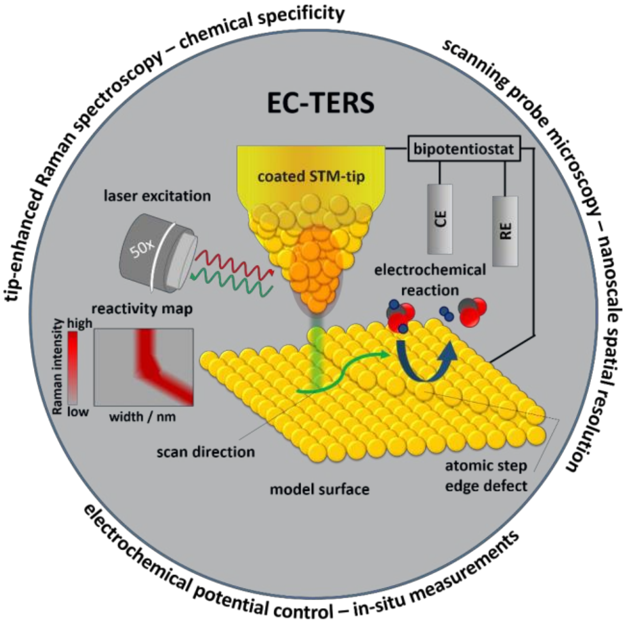

Figure 1: Schematic of EC-TERS imaging platform. Reproduced from *(2)*.

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Self-Powered Electrochemical Systems for Biosensing and Nanoparticle Synthesis Applications

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Since the introduction of the first expounded triboelectric nanogenerator (TENG) in 2012, the theoretical and practical aspects of the TENG have been researched as an alternative energy harvesting technology to convert mechanical energy into electricity efficiently. Numerous self-powered sensing systems have adopted the TENG as a power source to further explore its versatile applications toward different targets. In this study, we employed a TENG to replace a traditional power supply for synthesizing different metallic nanoparticles using an electrochemical approach. Carbon fibers were adopted as the conductive substrates to grow the metallic nanoparticles, where the size and density of the nanoparticles on carbon fibers can be controlled by the electric output of the TENG. Additionally, we demonstrated that the as-prepared carbon modified and integrated with the TENG to construct a wearable self-powered sensing system exhibited significant selectivity and sensitivity toward lactate detection. Furthermore, the design of the sensing unit was favorable regarding its adaptability and flexibility to fit human body shapes and postures. As demonstrated in this study, the as-prepared self-powered sensing system could detect the lactate concentration in human perspiration, which can be an ideal wearable device for end users who seek real-time monitoring of their physical condition. This study concludes with a proposal for noninvasive biosensors, which provide boundless potential for future cross-field applications.

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Electroactive Supramolecular Ionic Material for Biosensing and Electronic Device

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Over the past two decades, functional supramolecular materials prepared with noncovalent interactions have attracted enormous attention because of their unique applications in electronics, photonics, light-energy conversion, biosensing, and catalysis. Recently, supramolecular materials with water-stability and adaptive encapsulation properties have become particularly attractive especially in biosensor development since most biological processes take place in aqueous environments and biological molecules such as proteins and enzymes are generally active in water. Moreover, the ability to encapsulate functional molecules in supramolecular networks enables the materials to hold great promise in tailoring and improving their functions for target-oriented applications. So far, several kinds of water-stable and adaptive materials have been developed, mainly based on metalcoordination interactions. As a result, it is imperative to explore other kinds of noncovalent interactions for the development of water-stable and adaptive materials with excellent properties.

Ionic interaction between oppositely charged species represents one of the strongest noncovalent interactions and has been widely used in self-assembly, typically as electrostatic self-assembly in solid state and ionic self-assembly in solution. All this work suggests that Coulombic interaction could be used as the noncovalent interaction to form supramolecular materials by self-assembly. While wide availability of charged species and the simplicity of their synthesis allow the ionic interactions to be used in synthesis of various functional materials, it remains a great challenge to utilize this kind of interaction to develop functional supramolecular materials with water stability and adaptive encapsulation property. This is because, on one hand, most of the charged species could easily dissolve in water because of the high dielectric constant of water ($\varepsilon = 78.5$, at 25 °C) and thus the electrostatic interactions become significantly weakened in water. On the other hand, the large lattice energy in ionic compounds essentially limits their encapsulation property. Very recently, this interaction was utilized to create supramolecular ionic networks and supramolecular polymers by using multiple electrostatic bonds. This implies that ionic interaction could potentially provide the possibility to form water-stable and adaptive supramolecular materials by rationally designing the structure of the building blocks. However, such potential has not been explored so far.

Herein, we demonstrate a series of water-stable, adaptive, and electroactive supramolecular ionic materials (SIM) that is formed from the aqueous solutions of imidazolium-based dication and dianionic through ionic self-assembly. The formed SIM not only shows good thermostability and unique optical and electrochemical properties that are raised from precursors of the SIM, but also exhibits good water-stability, salt-stability, and adaptive encapsulation properties toward some heterocyclic cationic dye molecules. Firstly, we systematically studied the self-assembly behavior based on different carbon chains in imidazolium dications and its structure. Secondly, we found these SIM bears good adaptive inclusion property towards organic dyes and inorganic salt. Based on this, some kinds of biosensors including fluorescence and electrochemistry have been developed. Finally, the electronic property of this kind of SIM was investigated. And we found its electric conductivity was strongly dependent on the humidity. Based on this property, the solid electronic device with high sensitivity and stability was developed. The present study not only opens a new avenue to the preparation of the supramolecular materials, but also provides a versatile platform for (bio)sensing and electronic devices.

In Vivo Electrochemistry to Understand Physiological Roles of Ascorbate

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To understand the molecular basis of brain functions, researchers would like to be able to quantitatively monitor neurochemicals in vivo. However, the chemical and physiological complexity of the central nervous system (CNS) presents challenges for the development of these analytical methods. We used the redox nature of neurochemicals at the electrode/electrolyte interface to form a basis for selectively monitoring neurochemicals. In this presentation, I would introduce the recent process in our group on in vivo monitoring ascorbate in rat brain.

1) Carbon nanotubes (CNTs) provide an electrode/electrolyte interface for the selective oxidation of ascorbate and, based on this, we have developed both in vivo voltammetry and an online electrochemical detecting system (OECS) for continuously monitoring ascorbate in CNS.

2) By using the CNT-based OECS, we compared the dynamic regional changes of extracellular ascorbate level in four different brain regions 1 h after global cerebral ischemia induced by two-vessel occlusion (2-VO). We also compared the change in the level of ascorbate in the different ischemia model (i.e., two-vessel occlusion (2-VO) and left middle cerebral artery occlusion (LMCAO) in striatum.

3) We also demonstrated the validity of the OECS for ascorbate detection as a platform for in vivo evaluation of neuroprotective efficiency of antioxidants by studying the dynamic change of hippocampal ascorbate during the acute period of cerebral ischemia and its responses to intravenous administration of antioxidants including ascorbate and glutathione. instructions are an example of what a properly prepared meeting abstract should look like.

Biocompatible Coatings for Mg Alloys

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Magnesium and its alloys are promising materials for biodegradable implant applications. However, the degradation rate in the biological environment should be adjusted for the specific application, to match the healing behavior of the surrounding tissue. For the control of corrosion, research has targeted development of new alloys as well as coatings and surface modification of Mg. This presentation will discuss challenges in developing suitable coatings for Mg for biomedical applications. The requirements for such coatings are multifunctional, in that the coatings should be biocompatible, biodegradable and possibly also bioactive. Many different approaches have been explored, such as coatings based on biodegradable synthetic or natural biopolymers. The presentation will describe methods to successfully coat highly reactive Mg alloy surface in aqueous solutions, based on developing suitable pre-treatments of the surface. Immersion testing and electrochemical experiments revealed information on the corrosion protection properties of the coatings as well as on the time-dependent degradation of the coatings. Influence of the electrolyte composition on the performance of the coatings was studied, including the effect of proteins on the corrosion behavior. The exact composition of the type of simulated body solution as well as addition of proteins can very strongly influence the corrosion behavior. The effects are highly complex in that for instance proteins show a time-dependent and strongly system-dependent influence on the corrosion rate; both accelerating and inhibiting effects by proteins in solution can be observed.

Electrode system for Large-scale Reverse Electrodialysis: Water electrolysis, Bubble resistance, and Inorganic scaling

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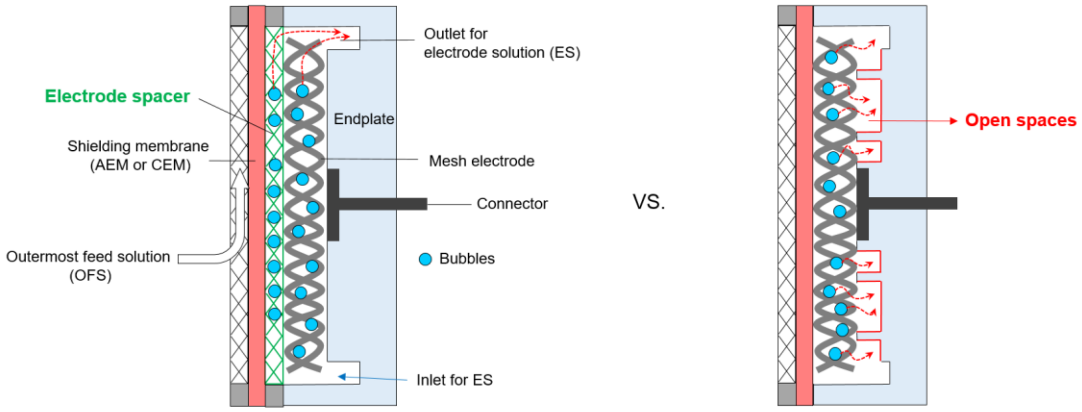
It is generally accepted that the effect of electrode resistance is not predominant in determining the performance of reverse electrodialysis (RED), because the contribution of electrode resistance to total internal resistance decreases as the number of cell pairs increases[1-3]. However, this is not true under the condition in which gas is continuously produced by water electrolysis owing to the large stack voltage in pilot-scale applications. We verified that the bubble resistance of the electrode spacer in a conventional endplate causes the electric power of a RED system with 1,000 cells to decrease by more than 20% under the specific condition in which the outermost feed solution (OFS) at both electrodes and the electrode solution (ES) are river water. This configuration, called OFS(river)/ES(river), is the best for minimizing inorganic scaling and toxic gas evolution. Another problem associated with the conventional endplate is fluid congestion owing to very narrow spaces, which causes sudden pH changes and deteriorates further with inorganic scaling. To address these issues, we removed the electrode spacer from the electrode system and utilized an open-type endplate with interconnected open spaces. This endplate maintained high electric power without the bubble resistance and suppressed the abrupt changes in the pH around the electrodes and the shielding membranes. We believe that our approach will be useful in the search for an optimum electrode design for RED systems on the industrial scale.



Enclosed-type endplate with electrode spacer

Open-type endplate without electrode spacer

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Intrinsic Cu nanoparticle decoration of TiO_2 nanotubes: A platform for efficient noble metal free photocatalytic H_2 production

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The use of titanium dioxide (TiO_2) for photocatalytic applications has been intensively investigated for years due to appropriate electronic properties, chemical and photocorrosion resistance, as well as the low cost of the material [1]. Although TiO_2 has a suitable conduction band position for the photocatalytic H_2 formation reaction, the hydrogen evolution reaction from water on a TiO_2 surface is kinetically hampered. To tackle this problem, typically decoration with noble metals such as Pt, Pd, Au that act as a co-catalyst is employed. However, these noble metals are costly and a variety of pathways for replacing these elements have been explored. One of the promising substitutes for noble metals are copper and copper-compounds. The fabrication of copper co-catalyst loaded TiO_2 nanotubes is conventionally carried out by chemical methods such as hydrothermal, impregnation, photo-deposition and electrochemical deposition [2]. However, a most straightforward and unique method to modify anodic TiO_2 nanotube properties is employing, instead of pure Ti metallic substrate, a Ti-X alloy in the anodization process, were X is another metal. During anodizing the second metal can be simultaneously oxidized and doped into the TiO_2 lattice (in substitutional or interstitial position), giving the nanotubes a specific functionality [3–5]. A number of such intrinsically doped nanotube arrays have been reported, namely using Nb, Ta, Ru and etc., alloyed in Ti [3–5].

In this work, we grow intrinsically Cu doped TiO_2 nanotubes (TiNTs) by self-organizing anodization of Ti-Cu binary alloys. We demonstrate that up to a copper concentration of 1.5 at.% in the alloy, self-ordered Cu^{2+}-doped nanotubes can be grown. Under UV illumination the Cu^{2+} ion-doped oxide structures can be converted to nanotubes that carry metallic nanoparticles (NPs) uniformly decorated TiNTs. We investigate the formation of these metallic nanoparticles under UV illumination by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and electron paramagnetic resonance (EPR). The resulting intrinsic copper doped and decorated TiNTs provide a strongly enhanced photocatalytic activity for H_2 evolution in comparison to pristine TiNTs. Key is the light induced conversion of the intrinsic Cu doping to metallic copper nanoparticles that act as a stable co-catalyst for H_2 generation.

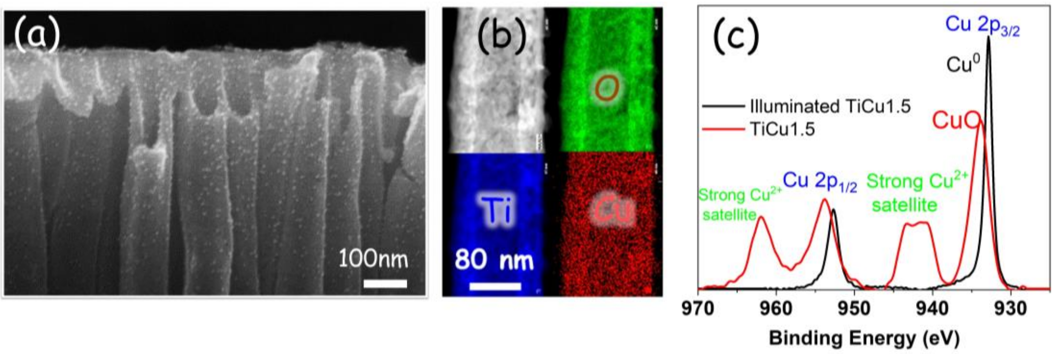

Figure 1. (a) SEM images of intrinsically decorated Cu nanoparticle TiO_2 nanotubes and (b) EDS map of TiO_2 nanotubes grown on the 1.5 at.% Ti-Cu alloy (c) high resolution XPS spectra of the Cu2p for TiCu1.5 before and after UV illumination.

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Conductive Cu doped TiO_2 nanotubes for enhanced photoelectrochemical methanol oxidation and concomitant hydrogen generation

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Ever since Fujishima and Honda reported on the photoelectrolysis of water into H_2 and O_2 using a rutile titanium dioxide single crystal, TiO_2 has been widely explored for applications in photoelectrochemical (PEC) water splitting [1]. In a conventional PEC device, the reduction and oxidation reactions occur at the surface of photoelectrodes. Therefore, a larger specific surface area of the photoanode represents a great advantage [2]. An efficient route to obtain highly defined nanoscale photoanodes is the anodic growth of self-organized TiO_2 nanotube layers on Ti. However, the efficiency of using pure TiO_2 as a water splitting photoanode – even in a nanotube form – is still low due to the fact that only a sluggish charge transfer kinetics to H_2O is obtained [2]. One way to enhance the overall reaction rate of the photocurrent is to use hole-capture agents that facilitate the oxidation reaction, such as various alcohols, namely methanol. A further enhancement of the reaction can be the use of additional co-catalysts for catalyzing methanol photoelectrochemical and electrochemical oxidation – typically these are noble metal based catalysts [3]. An inexpensive alternative could be copper that has been reported as an efficient electrode for methanol electro-oxidation. [4]. It is therefore conceivable to design a copper doped titania structure to create an efficient photoanode for methanol oxidation. However, copper doped titania has never been reported for photoelectrochemical methanol oxidation. The key obstacle is that copper doping (Cu^{2+} and Cu^{+}) drastically reduces the conductivity and photo-conductivity of a TiO_2 scaffold [5] and thus prevents the practical use of Cu doped-titania as electrodes or photoelectrodes. In previous work, we showed that optimized annealing of TiO_2 nanotubes in Ar/H_2 can not only drastically improve the conductivity of TiO_2 nanotubular structures but also preserve the semiconductor properties of TiO_2, thus providing efficient photoelectrodes [6].

In this work, we produce TiO_2 nanotube arrays intrinsically doped with copper and establish sufficient conductivity to use them as efficient photoanodes for methanol oxidation in a photoelectrochemical hydrogen generation setting. Firstly, Cu doped TiO_2 nanotubes were produced by anodizing a Ti-Cu binary alloy. By subsequent thermal reduction of the structure in an Ar/H_2 environment, conductive copper doped TiO_2 nanotubes (TiCuTN-Ar/H_2) can be achieved with an approximately 10^3 times higher conductivity than the non-reduced material. When these reduced Cu doped TiO_2 nanotubes are used as photoanode, copper species embedded in the TiO_2 wall catalyze the methanol oxidation reaction. As a result of the combined effect of conductivity and catalytic effect of Cu, such a reduced Cu:TiO_2 nanotubes can generate a photocurrent of 0.76 $mA.cm^{-2}$ at 1 V vs. RHE, under AM1.5 (100 mW/Cm^2) irradiation – in a 50:50 MeOH/water solution – this is 33 times higher than for pristine Cu:TiO_2 nanotubes.

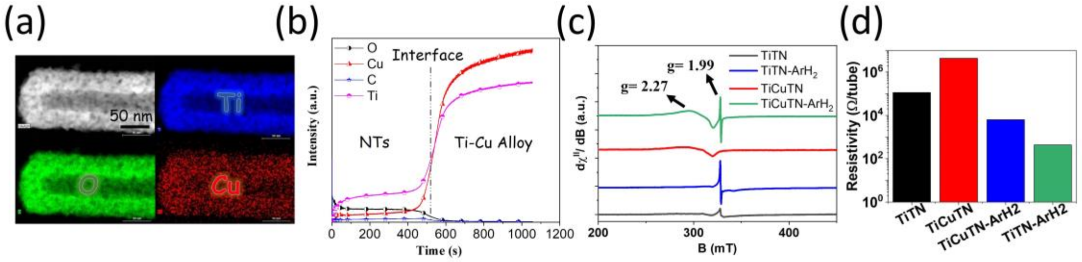

Figure 1. (a) EDX map of O, Ti and Cu, (b) GDOES depth profile of the Cu-doped TiO_2 nanotubes, (c) EPR spectra recorded at 123 K of pristine TiO_2 and TiCu nanotubes and the Ar/H_2 treated samples, and (d) resistivity of pristine TiO_2 and TiCu nanotubes and the Ar/H_2 treated samples.

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Exploring the Interplay Between Organic Synthesis and Electrochemistry. Capitalizing on a Synergistic Relationship

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Electrochemistry has long held potential as a tool for constructing a wide variety of organic molecules, and the organic chemistry community is both recognizing and impressively exploiting that potential with increasing regularity. Those efforts have taught us a great deal about how to think about electrochemical reactions and how to use the technique to accomplish new transformations that enrich the synthetic enterprise.

Interestingly, the relationship between organic synthesis and electrochemistry can also be viewed in the opposite direction with the new synthetic chemistry being developed offering exciting opportunities to expand the scope of electrochemical experiments. Central to this idea is the site-selective generation of chemical reagents, a technique that allows for the construction of complex molecular surfaces on an addressable array of electrodes. Efforts along these lines are setting the stage for the use of electrochemistry to monitor the binding behavior of small molecule libraries with biological targets in "real-time", experiments that afford a previously unknown level of quality control over the library.

Not surprisingly, the exploration of these new electrochemical tools is also beginning to "give back" to the synthetic arena with preparative scale applications arising from the concept of site-selective reagent generation.

In the talk to be given, this interplay between organic synthesis and electrochemistry will be highlighted with an emphasis on how each area of research can be used to advance the other.

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A Bio-Solar Cell with Thylakoid Membranes and Bilirubin Oxidase

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Mimicking the natural photosynthesis is expected to be a fundamental technology to realize a sustainable energy economy. It is called artificial photosynthesis. A bio-solar cell is one of artificial photosynthetic devices and extracts the excited electrons to an electric circuit outside the photosynthetic system. We constructed a bio-solar cell designed from photosynthesis. The bioanode comprises thylakoid membranes from spinach on water-dispersed multi-walled carbon nanotubes immobilized on a gold-spattered indium tin oxide electrode.

When the electrons transfer from thylakoid membranes to an electrode, some artificial mediators may be utilized. The electron transfer kinetics between thylakoid membranes and mediators obeys a linear free energy relationship. Characteristics required for desirable mediators in photo-driven bioanodes of bio-solar cells are high electrode kinetics, high stability, suitable solubility, and negative redox potential. In addition, the mediators have to have high oxygen (O_2) resistance, because O_2 evolution occurs at the bioanode with PSII functions. $[Ru(NH_3)_6]Cl_3$ was used as a soluble mediator, since its formal potential is rather negative and $[Ru(NH_3)_6]^{2+}$ has strong resistance to autoxidation.

On the other hand, we used bilirubin oxidase (BOD) for the biocathode. BOD is one of multicopper oxidases, catalyzes four-electron reduction of O_2 to water, and transfers electrons directly from an electrode to O_2 with relatively low overpotentials. The active site of BOD contains four copper atoms divided into three types according to their spectroscopic and magnetic properties: type I (T1), type II and type III coppers. In direct-electron-transfer (DET)-type bioelectrocatalysis, the T1 copper works as an electron acceptor from electrodes. In this study, we used recombinant BOD, which is produced by expressing the gene of BOD from *Myrothecium verucarria* in *Pichia pastoris*. The recombinant BOD has higher activity and thermostability than the wild-type BOD from *Myrothecium verucarria*. We utilized a gas-diffusion-type bioelectrode which passively supplies O_2 from the gas phase to BOD on the bioelectrode to realize a high-speed O_2 supply.

The bioanode exhibited a photocurrent at a density as high as 0.2 mA cm^{-2} at 0 V and a photon flux density of 2 mmol m^{-2} s^{-1}. The biocathode comprises recombinant bilirubin oxidase expressed in *Pichia pastoris* for DET-type bioelectrocatalytic O_2 reduction. The two electrodes were coupled to construct a bio-solar cell without a separator. The cell exhibited an open-circuit voltage of 0.61 V and a maximum power density of 50 µW cm^{-2} at a cell voltage of 0.42 V under quiescent conditions.

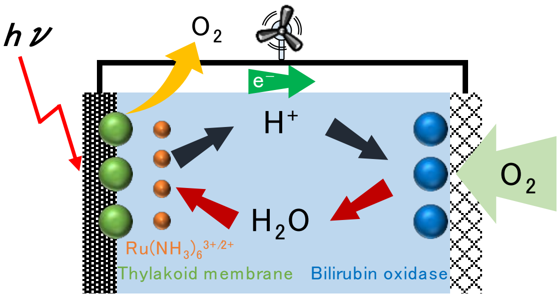

Fig. 1 Schematic of bio-sor cell

Highly Sensitive, Stable and Selective Hydrogen Peroxide Amperometric Biosensors Based on Peroxidases from Different Sources Wired by Os-Polymer: A Comparative Study

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ABSTACT

A comparison was made between two plant peroxidases, cationic horseradish peroxidase (HRP) and anionic tobacco peroxidase (TOP), to form the basis together with a highly cationic osmium polymer [Os(4,4′-dimethyl-2,2′- bipyridine)$_2$poly(N-vinylimidazole)$_{10}$Cl] $^{+2/+}$ ([Os(dmp)PVI] $^{+/2+}$) to prepare highly sensitive, stable and selective hydrogen peroxide biosensors. The two different plant peroxidases were individually immobilized onto graphite rod (G) electrodes by a three steps drop-casting procedure consisting of the subsequent deposition of an aqueous solution of ([Os(dmp)PVI] $^{+/2+}$), followed by a solution of poly(ethyleneglycol) diglycidyl ether (PEGDGE), used as a cross linking agent and finally an aliquot of a solution of cationic HRP or anionic TOP to make HRP/PEGDGE/[Os(dmp)PVI]$^{+/2+}$/G and TOP/PEGDGE/[Os(dmp)PVI]$^{+/2+}$/G based electrodes, respectively. Electrochemical experiments were carried out to investigate the influence of the surface charge of the enzyme and the charge of the polymer on the efficiency of the electron transfer (ET) between the enzyme and the wiring redox polymer and the efficiency for electrocatalytic reduction of H_2O_2. In the case of HRP a decrease in the ET rate was observed due to the repulsion between this enzyme and the polymer, both positively charged, whereas with TOP there was an enhanced ET rate due to the attraction between the anionic enzyme and the cationic polymer. The effects of enzyme loading and pH were investigated. Both optimized peroxidase modified electrodes exhibited a wide dynamic response range (1-500 μM H_2O_2) and a low detection limit (0.3 μM H_2O_2). The TOP based electrode showed a higher sensitivity (470 nAμM^{-1}cm^{-2}) compared to that of the HRP based electrode (300 nAμM^{-1}cm^{-2}) and an improved long-term stability (decrease in 17.3% upon 30 days compared with 50% for HRP). Both enzyme electrodes showed a response time of 3 s. The HRP based sensor was more sensitive to the presence of phenolic compounds acting as alternative electron donors, whereas the TOP based sensor was virtually interference free. Both HRP and TOP based electrodes were successfully tested in contact lens cleaning samples and real “spiked” samples from different sources such as tap water, milk and dairy products.

Keywords: H_2O_2; HRP; TOP; wiring; osmium polymer

References : *Solid State Ionics 314 (2018) 178–186*. doi.org/10.1016/j.ssi.2017.10.015.

Well-defined Pt(hkl)|solution interfaces: charge, ionic adsorption and acid-base properties.

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Abstract

The use of well-defined model electrodes benefits of the knowledge of the surface atomic density. This parameter is the key to correlate the charge transfer associated to any surface process to the stoichiometry of the corresponding electrochemical reaction. On polycrystalline materials, the number of surface atoms is unknown and the lack of this information makes difficult any quantitative analysis of data.

Comparison between different processes taking place at well-defined interfaces enables to gain information about the validity of Faraday laws in Surface Electrochemistry and validate charge density as a quantitative tool. Once understood, potentials of zero charge can be estimated for different single crystal Pt(hkl) electrodes and particularly for Pt(111), by using purely electrochemical techniques [2]. The results are corroborated by using more sophisticated auxiliary techniques.

The knowledge of the potential of zero free charge defines the adsorption of ions at the surface and the possible contribution of ionic pairs in this process. On the other hand, using electrolytes that do not contain to specifically adsorbed species enables to work at different pH values and approach interfacial properties related to acid-base equilibria [3, 4]

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Synthesis, Spectroscopic and Electrochemical Characterization of Benzyl Thio Substituted Phthalocyanines for Application in Electrocatalytic Detection of 4-Chlorophenol in Water

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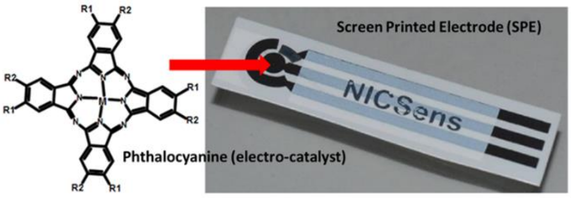

Scheme 1: Modification of a Screen Printed Carbon Electrode with Benzyl Thio Substituted Phthalocyanines.

Chlorophenols are toxic organochlorides of phenols primarily released from industrial and agricultural wastewater. Electrocatalytic detection of chlorophenols has been performed on Gold, Glassy Carbon and Platinum electrodes. Repeated detection cycles result in passivation of the electrode surface by thin films of phenolic polymers that result from the oxidation of the chlorophenols.

This work aimed to design a portable system for field detection of Chlorophenols, using a portable potentiostat with modified Screen Printed Carbon Electrodes (SPCE) (see scheme 1). Disposable SPCE sensors are becoming a trend with regards to application in electrochemical sensors [5]. Cobalt complexes 1, 2, 3 and 4 in figure 1 are used in this work to modify the SPCE surface, to serve as an electro-catalyst and prevent electrode fouling. In order to improve selectivity towards chlorophenols, molecular imprinted polymer (MIP) approach is used [1].

The MIP recognition element is added to the screen printed electrode by electropolymerizing of the monomer o-phenylenediamine (oPD), to form poly(o-phenylenediamine (PoPD), in the presence of pollutant of choice as a templet following a known method found in literature [1].

The surface morphology of various modified electrodes (PPY/SPE, PPY-GO/SPE, PPY-GO-CoPc/SPE and MIP/PPY-GO-BiCoPc/GCE) are characterized with surface techniques such as Tunneling electron microscope (TEM), X-ray photoelectron spectrometer (XPS), Atomic Force Microscope (AFM) to characterise the formation of PPY-GO-CoPc films. Cyclic voltammetry (CV) and Electrochemical Impedance spectroscopy (EIS) techniques are used to characterise the electrochemical behaviour of the electrode.

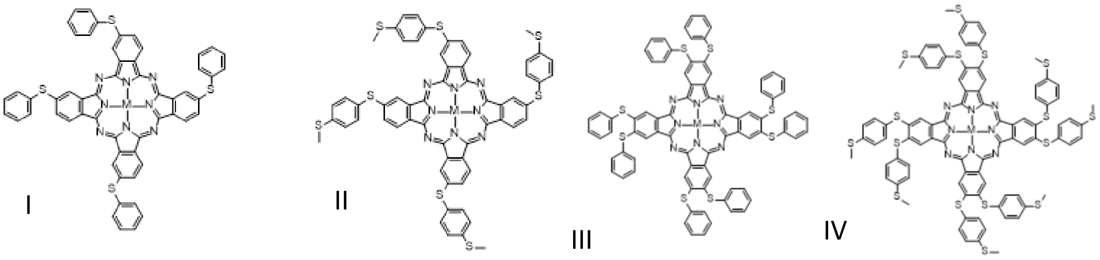

Figure 1: Structure of Phthalocyanine complexes prepared in this work Tetrakis Cobalt Pc (I and II) and Octakis Cobalt Pc (III and IV).

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Coupled kMC-continuum Modelling of Processes at Electrodes

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Processes at electrode surfaces are complex and often comprise besides electrochemical reactions some of the following processes: chemical reactions, adsorption, desorption, degradation and re-/deactivation. The processes are usually impacted by macroscopic conditions, such as concentrations and potentials. Furthermore, atomistic conditions may impact them. E.g., surface site topology may be heterogeneous or processes may occur only in the proximity of certain species.

Usually continuum models cover the macroscopic impacts, and molecular modeling methods the atomistic, rather stochastic effects. Approaches allowing to cover both, atomistic and macroscopic impacts at relevant time scales are rare, and such multiscale modeling is usually conducted sequentially, e.g. with macroscopic models using tabulated atomistic results. However, only direct coupling of both methods allows to study the multiscale interaction of atomistic and macroscopic conditions and processes. This talk illustrates how to couple kinetic Monte Carlo models of atomistic surface processes with processes modelled at the macroscopic level. It addresses numerical challenges and strategies to overcome them [1]. The working principle is illustrated using a simple sequential reaction mechanism as shown in Figure 1. Furthermore, its application to study the formation of the solid electrolyte interphase at Li ion battery electrodes is demonstrated [2]; heterogeneity in the structure, composition and growth on nm to µm scale are shown, as well as multiscale interactions. Finally, strategies for parameterisation of the multiscale model are discussed [3].

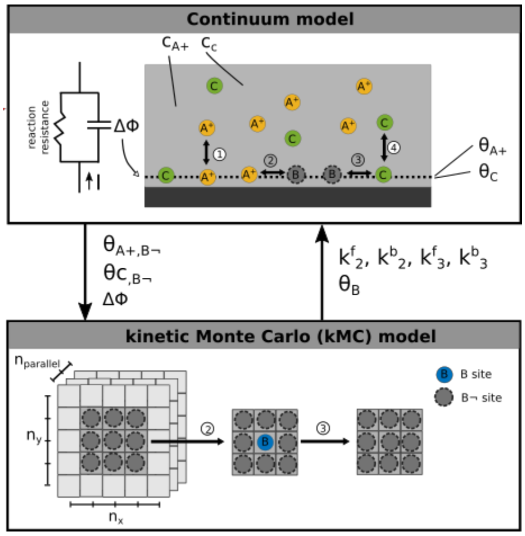

Figure 1: Dynamically coupled kMC-continuum model.

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Nanofabrication of Multifunctional Biosensing interface for Electrochemical Detection of Cytokines in Inflammatory Mice

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Cytokine are cell signalling molecules in our immune systems. The dynamic secretion of cytokines makes continuous monitoring of cytokines especially essential for the understanding of chemistry behind the biology of living organisms.[1] Detection of cytokine is challenging because of the low abundance, dynamic secretion process and the multiplex cytokine networks.[2] Enzyme-linked immunosorbent assays (ELISA) is the most frequently used method for cytokine quantification. ELISA requires lengthy analysis times and has limited sensitivity in some cases. Thus it is essential to develop a simple, reliable and sensitive approach for detection of cytokines. The choice of interface chemistry is critical for a successful sensor device and the sensing interface together with the recognition elements must be rationally designed to optimise the sensitivity, specificity, selectivity, reproducibility, and response time of the sensor.[3, 4] Forming such an efficient sensing interface is particularly essential for detecting analytes in a complex matrices such as blood, urine, saliva, and cell culture. It is desirable for the sensing interface to be integrated with a high surface area film which is thin enough to keep the biomolecules close to the sensing element to allow rapid signal response. Moreover, the interface together with the film must be sufficiently robust so that it remains intact during washing and sensing, and the film must not interfere with the transduction mechanism, and must be simple to fabricate. Nanotechnology has a profound impact on biosensor research, and provides significant opportunities to develop high quality biosensing interfaces.[5] In this talk, different strategies to fabricate the biosensing interfaces with nanomaterials such as graphene oxides for sensitive and robust detection of cytokines ex vivo and in vivo will be presented, respectively. Additionally, technologies for real time detection of multiple cytokines in whole blood samples will be realised by fabrication of multifunctional sensing interfaces. These sensing interfaces provide a universal platform for detection of a spectrum of analytes.

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The Electrodeposition of Tellurium from Non-Aqueous Solution

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Tellurium is an important constituent of a number of semiconductor compounds and alloys with important technological applications. These include thermoelectric materials (Bi_2Te_3, Sb_2Te_3, PbTe), semiconductor and narrow band gap infrared detector materials (ZnTe, CdTe, HgCdTe, HgTe, GeTe, etc.) and compounds and alloys for memory applications (Ag_2Te, $Ge_2Sb_2Te_5$). In addition, tellurium itself is an interesting material with a narrow band gap (0.35 eV) and a trigonal crystal structure comprising helical chains of Te atoms. The vast majority of work on the electrodeposition of tellurium and tellurium based materials has used acidic aqueous solutions containing TeO_2. In addition, in the literature there is much more limited body of work on the electrodeposition of tellurium from ionic liquids and from some non-aqueous solutions using $TeCl_4$.

In this work we have investigated the electrodeposition of tellurium from dichloromethane using both Te(IV) and Te(II) complexes. Dichloromethane was chosen because it is an example of a weakly coordinating solvent as it is aprotic and both a weak donor and a weak acceptor. As a consequence, dichloromethane is not expected to coordinate strongly with the dissolved Te complexes and to alter their complexation. In this study we have prepared and characterized several Te species and investigated their electrochemistry using both microelectrodes and macroelectrodes, and electrochemical quartz crystal microbalance (EQCM) measurements. Based on these measurements we are able to identify the different redox processes that occur, including reduction of Te(IV) to Te(II), electrodeposition of Te(0), surface catalyzed electrodeposition of Te(0), anodic stripping of Te(0) as Te(-II), and cathodic stripping of Te(0). Figure 1 shows an example of results for the electrochemistry of $[N^nBu_4]_2TeCl_6$ in dichloromethane containing 0.1 M $[N^uBu_4]Cl$ at a 25 µm Pt microdisc electrode.

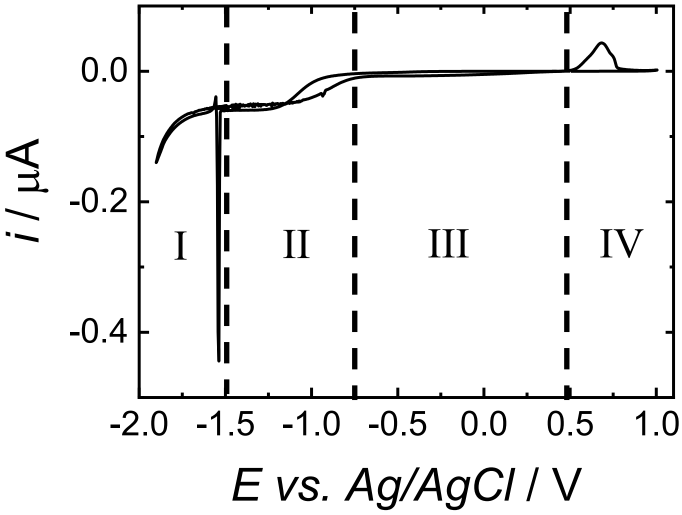

Figure 1. Voltammetry for 3.9 mM $[N^nBu_4]_2TeCl_6$ in dichloromethane containing 0.1 M $[N^uBu_4]Cl$ at a 25 µm Pt microdisc electrode. I – cathodic dissolution of Te(0); II – deposition of Te(0); III – surface catalyzed deposition of Te(0); IV – anodic dissolution of Te(0).

This work was conducted as part of the ADEPT project funded by EPSRC (EP/N035437/1).

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Understanding ORR in nitrogen doped graphitic materials

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Nitrogen-doped graphitic materials are promising catalysts for the oxygen reduction reaction in fuel cells, especially in alkaline media. However, the measured the overpotentials are generally higher than those measured for the reference material (platinum) in the same conditions. If the catalytic activity of these materials is to be improved, so that they can be applied in practical devices, the role of nitrogen atom and the reaction mechanism has to be elucidated. For these materials, the nature of the sites and the mechanisms explaining the observed activity are still under discussion. The measured ORR activity has been mainly investigated under the graphitic versus pyridinic nitrogen-dopant dichotomy approach. However, it will be shown that active sites, reaction mechanism, selectivity and even the origin of each behavior can be better understood when the stability of the possible active site and the contribution of charge from the surface are considered separately. In this communication, we will explore the role played by the nitrogen dopant using DFT calculations in combination with some experimental results using model materials. In the calculations, solvation water should be included in the models to reflect real conditions. It will be shown that carbon atoms are the active sites provided that several conditions are fulfilled. First, this active carbon atom should be able to transition from a sp^2 to a sp^3 hybridization state upon adsorption of the oxygen molecule to have a favorable interaction energy with the oxygen molecule. This transition is possible in destabilized carbon atoms, that is, those neighboring a nitrogen dopant. Second, a significant charge transfer to oxygen adsorbed should occur, so that oxygen species has superoxide characteristics. This charge transfer requires the presence of additional nitrogen dopants, which acts charge donors, even in distant positions. When the nitrogen dopant is in an edge of the graphene structure, a clearly favorable chemisorbed state for molecular oxygen was found when nitrogen-dopant is hydrogenated in an armchair edge. The chemisorbed state is further favored by additional available charge from other nitrogen. To demonstrate the applicability of this approach, the ORR was experimentally studied on an aza-fused π-conjugated microporous polymer, were the DFT calculations are used to understand the activity obtained experimentally. Finally, the whole mechanism of the reaction will be explored by DFT. The activity for the ORR is essentially linked to the edges where certain carbon atoms are sufficiently unstable or can be destabilized by means of neighboring nitrogen-dopants, and where reaction intermediates can be better relaxed and much less to the presence of specific nitrogen-dopants. Unfortunately, relatively high overpotentials are required for the complete reduction to water on these materials due to the strong correlation between the adsorption energies of the different intermediates. Moreover, the production of hydrogen peroxide appears unavoidable on these materials. These results can contribute to the understanding and future development of heteroatom-doped graphitic catalysts.

Exploring the electrochemical extraction of titanium from complex molten oxides systems.

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The electrochemical extraction of high-purity metals from their oxides using molten oxide electrolysis is a revolutionary pathway towards clean metal production. However, the high liquidus temperature of most oxide imposes very demanding constrains in the cell materials and makes it very challenging to experimentally measure the properties of the molten oxides electrolytes at a laboratory scale. In this work, a thermodynamic model has been used to overcome those limitations by predicting the temperature of important phases transitions, as well as the viscosity and activities of the fully molten system. We validated the model by comparing the predicted phases and phase transitions with measured values obtained from ultra-high temperature differential scanning calorimetry (DSC) and x-ray diffraction (XRD). Here, we discuss the effect of the experimental processing conditions, such as atmosphere, crucible material and electrolyte composition, in the production of titanium metal from a molten Ti-Al-Si-Ca-Mg oxide system.

Characterization of Solvent-in-Salt Electrolytes with Consideration for Solute-Volume Effects

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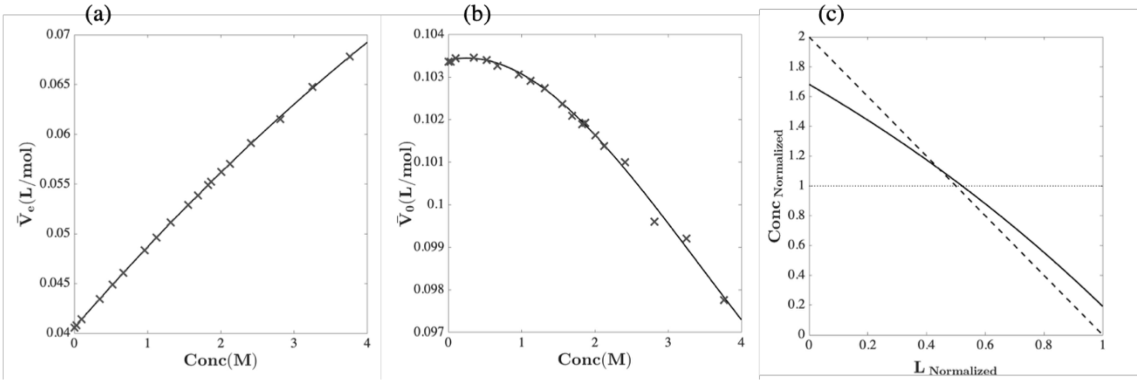
Models that predict the evolution of concentration gradients in isothermal binary electrolytes with current and time require accurate measurement of transport and thermodynamic parameters. We present experimental methods to quantify composition-dependent thermodynamic and transport properties including species partial molar volumes ($\bar{V}_i$) and thermodynamic Darken factor (χ) as well as transference number (t_+^0). We will also show how they are incorporated into models that consider solute-volume effects, especially in highly concentrated regimes.

Recent studies of highly concentrated 'solvent-in-salt' electrolytes suggest a number of favourable functionalities. In fact, for some solvent-in-salt systems t_+^0 has been observed to double in magnitude.[1] These findings have provided a new pathway to design concentrated electrolytes that improve rate capability and energy density in batteries.

Liu and Monroe showed that solute-volume effects in traditional Li-ion battery electrolytes (~1M) can enhance limiting currents by up to 10% and reduce concentration overpotentials.[2] Solvent-in-salt electrolytes have salt volume fractions far larger than traditional electrolytes. In highly concentrated regimes, the response may be dominated by effects such as the 'excluded-volume-effect', where density changes drive diffusion, and 'Faradaic convection', where interfacial reactions drive bulk flow.

We study lithium hexafluorophosphate in ethyl methyl carbonate ($LiPF_6$:EMC) across the entire solubility range. We also demonstrate a novel approach to measuring t_+^0 and χ by combining Hittorf experiments and a matrix of concentration-cell tests that more closely approximates the differential values of χ.[3] This method minimizes concomitant composition changes in concentration cells and remains valid up to the solubility limit. Solvent and solute partial molar volumes ($\bar{V}_0, \bar{V}_e$) are calculated from densitometry and used to quantify solute-volume effects. An extension to Newman's concentrated-solution theory then models composition and potential profiles in planar cells with lithium metal electrodes. A preliminary comparison of model predictions with and without solute-volume effects and experimental results from steady-state galvanostatic polarization and relaxation will also be made.



(a) Solute partial molar volume $\bar{V}_e$, (b) Solvent partial molar volume $\bar{V}_0$, (c) Non-dimensionalized composition profile with volume effects (solid —), and without (dashed ---).

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Electrochemical and colorimetric detection of HOTAIR long non-coding RNA

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Liquid biopsy is a new diagnostic concept that provides important information for identifying and monitoring tumours using body fluid samples during treatment and disease progression. Analysis of tumour specific biomolecules shed into the circulation, like circulating tumour cells, circulating tumour nucleic acids and how tumour-derived exosomes enable cancer screening, early stage diagnosis and evaluation of therapy response through minimally invasive means. Conventional serial biopsies are relatively tedious, suitable for centralised laboratories, expensive and require experienced personnel. However, techniques that are cheaper, and can rapidly analyse disease-related biomarkers are of utmost importance for health monitoring and biological applications. Electrochemical biosensors have emerged as reliable molecular sensing platforms in liquid biopsies for clinical diagnosis and prognosis.

Herein, we report a rapid and inexpensive sensor platform for the detection of cancer related long non-coding RNA HOX transcript antisense intergenic RNA (HOTAIR). HOTAIR sequences extracted from designated ovarian cancer cells and a small cohort of plasma samples derived from ovarian cancer patients were amplified isothermally using the isothermal reverse recombinase polymerase amplification (RT-RPA). During the amplification, biotinylated dUTPs were randomly added into the amplified product. Subsequently, HOTAIR amplicons were purified magnetically and isolated. Using well known avidin-biotin affinity, streptavidin coated horseradish peroxidase (HRP) was attached to RT-RPA products followed by HRP-catalysed colorimetric reaction in the presence of 3,3',5,5'-tetramethylbenzidine (TMB)/H_2O_2 system. Finally we implemented three potential readout methods for HOTAIR detection- *(i)* naked-eye observation of colour change for quick screening of target, *(ii)* quantitative absorbance measurement by UV-visible, and *(iii)* amperometric detection using electrochemical properties of TMB. The assay showed excellent reproducibility (% RSD = <5%, for n = 3) and sensitivity (10 cells/ per mL), while detecting HOTAIR in cancer cell lines and patient samples. The expression of HOTAIR in clinical samples was also validated with a standard RT-qPCR method. We believe that proof of concept assay reported here may find potential use in routine clinical settings for screening of cancer-related lncRNAs.

Electrogenerated Chemiluminescence Imaging of Electrocatalytic Activity at Single Nanoparticles

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Nanomaterials, especially noble metal nanoparticles, have attracted intensive interest because of their unique electrocatalytic properties, giving them potential in numerous applied fields including energy conversion and storage. Understanding the relationship between the structure and the electrochemical reactivity of metal nanoparticles can provide useful instructions for the design of ideal catalyst materials. Owning to their structural dispersion, the active catalytic sites of nanoparticles are heterogeneously distributed, and may fluctuate dynamically. Therefore, it is highly desirable to develop techniques with high resolution both in time and space to measure the electrocatalytic activity on single nanocatalysts instead of an ensemble. Herein, we studied the heterogeneous distributed electrocatalytic activity on individual 2D gold nanoplates using electrogenerated chemiluminescence (ECL) microscopy. The size, shape, and site-specific catalytic activity of 2D nanocrystals could be directly imaged at single particle level with submicron resolution. Furthermore, ECL microscopy allows continuous in-situ imaging, which elucidates the time-varying changes in spatial distribution of electrocatalytic activity on individual nanoplates, indicating that the corners and edges with more defect sites exhibit higher reactivity, but lower stability than the flat facet. Further, we employed ECL to image the catalytic oxidation of luminophore at single Au, Pt and Au-Pt Janus nanoparticles. Compared to monometal, the Janus particle structure exhibited enhanced ECL intensity and stability, indicating better catalytic efficiency. We believe the real-time and high-throughput ECL microscopy may lead to more comprehensive understanding of reactivity patterns of single nanocatalyst.

MAX Phases as an Electrocatalyst Support Material: A DFT Study

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The global increase in energy demand is causing increasing interest to be shown in the field of renewable energy. One of the potential new methods of green electricity generation is the hydrogen fuel cell. This uses hydrogen and oxygen to create electricity, with only water as a reaction product. However, before it is able to compete commercially with other methods of energy production, the issue of catalyst support material durability needs to be solved. Currently, carbon black is predominantly used to support the platinum catalyst, but the carbon black corrodes under the low pH and oxidative conditions present in a fuel cell, especially at the cathode.

A new class of material has been developed within the last 20 years which displays properties that could be suitable for use in a hydrogen fuel cell. These new materials are a combination of ceramics and metals and are called MAX phases. Some MAX phases display good electrical conductivity and excellent oxidation resistance, which are the precise properties required to be a good electrocatalyst support material. Out of the more than 60 different MAX phases that have been discovered, three of the most thoroughly studied are Ti_3SiC_2, Ti_3AlC_2, and Ti_2AlC. Therefore, it is proposed that MAX phases would be provide an excellent support material for the catalyst in hydrogen fuel cells.

To determine which of these would be the most suitable candidate to use as an electrocatalyst support material, it is necessary to understand more about their properties. To do this, the MAX phases have been modelled using density functional theory (DFT), which can give insight into both molecular and bulk properties of a material. The primary properties that have been investigated are the electrical conductivity and the oxidation resistance. By comparing the MAX phases against each other, it will be possible to determine which MAX phase, of the three, will be most suitable for use in hydrogen fuel cells.

Electrochemical and Surface Spectroscopy Study of the Passivity of a Duplex Stainless Steel

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Duplex stainless steels, containing ferrite and austenite phases, are increasingly used for various industrial applications. However the details of the passive state of the two phases are not clearly understood. This work reports an innovative methodology based on the coupling of two surface spectroscopies, X-ray Photoelectron Spectrocopy (XPS) and Time of Flight Secondary Ions Mass Spetrometry (ToF-SIMS) in order to resolve locally the analysis of surface oxide layers formed on austenite and ferrite phases of duplex stainless steels.

The native oxide film obtained after mechanical polishing and the passive film obtained by electrochemical passivation in 0.05 M H_2SO_4 were investigated. The effect of electrochemical passivation on the oxide layer composition and thickness is presented and discussed. Chromium and molybdenum are found to be more markedly enriched in the oxide layer formed on the ferrite phase surface. Nickel and nitrogen enrichments are found to be more pronounced under the oxide layer formed on the austenite phase.

The corrosion behaviour of duplex stainless steels will be discussed in the light of these new data.

The antibody assisted detection of human epidermal growth factor receptor on a cobalt porphyrin organic framework and gold functionalized graphene quantum dots modified electrode

Sixolile Centane and Tebello Nyokong

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In this work a novel simple, inexpensive and highly sensitive approach for the antibody assisted detection of the human epidermal growth factor receptor 2 (HER2) is presented. The sensor probe was fabricated by covalent immobilization of the antibody to the gold functionalized graphene quantum dots (Au@GQDs) and cobalt porphyrin organic framework (CoPOF) via an amide bond. The gold nanoparticles were used to enhance adsorption of the antibody onto the glassy carbon electrode (GCE), as well as retain the immunoactivity of the protein. The carboxylic porphyrin and GQDs were essential for electron transfer and as agents for covalent linkage via an amide bond. The sensor was characterized using cyclic voltammetry and impedance spectroscopy. Electron transfer properties of the electrode surface changes upon (i) modification, (ii) antibody and (iii) antigen interactions were displayed by changes in the impedance response. The experimental conditions for each step towards the HER2 detection were optimized considering concentration and pH. The surface of the electrode was explored using scanning electron microscopy (SEM). The performance of the sensor in terms sensitivity, reproducibility and selectivity in buffer and HER2 was explored.

Imaging single dielectric nanoparticle electrochemistry by interferometric microscopy

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High resolution optical microscopies have been proposed as promising alternative to image electrochemical processes at the nanoscale. Particularly adapted to image single nanoparticle electrochemistry, most of the optical microscopies have been devoted to plasmonic materials.

The detection and study of single NPs in an electrochemical environment is often reached by exploiting optical scattering properties. Under dark-field illumination, the change in the localized surface plasmon resonance of individual nanoparticles upon electrochemical activation has allowed imaging various electrochemical processes at the single NP level in 2D [1,2] or 3D [2]. However, this method is often limited to >40nm plasmonic NPs. Moreover even if informative, these strategies are often limited to qualitative description of NP transformation. The widespreading of optical-based electrochemical nanoscopies then relies on (1) the extension of their applicability to smaller and non plasmonic NPs and (2) the development of quantitative methodologies.

Some solutions have been proposed. Surface plasmon resonance microscopy is one of them, popularized for single NP electrochemical imaging by the groups of Tao and Wang [3]. Meanwhile, highly sensitive approaches, outperforming dark field microscopies, have been proposed. These microscopies, such as iSCAT[4b], exploit intereferometric detection principles [4,5] operated in standard reflection mode visualization. Interferometry provides enhanced sensitivity allowing to visualize down to 10nm individual NPs in solutions. This principle is also exploited in backside absorbing layer microscopy (BALM) which is the only one of these microscopies that can be operated udner an electrochemical context. It has allowed the imaging of the electrochemistry of single Ag NPs down to 10nm [5]. BALM also opens the route to imaging much more challenging electrochemical materials and processes. This talk will illustrate such performance through the imaging of the dynamics of single dielectric NPs. The case study of the quantitative description of the electrochemistry of single AgCl nanocristals will be detailed:

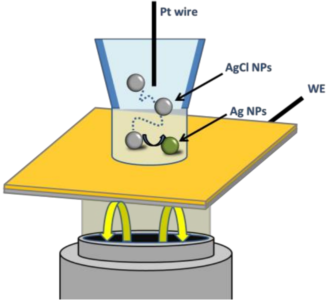

Figure. BALM monitoring of single AgCl nanocristal electrochemistry.

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Surface Heterogeneities Matter in Fast Scan Cyclic Voltammetry Investigations of Catecholamines in Brain with Carbon Microelectrodes of High-Aspect Ratio: Dopamine Oxidation at Conical Carbon Microelectrodes

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Carbon based electrodes are commonly used for measurement of neurotransmitter concentrations and their dynamics in living brain. By employing fast scan cyclic voltammetry (FSCV), it is possible to distinguish between the neurotransmitters (if several of them are present in the investigated region) as well as to follow their rapid changes [1]. The advantage of carbon electrodes is that the catecholamine neurotransmitters are oxidized through a surface activation step. From the other hand, it is well established that carbon materials feature heterogeneities having different electrochemical activity [2], the complication generally bypassed by the calibration.

In this work [3], we demonstrated that carbon surface heterogeneities do affect the electrochemical signal. Peak analysis of the background subtracted voltammograms recorded at vast range of scan rates (50 – 5000 V/s) employing commercially available conical graphite electrodes reveal that the expected $i_p \propto v$ relationship is not followed. That is the peak current dependence involves a pattern of transitions between the limiting $i_p \propto v$ behaviors. A change in the oxidation mechanism cannot be invoked to explain these peculiar variations since peak potential varies linearly with $\lg(v)$.

The observed comportment can be rationalized by presence of at least two types of mesoscaled domains with different electrochemical reactivities and surface dynamics properties. At low scan rates (<100 V/s) dopamine molecules that initially adsorbed onto non-electroactive domains have enough time to migrate toward highly electroactive ones so all molecules initially adsorbed on the whole electrode surface may be oxidized during one FSCV cycle. Current peak intensities then increase proportionally to the scan rate. However, above 100 V/s, dopamine migration between sites starts to be kinetically limited so that FSCV current peak intensities do not increase any more proportionally to the scan rate. Ultimately, i.e., above 1000 V/s, the dopamine exchange between sites is almost totally blocked so only dopamine molecules initially adsorbed on the electroactive surface domains may be oxidized; the current peak intensities then increase again proportionally with the scan rate though with a smaller slope than that observed at small scan rates.

These results emphasize two important points: (i) surface heterogeneities of carbon electrodes non-negligibly affect electrochemical measurements. Notably, employment of various scan rates may result in dissimilar outcomes of the experiment due to different populations probed at the electrode surface;
(ii) results of calibrations should be taken with care. Indeed, not all pathways towards electrochemically active domains at carbon electrode surface undertaken by neurotransmitter molecules in bulk solution where a calibration is performed could be available in case when the electrode is placed within the brain, a highly non-uniform medium in terms of mass transport properties and arrangement of the neurotransmitter releasing sites.

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Arc Generation Behavior During Anodic Oxidation of Aluminum Alloys in Aqueous Solutions

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Anodic oxidation of aluminum alloys can result in the formation of thick oxide films with regular pores or irregular pores, depending on type of aqueous solutions. The formation of anodic oxide films with irregular pores are achieved normally together with generation of arcs in alkaline type of electrolyte and it is called ‘Plasma electrolytic oxidation (PEO)’. The arcs generated during the PEO treatment are orange, red or white in color. The arcs are generated randomly, linearly or locally and composition and structure of the PEO films are critically dependent upon the generation behavior, lifetime and size of the arcs. The arcs are also accompanied with sounds. In this presentation, arc generation behavior of Al alloys is examined in terms of color, size, density and moving behavior of the arcs under application of DC and AC at 310 Hz in aqueous electrolytes containing various anions. The relationship between arc generation behavior and PEO film morphology is also discussed in detail.

Monitoring Changes in Electrolyte Behavior of Commercial Li-ion Cells using NMR Spectroscopy

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Batteries are ubiquitous, and their domain of application is constantly growing. In particular, lithium (Li)-ion battery technologies have been surging due to their combined unique features of high energy, power density and long life. Thus, they are being intensively pursued for a wide range of consumer electronics including cell phones, laptops, power tools, the electric vehicle market and grid energy storage.

However, Li-ion batteries can suffer from capacity fade during cycling. Capacity loss as well as power fade could be due to several complex degradation processes that occur during cycling. Some of these processes include Li deposition, electrolyte decomposition, phase changes of electrode materials and the formation of the passivating solid electrolyte interface (SEI) layer over the electrode surfaces. Herein, we pinpoint on examining the degradation behavior of electrolytes. They are crucial to the safety and durability of Li-ion batteries[1] and despite this, the understanding of their degradation mechanism is still imprecise. Hitherto, various studies have been performed on different types of cells to understand the decomposition of the electrolytes by analyzing either the composition of generated gases and/or the composition and morphology of the resulting SEI on carbon surfaces, rather than the compositional changes of the electrolyte itself.[2-4] Extracting electrolytes directly from commercial cells could be challenging, as it can be trapped into the electrodes and separator pores, thus not readily be available for further analysis. Lately, few studies report on the extraction of electrolytes from jelly roll of Li-ion cells with supercritical and subcritical CO_2[5] while others report on the solid phase microextraction complemented with GC-MS.[6]

Herein, we illustrate a simple and effective electrolyte extraction methodology from commercial LG 18650 cells. With the use of liquid-state nuclear magnetic resonance (NMR) spectroscopy we track the changes in electrolyte composition prior and upon cell cycling, while also obtaining information about salt concentration. These changes can be due to various mechanisms including: oxidation at the positive electrode, reduction at the negative electrode, transesterification of the linear carbonates and dimerization of ethylene carbonate (EC) and linear carbonates. We present NMR analysis that monitor some of these changes and highlight the impact of these reactions throughout cell lifetime. With the achievement of such information, this methodology stands on a high platform that can enhance the understanding of failure mechanisms in commercial battery cells and help build robust mathematical models.

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Approaches for improving enzyme electrode performance for application in biosensors and biofuel cells

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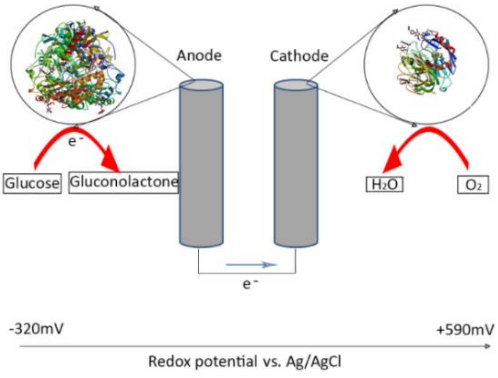
In recent decades there has been increased interest in implantable or semi-implantable biomedical devices. These devices include systems such as sensors, pacemakers and insulin pumps. Currently these devices are powered using batteries which are reliant on re-charging or sufficient reagents contained within. An alternative route towards powering such devices is fuel cell technology, using readily available *in-vivo* substrates (glucose and oxygen) as fuel and oxidant. This is difficult to achieve using chemical catalysts as they are non-selective and operate under harsh conditions (pH and temperature). Enzymes as catalysts immobilised at electrode surfaces offer an alternative route towards powering of such devices as they are selective and operate under physiological conditions (pH 7.4, 37 ºC).

Our research focuses on co-immobilisation of osmium based redox polymers with specific enzymes on electrode surfaces. Tuning of the redox potential of the osmium redox centres to the enzyme active site improves electron transfer to electrode surface. Combining enzyme and redox centre with nano supports such as carbon nanotubes achieves higher current densities and greater power outputs. This is achieved through refinement of the immobilisation procedures as well as optimisation of the enzyme electrode components.

A design of experiment (DoE) approach for optimisation of electrode surface chemistry to improve current density was utilised. The DoE approach improved current density by >50% over traditional one factor at a time (OFAT) approaches, with current densities of 1.2 mA cm^{-2} in biologically relevant glucose concentrations (5 mM) [1]. Testing of fuel cell electrodes in artificial plasma produced 49% less power than those tested in PBS. Glucose oxidising electrodes were tested in the presence of each component of artificial plasma to identify which plasma components have the greatest effect on performance. Glucose oxidation current responses and stability of electrode performance over 12 hours was recorded. Electrodes tested in the presence of uric acid produced the lowest current densities and had the lowest operational stability after 12 hours [2].

Electrodes were prepared with different glucose oxidising enzymes to identify if the uric acid affects the enzyme or another component of the biofilm. Electrodes prepared using glucose oxidase were the most stable in the presence of uric acid while those prepared with cellobiose dehydrogenase had the lowest stability in the presence of uric acid [2]. This is an important finding for continuous glucose monitoring devices as well as for inclusion in fuel cell assemblies. The results show the importance of enzyme selection for *in-vivo* applications.



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Zea mays lea silk mediated bio-synthesized NiO nanoparticles as cathode material for assymmetry supercabattery

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Abstract

We used aneco-friendly, simple, cost effective and sustainable green synthesis method mediated by maize (*Zea mays L.)* dry silk extract to synthesize NiO nanoparticles (NPs). Structural characterizations by X-ray diffraction (XRD)and HighResolution Transmission Electron Microscopy (HRTEM) show that the NiO NPs have a face-centered cubic structure (space group: *Fm3m*) with spherical and quasi spherical NPs of average diameter of 10-20 nm. The supercabattery properties of the NiO NPs were studied using cyclic voltammetry (CV), galvanostatic charge discharge (GCD) cycles and electrochemical impedance spectroscopy (EIS). A capacity of 54 C g^{-1} was obtained at a scan rate of 5 mV s^{-1} and capacity retention of 60% after 2000 GCD cycles. Asymmetric devices were made using activated carbon anode and NiO NPscathode. The device with cathode/anode mass ratio of 1:1 gave superior electrochemical energy storage capabilities compared to others giving a specific capacity of 29 C g^{-1}at a current density of 0.25 A g^{-1}.Therefore, the *Zea mays lea* silk mediated bio-synthesized NiO NPs could be a promising material for electrochemical energy storage applications.

Key words: asymmetry supercabattery, nickel oxide,green synthesis, electrochemical, energy storage, *zea mays L.*

Scanning Electrochemical Microscopy (SECM) Study of Redox Potential Impact on Chalcopyrite Leaching

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Chalcopyrite ($CuFeS_2$) is not only the most abundant but also one of the most refractory copper sources. For low grade chalcopyrite ores, conventional pyrometallurgical methods for extracting copper are usually not economically viable whereas a hydrometallurgical approach could be a potential solution because of the advantages of lower capital costs and lower energy consumption. To date, the leaching kinetics of chalcopyrite are slow and remain to be a challenge. The passivation formation during leaching process is one of the most important reason that hinders the dissolution rate of chalcopyrite. We aim to understand the impact of redox potential and the chloride on the chalcopyrite leaching in acidic leaching environment [1-3].

We know that leaching of minerals is not a surface uniform reaction process [4]. Especially during initial stages, leaching is restricted to microscopic domains associated with various surface inhomogenities. Electrochemical methods often employed to study minerals leaching. This work found that the anodic polarization experiments showed distinct active and passive regions for chalcopyrite in different pH leaching solutions. We have demonstrated that SECM allows for straightforward characterization of copper-bearing mineral samples and provide localized electrochemical information [5-7]. It is shown that leaching of the mineral samples can be monitored directly in the leaching medium.

A platinum microelectrode with a diameter of 25 μm was employed as a probe to detect iron and copper ions dissolved from the chalcopyrite electrode in the active-dissolution, passive and trans-passive region during anodic linear voltammogram polarization. The dissolution of both iron and copper ions from the chalcopyrite electrode surface can be monitored by the probe. The results showed that the concentration of the dissolved iron and copper ions were depending on the substrate surface chemistry and mineral crystal orientation. For example, both ferrous and ferric ions were detected during the chalcopyrite anodic dissolution process, however, ferrous ions was detected earlier than ferric ions in the active-dissolution region, but ferric concentration was higher than that of ferrous in both of the passive and trans-passive regions. The ferrous ions were found to be surface-adsorbed and released immediately after aborting the anodic polarization of substrate, indicating ferrous ions might be partially oxidized on the substrate surface during polarization. Cuprous ions were also detected in the active-dissolution region with the addition of 2 M chloride ions.

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Group 4 and 5 Metal Oxide Cathode Catalysts for Advanced PEFCs

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Considering our future sustainable growth, renewable energies should be the primary energy. In that way we need technologies to store and transport renewable energies. Green Hydrogen is the hydrogen from water using renewable energies. The environmental impact factor was defined as a ratio of an annual quantity of materials produced by energy consumption of mankind to a natural movement on the earth. By the comparison of environmental impact factor, the Green Hydrogen could keep our environment more than 2 orders of magnitude cleaner compared to that of fossil fuels [1]. With using Green Hydrogen, we could produce clean electricity through fuel cells without any pollutants. Polymer electrolyte fuel cells are expected for the residential and transportable applications, due to their high power density and low operating temperature. However, the estimated amount of Pt reserve is limited and its cost is high. The instability of Pt cathode and carbon might be the big problems to improve the stability of the present PEFC system. A stable nonprecious metal oxide cathode with stable metal oxide support might be the final goal for the cathode of PEFCs. In the future energy system fuel cells should be operated at higher efficiency such as 60 %(HHV) or more. To achieve this high efficiency or high operation voltage, their operation temperature might be higher than 120 ºC for future PEFCs. At these high potential and temperature Pt and carbon are no more stable for long time operations. We need new materials, such as metal oxides that should be stable in acid and oxygen atmosphere. We are developing non precious metal oxide cathode for polymer electrolyte fuel cells using group 4 and 5 metal oxides. The highest onset potential of the $Ti_xNb_yO_z$ +Ti_4O_7 was over 1.1 V vs. RHE at 80 ºC [2]. No degradation of the ORR performance of $Ti_xNb_yO_z$ + Ti_4O_7 was observed during both start-stop cycle and load cycle tests. The ORR activity depended on the heat treatment temperature of oxides. Especially we got the highest ORR activity in reducing atmosphere at 800ºC. Ti^{3+} on the surface of the titanium oxide catalyst might affect the ORR reaction. The ORR activity of ZrO_x catalyst that was made by the arc-plasma deposition depended on the thickness of the catalysis layer. The maximum ORR current was obtained at the thickness of 2 nm. The tunneling current might help the electron conduction for ORR. Considering these factors we could improve the ORR activity of group 4 and 5 metal oxide cathodes with oxide support [3]. We are also doing other fundamental researches to develop these new materials. These new material could contribute to promote the Green Hydrogen Energy System.

Acknowledgement
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Environment-friendly Treatments of Fabrics Using Electrochemically Generated O_3-water with UV Irradiation

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Recently, application of advanced oxidation technologies (AOTs) for environmental purification have received growing attention [1]. Especially electrolysis with boron-doped diamond (BDD) electrodes make it possible to generate various highly active oxidants such as O_3 which can oxidize aqueous contaminants [2]. In this study, we introduce recent studies about environment-friendly "AOT-treatments" of fabrics by using of O_3-water with UV irradiation instead of conventional treatments (scouring and bleaching) with environmentally persistent reagents. Fig. 1 shows the photographs of cotton bleaching by AOT. Cotton fabrics were treated by O_3-water (1.0 ppm, 1.5 L/min, continuously generated from tap water) with UV irradiation (170 mW/cm^2 @310-380 nm). After treatments, the fabrics were dried under room temperature and analyzed by reflection spectra. Fig. 2 left shows the reflection spectra and photographs of cotton fabrics. After 60 min of AOT, the spectrum and whiteness of the cotton are almost the same with conventional chemical-bleached one. The AOT-bleaching is not only effective after scouring but also before scouring (Fig. 2 right). In addition, hydrophobic surface of the cotton was converted to hydrophilic surface by AOT. These results indicate that any impurities such as waxes in fabrics are also able to be removed by AOT. Therefore, AOT-treatment is attractive to reduce energy consumption and cut waste in the fabric processing.

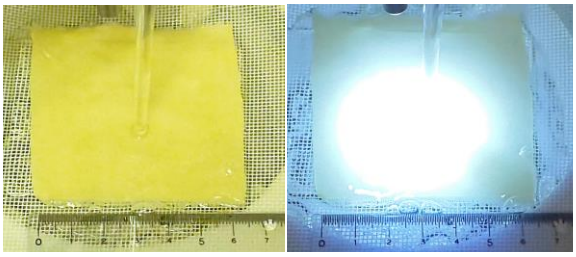

Fig. 1. Cotton bleaching by O_3-water treatment (left) and O_3-water with UV irradiation (AOT, right).

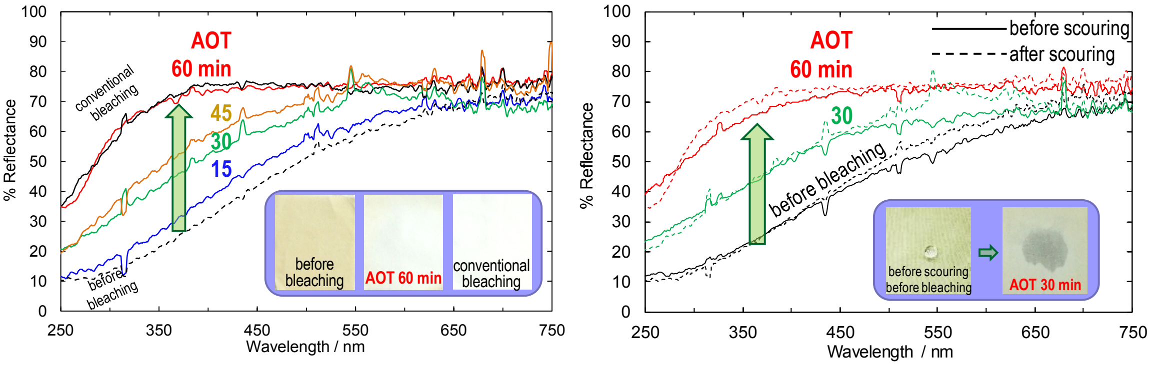

Fig. 2. Reflection spectra and photographs of cotton fabrics. (left) Comparison of AOT and conventional chemical bleaching. (right) Effects of AOT before and after scouring.

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Electrochemical behavior and corrosion resistance of HSLA API 5L X65 pipes in CO_2 saturated aqueous media

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Abstract

According to report issued by the International Energy Agency, CO_2 represents 58% of global greenhouse gases (GHG) emissions [1]. To reduce global warming to about 2.0 to 2.4° C compared to the pre-industrial period, as established in different climate agreements, it is estimated that by 2050 CO_2 emissions should be reduced by 50-85% compared to 2000 levels [2]. In this context, the development and implementation of carbon capture and storage (CCS) technologies has become a priority for government agencies and energy companies. Briefly, the process consists of capturing CO_2 from large emitting sources (mainly power plants that consume fossil fuels) and transport it in supercritical conditions to geological formations, such as deep saline aquifers, oil and gas reservoirs, and deep and non-mining coal beds [3], which do not present environmental risk. To become economically viable, ideally, transport should be made using High Strength Low Alloy (HSLA) steel pipes already in use for oil and gas transportation. In addition, certain degree of contamination of the CO_2 flow must be admitted, not only due to the differences in the emission sources but also due to the possibility of using the piping infrastructure already available. In the present work EIS and microstructural characterization (SEM and OM) were employed to compare the corrosion resistance of an HSLA steel and an ASTM A36 steel in CO_2-saturated aqueous solution in the presence of acidic contaminants (namely HCl and HNO_3). For both steels, the EIS diagrams are composed by a single depressed capacitive loop, which diameter decreases with the addition of the contaminants. As expected, the results showed a better corrosion resistance of the HSLA steel when compared with the ASTM one, which could be ascribed to the superior pearlite content of this latter. To interpret the results, the EIS behavior as a function of immersion time will be acquired, which will be interpreted on the basis of electrical equivalent circuit fitting.

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Noble Metals Modified Nickel Materials for Electroanalysis and Electrocatalysis

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Metal nanoparticles (NPs) have been attracting active attention as functional units for electrode modifications because they can change the electronic communications on the conductive materials. If we would like to attach gold NPs (AuNPs) on the ITO surfaces, the functional bridging reagents such as (3-mercaptopropyl)-trimethoxysilane have been adopted. While many successful results have been obtained using the bridging reagents, our group proposed a simple methodology to attach AuNPs on the ITO surfaces. Namely, by applying a seed-mediated growth method to the surface modification, the crystal growth of AuNPs on the ITO surfaces could be performed from the Au nanoseed particles physically adsorbed on the ITO with keeping adhesion contacts [1]. As the results, successful electroanalysis could be performed using thus prepared AuNP-attached ITO electrodes [2].

Although we utilized the absorption of Au nanoseed particles on Ni surface in the previous work [3], Au can be deposited on Ni surface using a very simple method. That is, because the oxidation potential of Ni to Ni ions is relatively negative, it is expected that Au deposits on Ni electrodes by the simple galvanic replacement reaction. When we use a wire of Ni as a base electrode, the modification of AuNPs was possible by just immersing a Ni wire into an aqueous solution of $HAuCl_4$. The modified states of Au were evaluated by observing SEM images and cyclic voltammograms of H_2SO_4, glucose etc. As the result, it was found that low concentrations of $HAuCl_4$ could change the electrochemical characteristics from those of a bare Ni wire electrodes [4].

Starting from the modification of Au on Ni wire electrodes, we explored the modification of Pd on Ni wire electrodes and Ni microparticles for applying the prepared nanocomposite materials to electrocatalysts, in particular, for ethanol oxidation in alkaline aqueous solutions. Furthermore, the modification of PdAu and PtAu on Ni wire electrodes have shown interesting promotion of the modification or deposition reactions. These progresses of the noble metals modification on Ni materials and their applications will be presented in the meeting.

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Toward highly reversible poly-anion cathode materials Na-ion batteries

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Development of highly reversible multi-electron reaction per redox center in NASICON-structured cathode materials is desired to improve the energy density of Sodium-ion batteries.[1] In the last several years, we investigated several polyanion compounds such as $Na_3VCr(PO_4)_3$ and Na_2FePO_4F as model systems to understand multiple-electron exchange process in these materials. Combining a series of advanced characterization techniques such as ^{23}Na solid-state nuclear magnetic resonance (ssNMR), X-rayAbsorption Near Edge Structure (XANES),*in situ*XRD and High-angle annular dark Field (HAADF)-STEM,we reveal that, V^{3+}/V^{4+} and V^{4+}/V^{5+} redox couples in the materials can be accessed, leading to 1.5-electron reaction. In addition, anirreversible V/Na1 antisiteis also found after cycling, resulting in the fast capacity fade at room temperature. Nevertheless, the lost electrochemical performance and changed structure can be partially recovered by over-discharging.

Besides, we showed the irreversibility of the phase changes could be largely suppressed at low temperature, and thus leading to a much improved electrochemical performance.[2] The long- and short-range structural evolution of Na_2FePO_4F during the cycling were also studied through *in situ* high energy X-ray diffraction (HEXRD), *ex-situ* ssNMR and first-principles DFT calculations. Na_2FePO_4F undergoes two processes of two-phase reactions along the cycling. Furthermore, $Na_{1.5}FePO_4F$ was identified by DFT calculations with a new space group *P2₁/c,* which was in good agreement with the XRD and ss-NMR results. *Ex-situ* ssNMR spectra were employed during the first cycle, whose results showed that the distribution of the Na ions in different sites. This study clearly elucidates the electrochemical mechanism of Na_2FePO_4F in a Na-ion battery system. [3]

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Secondary Alcohols as Rechargeable Electrofuels: Electrooxidation of 2-Prpoanol at Pt-Based Electrodes

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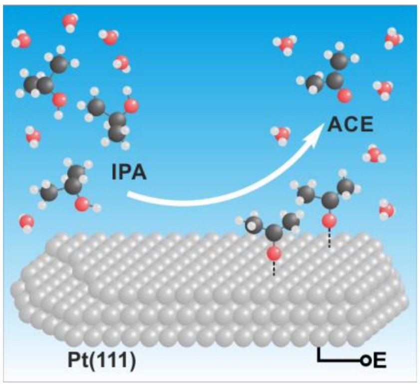
Isopropanol (IPA) and its dehydrogenated counterpart acetone (ACE) can be used as a rechargeable electrofuel. In a fuel cell application, IPA can be oxidized electrochemically to ACE and, subsequently, ACE can be re-hydrogenated catalytically to IPA. We envisage that latter "recharging step" could be realized via transfer hydrogenation from a liquid organic hydrogen carrier (LOHCs). In this way, it would be possible to implement a highly efficient direct fuel cell technology to convert chemical energy stored in LOHCs (with very high energy density) to electricity.



In order to obtain a better understanding of the underlying electrocatalytic processes, we investigated IPA oxidation on Pt single crystals, polycrystalline and nanostructured Pt electrodes, on commercial Pt/C catalysts, and on PtRu/C catalysts. We used electrochemical infrared reflection absorption spectroscopy (EC-IRRAS) in combination with density functional theory (DFT), cyclic voltammetry (CV), and differential electrochemical and electrochemical real-time mass spectrometry (DEMS and EC-RTMS).[1,2]

On Pt electrodes, the onset for IPA oxidation is observed at 0.3 V_{RHE}, where ACE is formed at the Pt electrodes with high selectivity. The only side reaction observed is the formation of small amounts of CO_2. Noteworthy, the total oxidation to CO_2 competes with the ACE formation but it is efficiently suppressed as long as IPA is present in solution. The ACE formed adsorbs strongly on the Pt electrodes and poisons the catalyst. The poisoning by adsorbed ACE is the limiting factor for the oxidation of IPA using pure Pt electrodes. By using PtRu alloy catalysts, the onset potential is shifted to lower potential (0.1 V_{RHE}) and the poisoning effect is reduced dramatically. We discuss the origins of this effect in relation to the future development of improved IPA electrooxidation catalysts.

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Spectroscopic and electrochemical sensing protocols based on dihydropteroate synthase inhibition for the detection of sulfonamide antibiotics.

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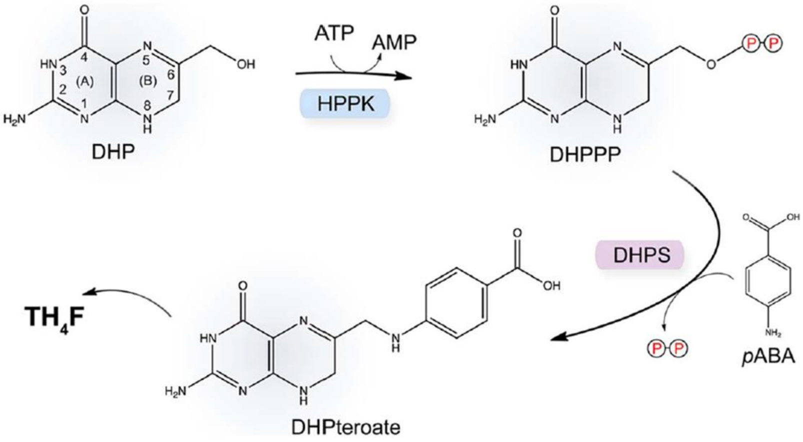
Dihydropteroate synthase (DHPS, EC: 2.5.1.15) an enzyme which catalyzes the reaction of 6 hydroxymethyl-7,8-dihydropterin-pyrophosphate with p-aminobenzoic acid (p-ABA) to yield 7,8-dihydropteroate and pyrophosphate (Morgan et al 2011). Dihydropteroate synthase (DHPS) is a key enzyme in bacterial folate synthesis and the target of the sulfonamide class of antibacterial compounds (Fernley et al 2010). DHPS enzyme as a protein that forms α/β barrel structure, with a highly conserved binding pocket for recognition of the pterin substrate, DHPPP (6-hydroxymethyl-7,8-dihydropterin pyrophosphate). There is a fixed order of substrate binding which sees the pyrophosphate substrate binding first, followed by the second substrate, pABA (p-aminobenzoic acid). The pyrophosphate moiety is key to the recognition of pABA or inhibition by sulfonamide drugs. The synthesis of folic acid is interrupted, when the sulfonamide drugs bind to the pterin substrate, instead of pABA.



Scheme 1: Folic acid synthesis pathway

In developing biosensors for electrochemical screening of sulfonamides using DHPS inhibition, it is necessary to include 6-hydroxymethyl-7,8-dihydropterin pyrophosphate (DHPPP) or its analogue inorganic pyrophosphate as one of the sensing components to be able to recognize the sulfa drugs. The approach of using spectroscopy to measure the enzyme activity decrease, in the presence of the inhibitor is typically used as the basis of the sensing protocol.. In this presentation we will show the inhibition effect of selected sulfonamide antibiotics on the synthase driven folic acid pathway. Construction aspects of the biosensor assembly will be highlighted using spectroscopy, electrochemistry and microscopy. UV/vis spectroscopy and in particular electrochemical impedance spectroscopy will be employed to evaluate the inhibition of the enzyme-pterin substrate by pABA (control system) and subsequently by sulfonamide class antibiotics.

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The Application of Hydrogen Substituted Graphyne in Lithium-sulfur Battery

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Lithium-sulfur batteries (LSBs) with a high theoretical specific capacity (1675 mAh g^{-1}) and a remarkable mass energy density (2600 mWh g^{-1}), low price and environmental benignity, are expected to generate electrochemical rechargeable battery with high-energy density[1]. However, inadequate efficiency of active sulfur, inferior cycling durability and poor rate capability plague its commercial application in large scale, which may due to isolated sulfur and discharging species (Li_2S_2, Li_2S), the shuttle effect of lithium polysulfides (LiPSs) and the irreversible volume expansion of sulfur during the lithiation/delithiation processes[2]. Herein, as shown in Fig. 1a, based on the dynamic nature of alkyne metathesis reaction, the hydrogen substituted graphyne (HsGY) film was successfully synthesized on the gas/liquid interface using 1,3,5-tripynylbenzene (TPB) as the precursor. A melt-diffusion strategy was adopted to synthesize the HsGY@S composite, which was applied in LSBs (Fig. 1b). The morphology, composition, structure and electrochemical performance of the as-prepared HsGY@S were effectively characterized by FESEM, TEM,AFM,EDS,XPS,XRD,FT-IR,Raman spectroscopy, solid-state NMR, and electrochemical tests. The results indicate that the unique structure of HsGY makes it had high Li^+ mobility, rapid Li^+/e^- transfer and short sulfur energy-storing unites. The micropores (~1 nm) of HsGY could encapsulate the sulfur and essentially confine soluble polysulfide (LiPSs) dissolution via physical confinement and chemical adsorption, therefore alleviating the "shuttle effect" in LSBs system. The HsGY@S composite containing 75% sulfur exhibits small polarization, fast reaction kinetics, excellent cycling and rate properties with a reversible discharge capacity of 557 mAh g^{-1} at 2 C after 200 cycles (Fig. 1(c, d)). This work successfully synthesizes HsGY/HsGY@S and provides a new idea for advanced LSBs with high reversible capacity and stable cycling performance. It also could be used as a promising material applied in other practical storage systems in the future.

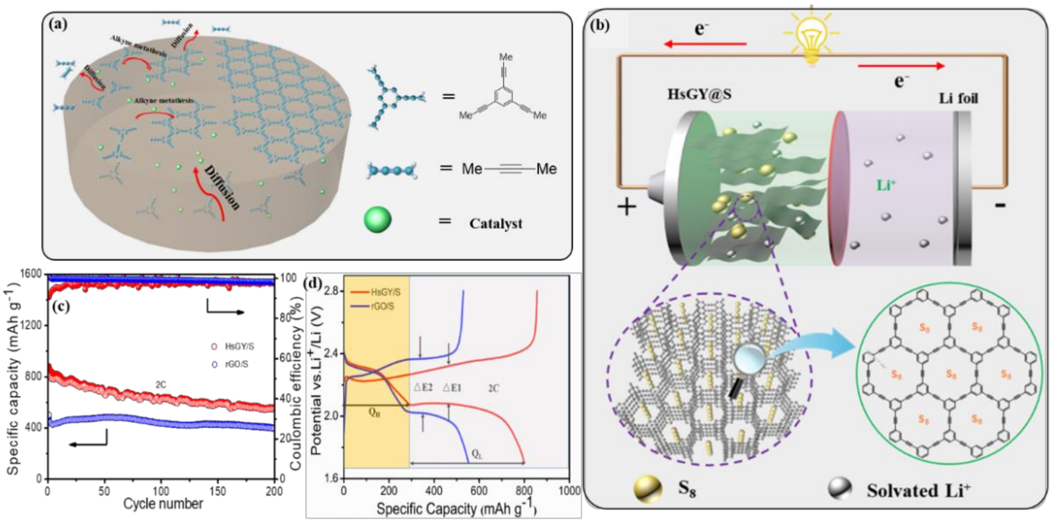

Figure 1. (a)schematic illustration of the HsGY synthesis; (b) the electrode configuration for the designed LSB with a HsGY@S electrode; (c) long-term cycling performance and Coulombic efficiency of the HsGY@S and rGO@S electrodes at 2 C; (d) first cycle galvanostatic charge/discharge profiles.

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Electrochemical gating of quantum interference in single-molecule junctions

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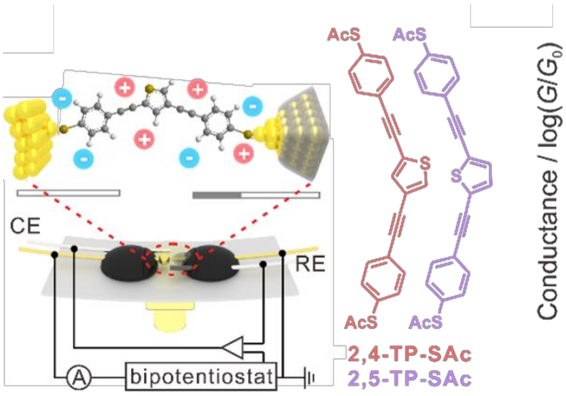
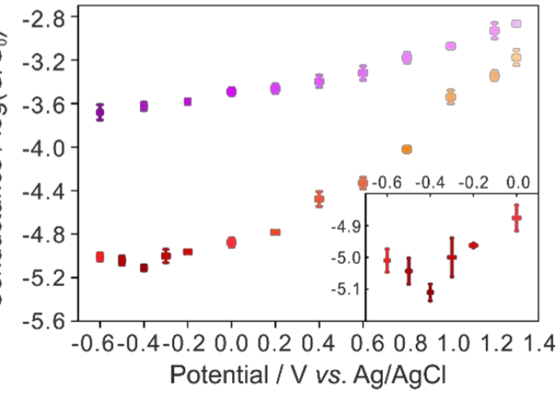
Quantum interference effects (QIE) have become an emerging area in single-molecule charge transport investigation, and controlling the electrical conductance and in particular the occurrence of quantum interference in single-molecule junctions through gating effects has potential for the realization of high-performance functional molecular devices[1,2]. Among the gating approaches, electrochemical gating provides a complementary and effective approach to manipulate charge transport in the electrochemically active or inert molecular junctions at room temperature, which offers the in-situ fine tuning of charge transport through single-molecule junctions[3,4].

We used an electrochemically gated, mechanically controllable break junction technique to tune the electronic behaviour of thiophene based molecular junctions that show destructive quantum interference features. By varying the voltage applied to the electrochemical gate at room temperature, we reached a conductance minimum that provides direct evidence of charge transport controlled by an anti-resonance arising from destructive quantum interference. Our molecular system enables conductance tuning close to two orders of magnitude within the non-faradaic potential region, which is significantly higher than that achieved with molecules not showing destructive quantum interference. Our experimental results, interpreted using quantum transport theory, demonstrate that electrochemical gating is a promising strategy for obtaining improved in-situ control over the electrical performance of interference-based molecular devices.

As a perspective, we will present our recent progress towards the charge transport through supramolecular devices.





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IrO_x Supported on Antimony-Doped Tin Oxide as A High-Performing Electrocatalyst For the Oxygen Evolution Reaction

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Hydrogen is a critical feedstock for several globally relevant industrial processes, such as the production of ammonia, methanol, paraffins and olefins. Additionally, hydrogen is an energy carrier for fuel cell technology. As anthropogenic carbon dioxide emissions continue to soar, it has become of great environmental importance to drive the production of hydrogen by renewable and sustainable means. Polymer electrolyte membrane water electrolysis (PEMWE) offers a means for the generation of high purity hydrogen with zero emissions. While this technology is promising, the slow reaction kinetics of the oxygen evolution reaction (OER), at the anode side of a water electrolyser requires the use of rare and costly platinum group metal oxides (IrO2 and RuO2) as electrocatalysts for feasible operation. Therefore, a significant issue faced in the large-scale implementation of PEMWE is in the reduction of the noble metal content in electrolyser anodes [1].

Supporting of iridium oxide on cheap and stable transition metal oxides has been shown to significantly reduce the content of iridium in OER electrocatalysts. This work focusses on the synthesis of iridium oxide supported on antimony-doped tin oxide using a novel, organometallic chemical deposition (OMCD) method [2,3]. The synthesised catalysts have been structurally characterised to understand the particle size, dispersion and oxidation state of the iridium using XPS and HRSTEM techniques.

Electrochemical activity and durability of the synthesized catalysts was tested using cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy. The performance and stability of oxide supported OER catalysts produced by the OMCD method will be discussed and compared to those prepared by wet synthesis techniques, as well as to unsupported and commercial OER catalysts.

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Theoretical Insights into the pH Effects in Electrocatalysis

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Electrocatalytic reactions exhibit diverse pH effects in kinetics and thermodynamics. For instances, the hydrogen evolution/oxidation reactions (HER/HOR) undergo two orders of magnitude decrease in reaction kinetics on Pt when traversing from acid to alkaline regime; doped carbon materials mostly exhibit much higher activity for the oxygen reduction reaction (ORR) in alkane than that in acid, while Pt-based materials give very similar ORR activities in the two type of media. Understanding the origin of these pH effects would of fundamental and applied significance. Herein, we present some theoretical and computational results on the pH effects in a few model electrocatalytic systems.

Iron phthalocyanine (FePc) is used as a model system for Metal-N_4 (MeN_4) macrocyclic complexes and Me/N-doped carbon electrocatalysts which have potential as low-cost alternative to Pt for the ORR[1]. Through charge-modulating DFT calculation, we derived the adsorption free energies for various ORR intermediates and the reaction free energies for various possible ORR steps at different constant potentials. The results showed that the rate determining steps of ORR are different in acidic and alkaline solutions, and the reaction barrier in alkaline solution is much smaller than that in acidic solution (Fig.1 a), which agrees with the experimental result that the ORR activity of FePc at pH of 13 is two orders of magnitude higher than that at pH of 1. The results for FePcs with different substituent groups indicated that the Fe(III/II) redox potential ($E_{\mathrm{II/III}}$) can serve as an descriptor of the ORR activity of the of FeN_4 center. However, different activity-$E_{\mathrm{II/III}}$ dependence was observed in acid and alkaline solutions. Our results also explain why the $E_{\mathrm{II/III}}$ (vs RHE) shifts positively with increasing the pH value in acidic solution but changes little with pH in alkaline solution (Fig.1b, c), namely, because that the adsorption free energy of OH increases with the increasing of pH in low pH but it is nearly constant in high pH (Fig.1 d). The weaker OH adsorption would result in more positive $E_{\mathrm{II/III}}$, therefore better ORR activity in alkali than in acid. Further electronic structure calculations revealed that the varied dependence of $E_{\mathrm{II/III}}$ on pH is related to the change of frontier molecular orbital with changed surface charge at different potential regions.

We also studied the pH effects on the mechanism and kinetics of hydrogen electrode reactions using DFT calculations and ab initio molecular dynamics simulations. The results allow us to obtain electrochemical adsorption isotherms of hydrogen on Pt and other catalyst surface at different pH values, understand the pH and potential-dependent volcanos, Tafel plots and reaction kinetics.

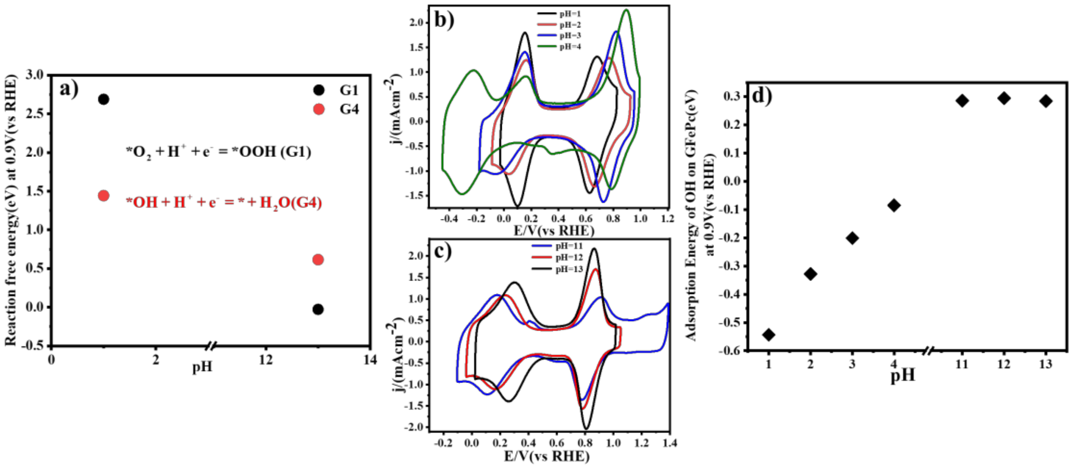

Fig.1 (a) Calculated reaction free energies of the rate-determining steps of carbon-supported FePc (FePc/C); (b, c) Experimental CVs of FePc/C in acid and alkaline solutions; (d) Calculated adsorption free energies of OH on FePc/C under different pH values.

Keywords: Electrocatalysis; pH effects; Iron phthalocyanine; Oxygen reduction reaction; Hydrogen

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Low-frequency SERS spectroscopy for in-situ and simultaneous observation of both sides of electrochemical interfaces

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Surface-selective spectroscopy is a powerful tool to study electrode/electrolyte interfaces. However, chemical and structural information at the solid and liquid phases of the interface has been separately studied using different spectroscopic methods: e.g., X-ray spectroscopy for solid phases and vibrational spectroscopy for liquid phases. For better understanding of electrochemical phenomena, it is preferable to develop a novel spectroscopic method that enables simultaneous observation of both sides of electrochemical interfaces. Recently, we have extended the detectable frequency range of surface enhanced Raman scattering (SERS) into the ultra-low frequency region down to 10 cm^{-1}, which corresponds to THz region, using a conventional spectrometer equipped with ultra-narrow notch filters [1]. This enables us to observe not only intramolecular vibrations but also extramolecular vibrations between weakly adsorbed molecules and substrate. When this low-frequency SERS is conducted on atomically defined metal surfaces like single crystal faces using nanoparticle-induced gap-mode plasmon excitation [2], the difference of the adsorption geometry is clearly observed. Moreover, SERS background can provide electronic information on the substrate, meaning that the vibrational information on molecular adsorbates and electronic information on substrate can be obtained in-situ and simultaneously using low-frequency SERS [3]. This would give deeper insight into catalytic and electrocatalytic reaction mechanisms. In this talk, we will demonstrate in-situ and simultaneous detection of chemical and electronic changes on both sides of electrochemical interface under various conditions.

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Improvement of Photoluminescence Property of Band-edge Emission from $AgInS_2/Ga_2S_3$ Core/shell Quantum Dots

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Semiconductor particles with several nanometer dimension possess optical properties determined by quantum confinement. Such semiconductor nanoparticles or quantum dots (QDs) have been receiving great attention and several kinds of QDs have been synthesized by the sophisticated methods to produce highly monodispersed QDs. The II-VI semiconductor QDs such as CdSe and CdTe have been extensively studied because they exhibit intense narrow band-edge emission from their characteristics as direct semiconductors. As a matter of fact, they have been increasingly finding commercial applications in liquid-crystal displays and television sets. However, high toxicity of cadmium is certainly a matter of concern, and now the QDs containing Cd face to a ban in many countries. The search for a replacement for toxic QDs with non-toxic alternatives has been, therefore, a high priority for persons who would like to exploit emission of QDs with high chromaticity.

I–III–VI semiconductor nanoparticles are promising candidates for non-toxic quantum dots [1,2]. It has, however, not been achieved yet to remove defect levels responsible for their broad-band emission. In the present study, coating of core $AgInS_2$ nanoparticles possessing a bandgap in the visible region with III–VI group semiconductors has been attempted. The prepared $AgInS_2/InS_x$ and $AgInS_2/GaS_x$ ($x = 0.8–1.5$) core/shell structures generate intense narrow-band photoluminescence originating from a band-edge transition at a wavelength shorter than that of the original defect emission, as shown in Figure 1. Microscopic analyses reveal that the GaS_x shell has an amorphous morphology, which is quite different from the typical shell materials such as crystalline lattice-matching ZnS. Single particle spectroscopy shows that the average linewidth of the band-edge photoluminescence is as small as 80.0 meV, which is comparable with that of industry-standard II–VI semiconductor quantum dots. In terms of photoluminescence quantum yield, a value of 56% with nearly single-band emission has been achieved as a result of several modifications to the reaction conditions and post-treatment to the core/shell nanoparticles. These results indicate the increasing potential of AgInS2 nanoparticles for use as practical cadmium-free quantum dots [3].

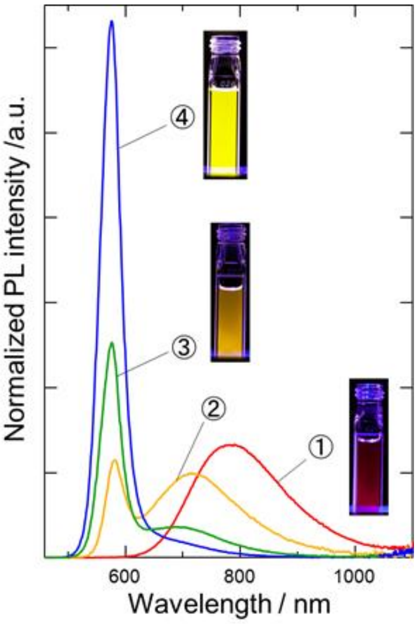

Figure 1 PL spectra of $AgInS_2$ (1), $AgInS_2/InS_x$ (2), $AgInS_2/GaS_x$ (3), and TOP-treated $AgInS_2/GaS_x$ (4).

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New approaches for the study of Electrocatalysis and Transport in Nanoporous Gold

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Nanoporous gold (NPG) is a nanoporous bulk material that is interesting for many applications, such as (electro-)catalysis, sensing, energy storage and energy conversion due to its large surface-to-volume ratio, easy preparation, good electrical conductivity, high catalytic activity and chemical as well as structural flexibility. Samples with a homogeneous structure up to several mm in size can be obtained by dealloying a silver-gold alloy in concentrated nitric acid or by applying a potential program that allows tuning of pore and ligament sizes as well as residual silver content. By understanding the complex interplay of structure and properties, a rational design of catalysts should be possible.

The filling of the nanoporous material into a cavity microelectrode enables an effective study of this material because many samples can be obtained from a powdered monolith. This has been used for the application of surface interrogation mode [1] of scanning electrochemical microscopy (SECM) to porous electrodes inside a cavity electrode [2]. Interestingly, the surface oxides are reduced throughout the three-dimensional material without significant diffusional blurring. This is ascribed to the mediator regeneration mechanisms inside the pore space. Digital simulations support our findings.

To investigate mass transfer inside the porous network of NPG with different morphologies we used SECM approach curves in the feedback mode with ascorbic acid as an irreversible redox mediator. This allows first, to obtain a relative effective diffusion coefficients of the used compound in the porous material. If solute-wall interactions are negligible, the porosity can be extracted when making assumptions about the tortuosity of the material. We found that the Bruggeman relation leads to good agreements between measured and simulated approach curves for this material similar to many other porous electrode materials [3]. Based on the results of a large number of individual simulations, a new analytical expression is proposed that can be used to obtain porosity values from SECM approach curves. This approach can be particular useful when following coarsening processes in an electrochemical cell under avoidance of transfer to a scanning electron microscope environment.

Furthermore, X-ray photoelectron spectroscopy (XPS) was used to identify the composition of NPG and compositional gradients in NPG. The distribution of residual silver was obtained from binding energy shifts of Ag in NPG that are sensitive to the local composition of the alloy. The Ag 3d peak is shifted to lower binding energies with increasing dilution of Ag in the silver-gold alloy. After a calibration of the binding energy for different silver-gold alloys we could confirm earlier studies which showed that Ag is not homogeneously distributed in NPG but forms Ag-rich regions [4,5]. In addition, XPS showed that the electrochemical cycling in methanol-containing solution resulted in a compositional change of the NPG [6]. Synchrotron X-ray photoelectron spectroscopy with tunable excitation energy and tunable information depth further showed a rather strong enrichment of Ag at the surface of the ligaments.

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Surface Plasmon-Driven Chemical Reactions on Silver Electrodes of Nanostructures

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On noble metal electrodes of nanostructures surface plasmon resonance (SPR) provides a pathway to efficiently absorb and confine light to nanoscale surface electrons, thereby bridging photonics and photoelectrochemistry. We have studied the surface-enhanced Raman spectra of p-aminothiophenol (PATP) adsorbed on silver electrodes of nanostructures, which can exhibit the strongest surface plasmon resonance (SPR) from the collective oscillation of their conductance electrons of nanostructures among various metal materials. This not only produces the giant enhancement in electrochemical surface-enhanced Raman spectroscopy (SERS), but also results in plasmon-driven chemical reaction on metal nanostructures. From our previous studies, the molecule can be oxidized to p,p'-dimercaptoazobenzene (DMAB). Now the surface catalytic coupling reaction has been a typical model reaction, which involved to the SPR effect, but it must be necessary to investigate the reaction mechanism and kinetics under experimental conditions.

In this work, we further studied SPR-enhanced photoelectrochemical synergistic reactions by SERS to improve chemical reaction activity and examine changes in reaction selectivity. (1) We first demonstrate that hot carriers arising from SPR decay contribute to the surface catalytic coupling reaction of PATP on a silver NP electrode. Our experimental results support the hot hole participates the surface catalytic coupling reaction of PATP adsorbed on silver electrodes. (2) By using potential step electrochemical SERS, we further inspect the kinetics of the surface catalytic coupling reaction by monitoring the time-dependent SERS intensity of the characteristic band at 1436 cm^{-1}, which can be attributed to the stretching vibration of the N=N double bond of p,p'-dimercaptoazobenzene (DMAB). We estimated the reaction rate constants based on the time-dependent SERS spectra of DMAB measured at different potentials. (3) Finally, we demonstrated a parallel reaction mechanism based on the observed SERS spectra of PATP adsorbed on silver nanoparticles modified smooth electrodes of silver. When synergistically combined with the modulation of pH to alkaline solution at electrochemical interfaces, SPR-enhanced photoelectrochemical reactions can be further gain reaction efficiency and selectivity for the formation of a new surface species at higher potentials. The electrochemical SPR effect provides a viable approach for studying the photoelectrochemistry through combining SERS at the interface of nanoparticle-modified metal electrodes and electrolytes.

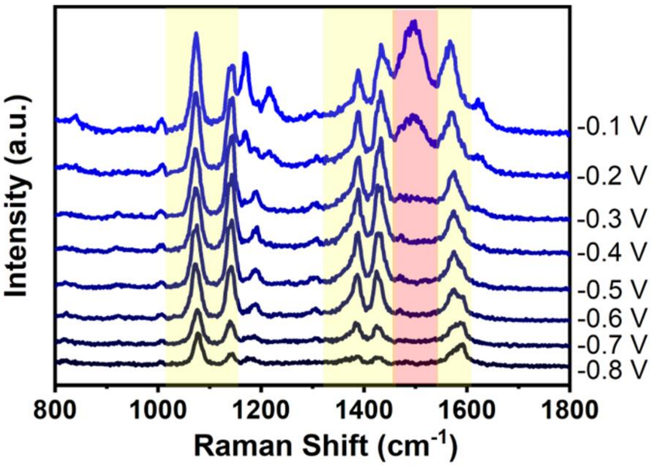

Figure 1. Electrochemical SERS for DMAB (yellow shade) and a new surface species (red shade)

Lab on a chip for the electrochemical quantitation and recycling of strategic materials

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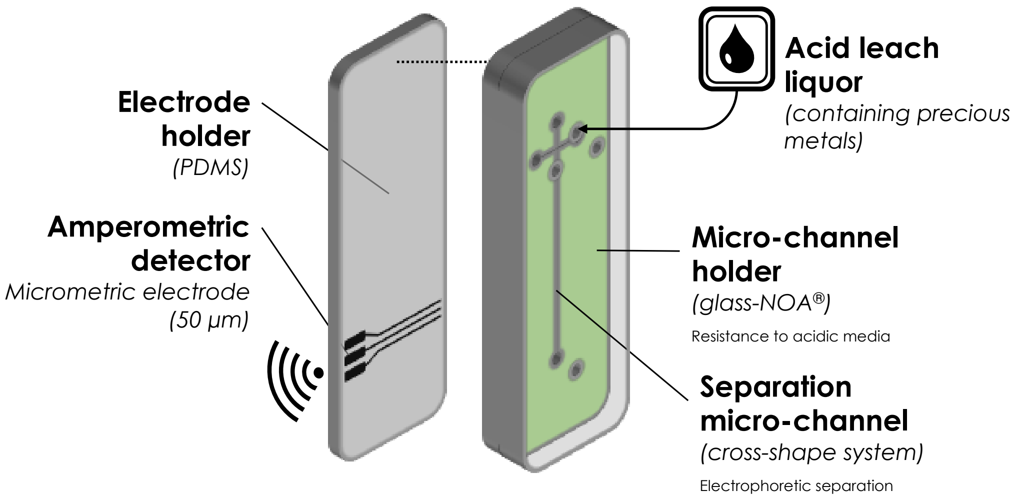
Metals subject to risks of economic fluctuations and of high importance for technological development are defined as strategic metals [1]. Some of them, such as platinum or gold, are used in the electronics industry in the manufacture of hard disks or certain printed circuit board connectors. Thus, waste electrical and electronic equipments (WEEE) have become sources of recoverable materials and their recycling is becoming a major economic and environmental issue. In this context, we were interested in their recovery in leach liquors [2].

We report on an innovative contribution to the recovery of WEEE, and more particularly precious metals, with the development of a laboratory on a chip (LOAC) dedicated to the analysis and recycling of metals present in low concentrations in an acid medium mimicking a conventional leach liquor (figure below).



A proof of concept was carried out to show the possibility of analysing strategic metals such as platinum and palladium. A LOAC has been developed using materials compatible with acidic solutions. In a cross-section design, this LOAC allows separating the different metal ions under an electric field and their electrochemical detection via the integration of original microelectrodes at the output of the microchannel. The incorporation of these electrodes not only allows the considered ions quantitation, but also the development of their capture in their metallic form for recycling purposes.

Acknowledgements
This work was financed by the Agence de l'Environnement et de la Maîtrise de l'Énergie (ADEME) and the "Urban Mines" Chair of the Paristech Foundation.

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Experimental and computational studies on sensing of DNA damage in Alzheimer's disease

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DNA damage plays a pivotal role in the pathogenesis of Alzheimer's disease (AD) therefore, an innovative ss-DNA/dopamine/TiO_2/FTO electrode strategy was developed to detect the genotoxicity upon photocatalytic reactions. This study involves a computational and electrochemical investigation towards the direct measurement of DNA damage. Computational chemistry was useful to resolve the intricate chemistry problems behind electrode constructions. The computational protocols were simultaneously carried out comprising of density functional theory (DFT) calculations, Metropolis Monte Carlo (MC) adsorption studies, and molecular dynamics (MD) simulations. The DFT calculations elucidated the structural, electronics, and optical properties of the electrode components resulting in a good agreement with the experimental parameters. The MC simulations carried out using simulated annealing predicted the adsorption process within layer-by-layer electrode as well generating reliable inputs prior to MD simulations. A 100 ns MD simulations were performed using a canonical ensemble provided information on the thermodynamics parameters such as total energy, temperature and potential energy profiles, including radius of gyrations and atomic density profiles. Binding energies calculated from the MD trajectories revealed increasing interaction energies for the layer-by-layer electrode, in agreement with the experimental characterization studies. Experimentally, the ss-DNA was electronically linked to TiO_2/FTO surface through dopamine as a molecular anchor. Electrochemical measurements using cyclic voltammetry and electrochemical impedance spectroscopy were employed to characterize the electrode modifications. The square wave voltammetry was subsequently used to measure the DNA damage and the ability of antioxidant treatment using ascorbic acid (AA). The presence of AA significantly protected the DNA from the damage, and therefore used as a potential treatment in AD. The electrochemical characterizations were in a good agreement with the theoretical investigations (i.e. HOMO-LUMO DFT levels and binding energies). In addition, guanine residues predicted by DFT as the most reactive sites of the ss-DNA involved in the genotoxic reactions. Overall, the theoretical studies successfully validated the experimental study as well as providing the molecular basis of interaction phenomena towards electrode constructions. Our results highlight the potential application of this methodology to screen the genotoxicity in Alzheimer's, suggesting the important role of theoretical studies to predict the molecular interaction and validation of the DNA-based sensors and bioelectronics.

Keywords: Titanium dioxide, Fluorine-doped tin oxide, Cyclic Voltammetry, Square wave voltammetry, Density Functional Theory, Molecular dynamics simulations, Monte Carlo Simulations, DNA-sensors.

Advanced lifetime analysis of CCCV and pulse-charging routines for li-ion batteries

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Fast charging strategies of lithium-ion batteries, especially for the e-mobility sector, demand for the best adjustment between charging time and cycle life. Excessive charging rates give rise to lithium plating and/or dendrite growth, thus increasing the capacity fade and /or internal shorts of the battery dramatically. In [1] the impact of different charging protocols on battery aging has been shown.

In this work, the standard CC-CV (constant current – constant voltage) charging protocol is compared to a time-saving pulse charging protocol, and the respective capacity fade over lifetime was used as benchmark. For better comparability, the pulse-charging and the standard CC-CV charging protocols were adjusted with respect to the total charging intensity (average charging current). First, suitable test sequences regarding (i) length and intensity of the charging pulse, (ii) length of the resting time between the pulses, and, (iii) the reduction rate after reaching the cut off voltage of 4.2 V have been developed. Second, test conditions as temperature and SoC range were set equal for both routines. Whereas discharging rate was kept at 1C (within the specification), charging intensity was accelerated and set at 2C (200% of the specification). All experiments were performed with commercial high-energy cells (Kokam 560 mAh) made of a NCA-LCO blend cathode and a graphite anode. The extensive experimental data set gathered from ten different charging protocols will be discussed in detail. The pulse charging protocol (1C discharge, 2C charging intensity at 25°C) granted 250 full cycles before end of life (EoL: capacity < 80%). In contrast, the cells cycled with the CC-CV routine (1C discharge, 2C charge at 25°C) showed a pronounced capacity fade and reached the EoL within the first 50 cycles. Post-mortem analysis revealed deposits at the anode side, indicating lithium-plating as the major contribution to the capacity fade.

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Impedance of a passive oxide layer at the OCP

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Different models can be used to describe the impedance of a passive oxide layer, such as the power-law model or the Young model. These two models tend towards a pure capacitor C_∞ at very high frequencies and to a resistor in very-low-frequency range. Between these two limiting cases, the behavior of the impedance corresponds to a CPE accounting for the power law model or a pseudo-CPE in the case of the Young model.

From a physical point of view, two kinds of conduction have to be taken into account in an oxide layer: an electronic conduction and an ionic conduction. The electronic conduction is characterized by a pure resistor $R_{\text{ox,e}}$, and the ionic conduction, which corresponds to the presence of vacancies, is indeed the impedance of the passive oxide layer.

At the open circuit potential, the cathodic reaction (e.g. the oxygen reduction reaction) occurs at the interface between the oxide and the electrolyte and the electrons are transferred to the substrate *via* the electronic resistor $R_{\text{ox,e}}$. In parallel to this electronic path, the ionic path is characterized by the double layer capacitance at the interface between the electrolyte and the passive oxide layer in series with the impedance of the passive oxide layer.

This model thus corresponds to two impedances in parallel, one corresponding to the anodic branch and the other corresponding to the cathodic branch. To extract all parameters from the experimental data, it is necessary to measure the impedance over a wide frequency range. The capacitance C_{dl} plays a role only in very low frequency range; whereas, C_∞ plays a role only in very-high-frequency range, thus allowing their independent determination.

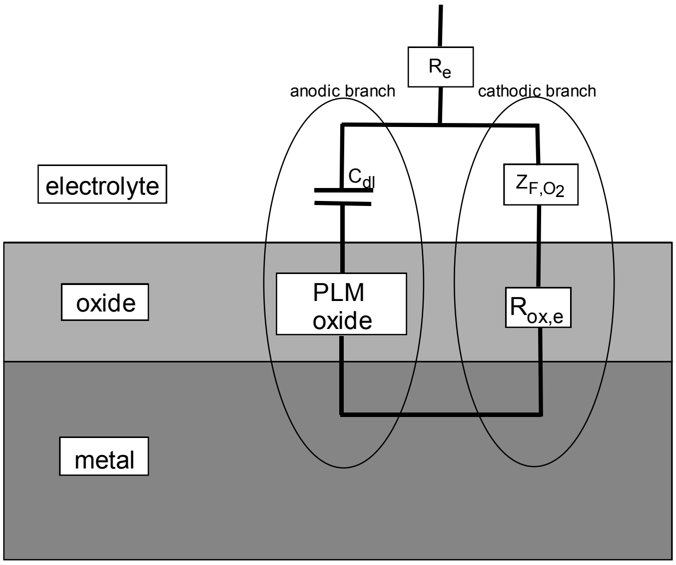

Figure 1: Electrical equivalent circuit showing the parallel contributions of anodic and cathodic reactions.

Polyoxometallate-based redox supercapacitors

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Redox active electrolytes coupled with high surface area carbon electrodes represent a new class of device called “redox supercapacitors” [1]. In this system, the electrolyte is the main source of accumulated charge, and consequently, this device possesses enhanced capacity respect to pure electrochemical double layer capacitor.

In this work, we exploited the possibility to use a novel redox electrolyte concept based on mixed aqueous-organic solvent and a polyoxometallate (POM) as redox moiety. The presence of organic solvent plays a multi-role in this system. Firstly, it enhances the cathodic electrochemical stability window (as shown in Fig. 1a); secondly, positively influences the reversibility of the redox reaction of the $PW_{12}O_{40}^{3-}$ anion at low potential, by stabilizing its reduced form. Finally, the physical properties of the hybrid aqueous/non-aqueous system inherit the merits from both aqueous (non-flammability, high conductivity) and non-aqueous (high electrochemical stability, low freezing point etc.) systems [2,3]. Last but not least, this novel redox electrolyte confers higher capacity to the system (Fig. 1 b & c).

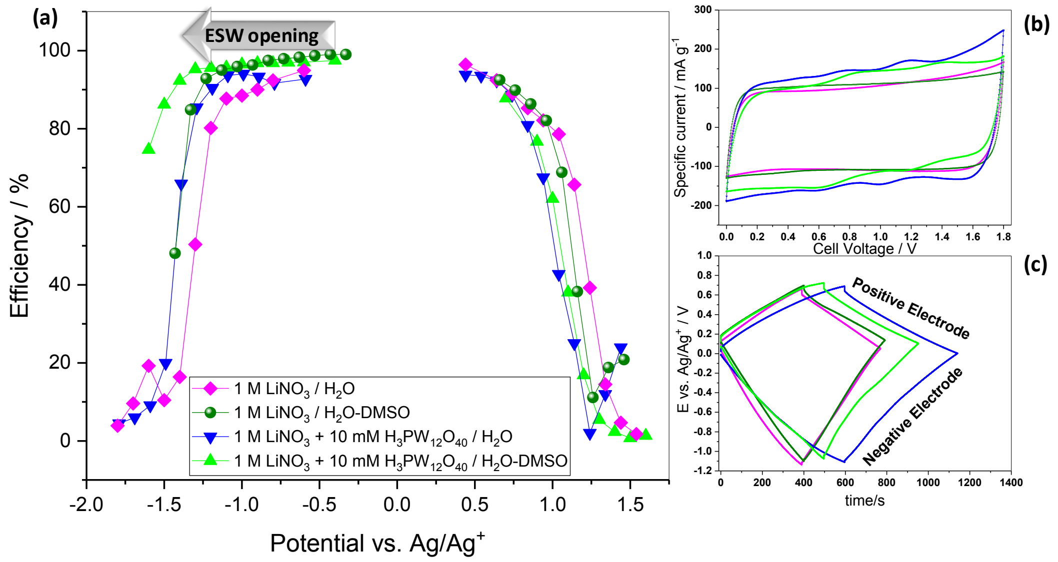

Fig. 1 – (a) Electrochemical stability window of AC electrodes and different electrolyte combinations; (b) cyclic voltammetry at 5 mV/sec and (c) galvanostatic cycle at 0.1 A/g of AC//AC capacitors in the different electrolytes (ratio PE:NE = 2:1)

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Organometallic Based Catalysts for Energy Production and Storage

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Organometallic complexes have intrinsically excellent characteristics as a new class of electrocatalysts for clean energy production in fuel cells and electrolyzers. The state of the art materials for those devices are based on precious metal nanoparticles dispersed on a conductive carbon based supports. Despite the fact that such materials have reached very high performance levels in terms of activity and stability, they still suffer from some intrinsic limitations that contribute to hinder the commercial development of fuel cells and electrolyzers on a large scale. Organometallic-based electrocatalysts may help to overcome such limitations. For example, those devices exhibit remarkably high selectivity for alcohol electrooxidation towards carboxylic compunds of industrial relevance. Additionally, precious metal loadings can be reduced significantly by using single site organometallic catalysts where each metal atom is potentially active. Here we present a Rh organometallic catalyst, [Rh(OTf)(trop$_2$NH){P(4-n-butyl-Ph)$_3$}] (trop$_2$NH=bis(5-H dibenzo[a,d]cyclohepten-5-yl)-amine; OTf$^-$ = $CF_3SO_3^-$ = triflate) that was successfully employed as anode both for Direct Alcohol Fuel Cells, named Organometallic Fuel Cells (OMFCs) and Alcohol Electroreformers, named Organometallic Electroreformers (OMERs). These devices exploit a biomass-derived alcohol (e.g. EtOH, 1,2-propanediol or glycerol) for respectively energy and hydrogen production and contemporaneously, the alcohol is converted in a high-added-value carboxylate, such as lactate. Therefore, we hypothesize the exploitation of OMFCs and OMERs as an essential component of the biorefinery platform. To the best of our knowledge, this [Rh(OTf)(trop$_2$NH){P(4-n-butyl-Ph)$_3$}] complex is the most active organometallic anode for OMFCs and OMERs ever reported. [1]

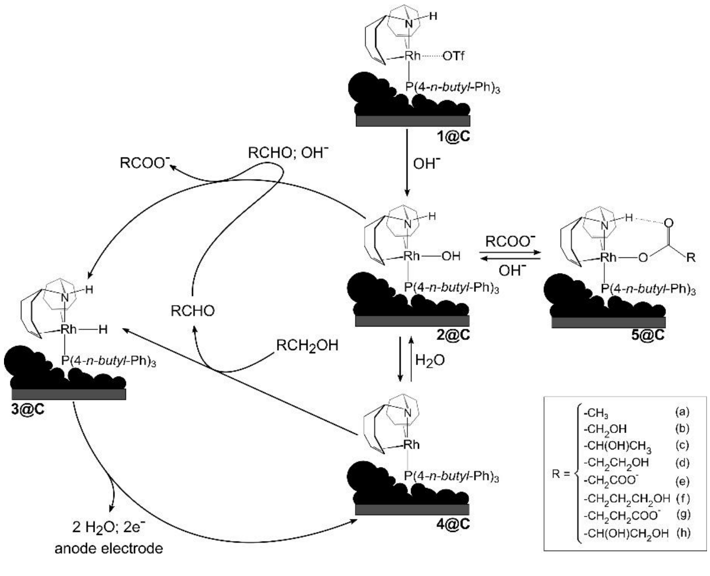

Figure 1: proposed mechanism for the alcohols electrooxidation occurring on the OMFCs and OMERs anodes coated with the [Rh(OTf)(trop$_2$NH){P(4-n-butyl-Ph)$_3$}] catalyst (1@C).

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Status, Challenges and Prospects for Zinc-Air Redox Flow Batteries

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A significant reduction in greenhouse gas emissions can only be achieved by increasing the installation capacities of wind and solar power systems. The intermittent and fluctuating power production by the renewable energies requires electrical energy storage systems to stabilize the electricity grid. Large-scale electrochemical energy storage technologies, such as all-vanadium or zinc-bromine redox flow batteries, have to meet the challenging long-term cost targets (e.g. < 150 $/kWh, DoE) [1]. The rechargeable zinc-air flow battery represents a promising storage technology with low environmental impact and compact system design. It uses zinc metal as abundant and inexpensive storing material. The second reactant–oxygen–is withdrawn from the surrounding air (Figure 1, left).
The main challenges of this system are non-compact zinc deposits during charging, leading to loss of active material and short-circuiting by dendrites as well as the high overpotentials and low stability of the bifunctional air electrode [2,3]. Overall, these issues accumulate in limited lifetime, deteriorating cycle stability and low energy efficiency, which impedes the application of the zinc-air redox flow battery as stationary energy storage system.

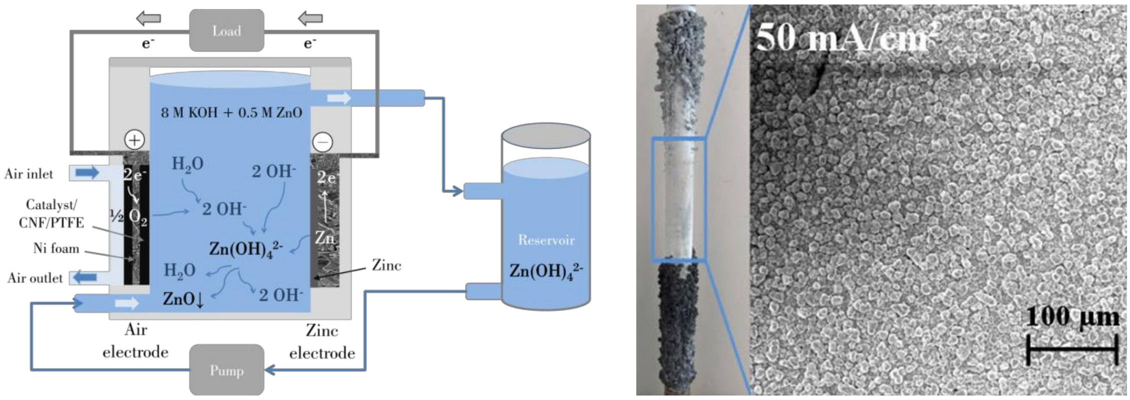

Figure 1: Schematic of a zinc-air redox flow cell (left); typical zinc morphologies obtained in a Rota-Hull cell for a wide range of current densities [5].

Strategies on improving both the deposit morphology of the zinc electrode (Figure 1, right) as well as the long-term stability of the bifunctional air electrode at practicable charge/discharge current densities of up to 50 mA cm^{-2} are discussed. Recent results on the long term cycle behaviour of the zinc and the air electrode during pulse interrupt charging in half cells and in unit zinc-air cells are presented [3,4,5]. Prospects are given for further improvements.

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Electrocatalysis at the tip: Evaluation of the OER activity of a single MOF-derived composite nanoparticle

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The advent of ultra-small electrodes marks a new frontier in 'single-entity' studies, breaking away from the traditional model of deducing nanoparticle behavior from bulk-continuum statistical ensemble analysis at macroelectrodes.[1] A detailed investigation of the nanoparticle, the subtle transformations occurring during activation, and the post-mortem changes in the aftermath of the electrochemical reaction remains elusive to 'single entity' studies due to the extreme technical challenges involved in handling a single particle.

Here, we present an exclusive attempt to elucidate the electrocatalytic response of a 'single' metal-organic framework (MOF)-derived nanoparticle using a unique 'particle at the stick' approach. The experimental design involves growth of a single MOF nanocrystal of Zeolitic imidazolate framework (ZIF-67) at the tip of a carbon nanoelectrode to produce a nanoassembly, which is stably robust to be sequentially analyzed by (TEM/SEM-EDX – electrochemistry and TEM/SEM-EDX (again). The nanoassembly successfully goes through the stages of pyrolysis and electrochemical study, in addition to interim microscopic (SEM/TEM-/EDX) investigation of the structure and compositional changes occurring inside the nanoparticle during each of these stages. Identical location TEM (IL-TEM) analysis substantiates the 'sacrificial' template nature of MOF, while post-electrocatalysis studies reveals agglomeration of Co ions within the Co-N/C composite during oxygen evolution reaction (OER). The extraction of the high current density profiles at extremely high oxygen evolution rates, up to 230 mA cm^{-2} at 1.77 V (RHE) and a remarkably high turn-over frequency (TOF) 29.7 s^{-1} at 540 mV overpotential underpins the usefulness of such architectures in establishing the particles' catalytic performance at industrially relevant reaction conditions and estimating the structure-property relationship without any macroscopic film effects.

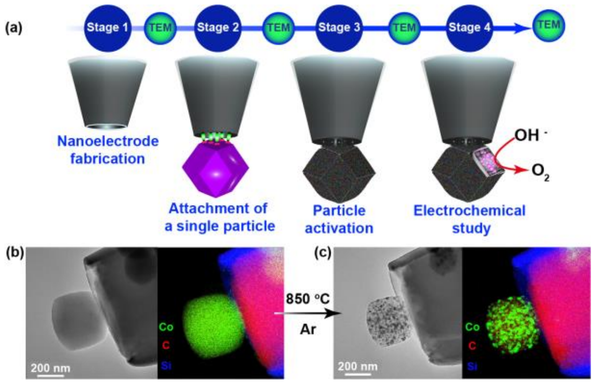

Fig. 1 (a) Flowchart of the various stages involved in the sequential analyses. (b) TEM image and corresponding EDX map of the ZIF-67@f-CNE nano-assembly. (c) TEM image and corresponding EDX map of the resulting CoN/C@CNE nano-assembly.

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Bipolar Electromechanical Activity of Conducting Polymers for Wireless Actuation

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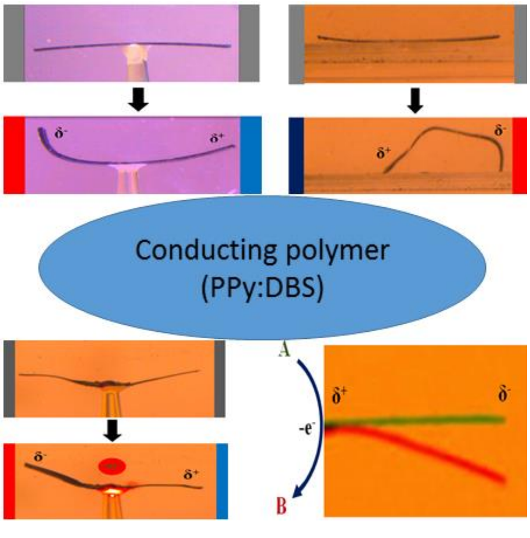
Bipolar electrochemical activity of conducting polymers can be used in order to achieve wireless actuation. During normal electromechanical deformation of conducting polymers, the two basic requirements are an electrical contact between the polymer and the power supply and a bilayer structure of the polymer. This can severely limit their application.[1] We could successfully overcome both of these critical issues based on a wireless actuation approach. In bipolar electrochemistry, a global electric field induces wireless electrochemical reactions at the two extremities of the conducting polymer, leading for example to a colour gradient and photoluminescence.[2, 3] Here, we demonstrate wireless actuation of electrochemically grown polypyrrole (PPy) objects doped with dodecyl benzene sulfonate (DBS) based on bipolar electrochemistry. The intrinsic asymmetric morphology of the two polymer interfaces constitutes the required bilayer structure, being a key factor for the directional bending in the presence of a constant electric field.[4] Furthermore, electric fields of alternating polarity allow triggering a crawling motion of a PPy strip.[5] The movement is the result of a triple symmetry breaking due to unequal oxidation states at the two extremities of the PPy. To increase the functionality of PPy, a miniaturized light emitting diode can be integrated into the PPy matrix for the purpose of simultaneous wireless actuation and light emission.[6] By further tuning and optimizing the electrochemical reactions, the wireless actuation can also be employed in a straight forward way as an optical read out of chemical and biochemical information.[7] Such systems might open up completely new perspectives, among others for wireless (micro-)robotics based on electrically and/or chemically triggered biomimetic actuation effects.



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Surfactant-free syntheses of precious metal nanoparticles for improved (electro)catalysts

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Platinum group metals are key yet scarce resources. Their scope of application ranges from chemical production and medicine to energy conversion. Precious metal (PM) nanoparticles (NPs) in particular are attracting nanomaterials to maximize the use of PM atoms. A vast amount of research has been dedicated to produce, process and exploit PM NPs. Wet-chemical methods leading to colloidal NPs are a popular approach due to the simplicity and control over the NP properties (composition, size, morphology etc.) achieved by this approach. Unfortunately, most colloidal syntheses require surfactants, detrimental for instance for catalytic activity since they typically block active sites. Surfactants often prevent the further large scale production of NPs. A major challenge is to then efficiently transfer the knowledge gained in research lab to industry-compatible production methods. This challenge can be addressed by designing new production methods of precious metal NPs.

Over the years, we focused on developing surfactant-free syntheses of PM NPs. Such syntheses allow on the one hand performing systematic study of PM NPs. So doing, a better understanding is gained on parameters influencing (electro)catalytic activities of NPs such as composition, size, loading on a support. Based on the surfactant-free ethylene-glycol synthesis we recently managed to discriminate between NP size and proximity effects, e.g. for the oxygen reduction reaction (ORR) catalyzed by Pt NPs.[1,2] The results show the strong influence of proximity effect that must be taken into account to optimize the design of supported PM NPs catalysts, Figure 1.

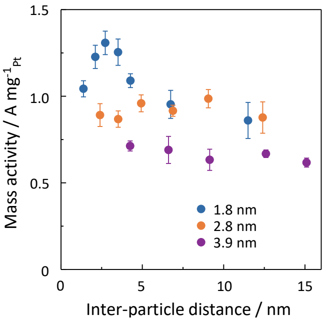

Figure 1. Size and proximity effects in the ORR for Pt NPs.

On the other hand, the gap between lab-scale research and large scale implementation can now be bridged. We recently developed a surfactant-free synthesis allowing the use of few and safe chemicals, easily scalable, leading to NPs that can easily be processed to catalysts with superior activities.[3] This 'colloids for catalysts' Co4Cat^{TM} process is here detailed together with and our recent achievements. The method is simple and generally applicable to Pt, Ru, Ir and Pd NPs. It consists in mixing and heating up a PM precursor in alkaline mono-alcohols without surfactants. The general approach is relevant for the room temperature preparation of small (3 nm or less) Pd nanoparticles for the ethanol oxidation.[4] The simplicity of the method makes this synthesis sensitive to experimental parameters typically screened in alternative colloidal syntheses. We studied the different nucleation and growth mechanism of Pt NPs and the influence of solvents,[5] cations,[6] metal precursor on the size control of the NPs.[7] we ultimately developed an ultra-fast (seconds) room temperature synthesis of PM NPs.[8] Pt NPs obtained by the Co4Cat technology a show superior performances compared to industrial catalysts for hydrogenations reactions. Ir NPs show extremely high electrochemically active surface areas and are suitable catalysts for the oxygen evolution reaction (OER).[3] We recently performed a detailed study of the effect of NP loading on the activity of these extremely active Ir NPs for the OER.[9]

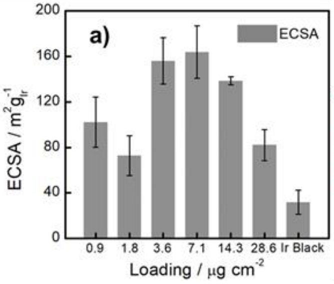

Figure 2. Loading effect on the OER for Ir NPs.

We then here show the multiple benefits of surfactant-free syntheses to develop various performant PM NP (electro)catalysts.

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Niobium-doped Titania as a Nanofibre Support for Iridium Oxide in Reversal Tolerant Anodes in Polymer Electrolyte Fuel Cells: The effect of dopant concentration on catalyst performance

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Durability is one of the major barriers to the large-scale commercialisation of promising polymer electrolyte fuel cells (PEFCs) as a relief mechanism for the current global energy challenges. The largest detractor from the durability of PEFCs is carbon corrosion, the most severe form of which occurs at the anode during the sub-stoichiometric supply of fuel. If such fuel starvation continues unabated, carbon corrosion causes cell failure, thereby increasing the lifetime cost of PEFCs.

A robust solution is the promotion of the oxygen evolution reaction (OER) as an alternative reaction to carbon corrosion by the inclusion of an iridium-based OER catalyst in the PEFC catalyst anode. However, this strategy will increase the cost of PEFCs due to the high cost associated with iridium. It is therefore vital that the OER catalyst be supported on a durable, cost-effective, and conductive material to maximise the efficiency of iridium included in the fuel cell.

Titania is an ideal support material given its high surface area, durability, low-cost and ease of synthesis. Its conductivity may be enhanced by substitutional doping of metal atoms in the lattice. Niobium is the most suitable dopant as it has a similar atomic radius as that of titanium, thereby minimising lattice strain. The upper theoretical limit for doping titania with niobium has been computationally predicted to be 25 at. % [1]. The use of nanofibres has been seen to improve the performance of electrochemical devices by increasing the charge mobility compared to nanoparticles [2].

In this work, rutile titania nanofibres having various niobium dopant levels (0 – 20 at. % Nb, in increments of 5 at. %) have been synthesised and used as support material for various loadings of iridium oxide (10, 30 and 60 wt. %). The structure of the support and catalyst has been confirmed with powder X-ray diffractometry (XRD; Co anode) by Rietveld refinement using TOPAS, Raman spectroscopy (532 nm source at 1 mW, 0 – 1000 cm^{-1}), and X-ray photoelectron spectroscopy (XPS; Al source). Particle morphologies, sizes and compositions have been determined using transmission electron microscopy with energy-dispersive X-ray spectroscopy (TEM and EDS), and were found to be 3 nm iridium oxide catalyst particles supported on niobium-doped titania nanofibres 100 nm in diameter. UV-vis spectroscopy has shown a decrease in bandgap with increasing dopant levels. The electrochemical performance has been tested in a three-electrode glass-cell (Pt foil as the counter electrode, SMSE as the reference electrode and a drop-cast thin film RDE as the working electrode) with 1 M $HClO_4$ as electrolyte. The OER activity of the synthesised materials has been determined using chronoamperometry techniques in the potential window of 1.5 - 1.7 V vs RHE, with the OER activity reported at 1.525 V vs. RHE [3]. Further, the durability of these materials has been studied through accelerated stress tests consisting of cyclic voltammetry in the potential window of 0.0 - 1.5 V vs RHE for 10 000 cycles. The electrochemical performance of the synthesised materials was compared to that of commercially available catalysts.

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Amperometric Gas Detection Using Planar, Low-Cost, Miniaturised Sensing Devices with Gelled Materials

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Amperometric gas sensors (AGSs) are widely used due to their many advantages, such as low-cost, portability, durability, wide linear range, high sensitivity and high selectivity.[1] Room temperature ionic liquids (RTILs) have been suggested as a replacement for conventional solvents/electrolytes in AGSs[2] – substantial research has been done to elucidate reactions and mechanisms of gases in RTILs, and their analytical utility in 'membrane-free' gas sensors. This research has translated to using microlitre droplets of RTILs on miniaturised devices such as screen-printed electrodes (SPEs) and thin-film electrodes (TFEs), with excellent results. However, the drawback to removing the membrane is that the RTIL is unstable and can flow when the electrode is subjected to tilting, shaking or agitation.

Our recent work has focussed on combining RTILs with polymers in order to create a gelled material that is robust and does not flow like a liquid.[3] These materials should be sufficiently conductive to enable the measurement of current, and also allow sufficient solubility of the gas. We have investigated polymers based on poly(methyl methactylate) (PMMA) and poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP), in addition to other hydrophobic polymers. We have used these materials in conjunction with miniaturised planar devices for the detection of oxygen[3] and ammonia gases,[4] and the explosive 2,4,6-trinitrotoluene (TNT).[5] In this talk, I will discuss the very low detection limits (less than 1 part-per-million for ammonia) that could be obtained on these devices, and the sensitivity improvements over common atmospheric contaminants (e.g. oxygen, moisture) that were observed by the addition of polymers. Overall, these materials show much promise for use in robust, low-cost, miniaturised sensors for various analyte species.

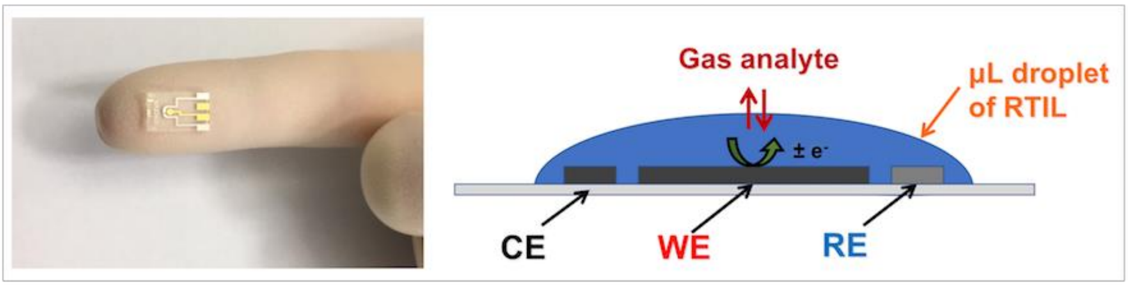

Figure 1. (Left) Photo of a commercially available thin-film electrode (TFE) device used in this work. (Right) Sketch of the side view of the TFE, showing the sensing processes when the sensor is exposed to a gaseous environment. CE, WE and RE = counter, working and reference electrode, respectively.

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Highly selective and efficient methane generation by carbon dioxide electroreduction on carbon-supported platinum catalyst without overpotential

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Electrochemical reduction of CO_2 without overpotential is one of the central issues to resourcify the CO_2 in the atmosphere which is increasing year by year. When a Cu electrode is employed, CO_2 reduction occurs as high as 60% Faradaic efficiency; but, it requires very high overpotentials of 1–1.5 V. That is hard to compete with the hydrogen evolution reaction (HER) at Pt electrode from a viewpoint of energy conversion efficiency. One idea to realize the CO_2 electroreduction without overpotential is to reduce a CO adsorbed on the Pt electrode that is well known and is easily generated by CO_2 reduction at around 0.05–0.35 V vs RHE.

Firstly, a mixture of CO_2 and Ar was fed to the Pt/C cathode of membrane electrode assembly by changing the mixing ratio. As a result of in-line MS analysis, CH_4 was obtained under a potential sweep from 0.2 to 0.1 V vs RHE with a Faradaic efficiency of ~3% by feeding 4–10 vol% CO_2. This CH_4 generation potential is almost the same as the theoretical one of E^0=0.169 V. In contrast, negligible small amount of CH_4 was found by the 100 vol% CO_2 feeding. Cyclic voltammogram measurements revealed that the adsorbed ratio of CO_{ads} and H_{ads} on the Pt is controlled by the gas feeding ratio of CO_2:Ar. This leads to a fact that the CO_{ads} and H_{ads} participate in the CH_4 production by the Langmuir-Hinshelwood mechanism. In addition, HER was observed at the electrode potential of <0.05 V vs RHE which does not encounter the CH_4 generation at 0.1–0.2 V vs RHE.

According to the above, the CO_2 reduction on the Pt/C is known to consist of sequential reactions of (i) $CO_2 \rightarrow CO_{ads}$ and (ii) $CO_{ads} \rightarrow CH_4$, where the two electrode potentials are not equal. By settling and stepping the former and latter potentials at 0.2 and 0.1 V vs RHE, a high Faradaic efficiency of ~7% was recorded by feeding 4 vol% CO_2, while ~0.3% at 100 vol% CO_2.

In conclusion, highly selective and efficient methane generation by the electroreduction of CO_2 was achieved on the Pt/C catalyst without overpotential by controlling the CO_2 concentration and potential step procedure.

Understanding Kinetic Performance of Carbon Felt Electrodes for Redox Batteries Using Individual Carbon Fibre Electrodes

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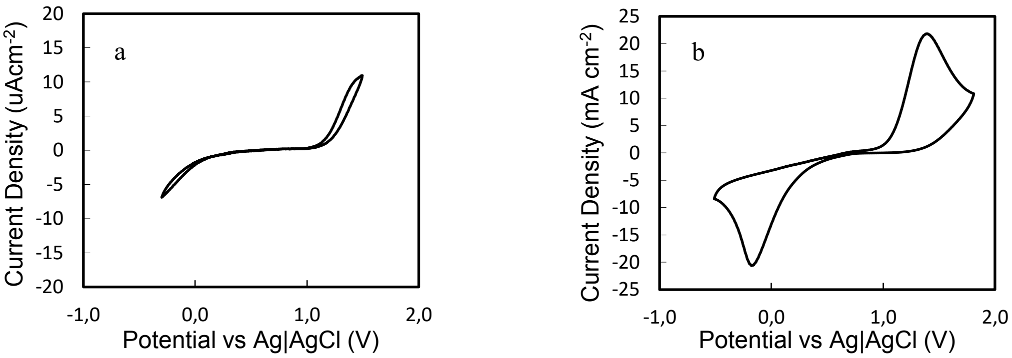
Vanadium redox flow batteries are a promising technology for providing large scale energy storage, for which performance improvements from modifying carbon felt electrodes has been studied in depth. Cyclic voltammetry (CV) results have been used to qualitatively describe kinetics on carbon felts, with reduced peak separations said to be a result of improved kinetics [1-3]. These results may be misleading, as electrode porosity and surface roughness have been shown to significantly alter CV results [4-7], thus incomplete compensation of these factors may be the cause of the wide distribution in the reported rate constants on carbon felt electrodes for vanadium redox reactions [8]. The use of individual carbon fibre (ICF) electrodes should enable greater insight into the kinetics of carbon felts, as the simple and defined geometry allows the effect of radial diffusion to be accounted for.

The effect of various oxidative treatments on the fibers was investigated using CV and XPS. Capacitance was calculated from the double layer charging observed in CV of ICF electrodes in sulfuric acid. Increases in fiber capacitance were observed for each oxidative treatment type with the greatest increase at thermally treated fibers. The ratio of carbon relative to oxygen and nitrogen on the surface was quantified using XPS, with no obvious link between capacitance and carbon ratios. The carbon fibres oxidized electrochemically in sulfuric acid had the greatest change in carbon ratios, but only a modest increase in capacitance. CV was then carried out in a vanadium solution to quantify the change in kinetic parameters of each fibre type. However, the poor kinetic activity coupled with the radial diffusion limits the usefulness of this approach.



Cyclic voltammetry of 25 mM $V^{4+/5+}$ in 0.5 M H_2SO_4, at 100 mVs^{-1}. a) Single carbon fibre, b) carbon felt.

Due to the poor kinetics of the and radial diffusion to the ICF surface, the overpotential required to observe CV peaks on single fibers was too great and therefore increasing the potential limits leads to unwanted side reactions. CV peaks were seen on using a carbon felt electrode; as the diffusion to the felt is linear not radial, the porosity of the felt likely reduces peak separation and wider potential limits did not lead to any obvious side reactions occurring. Without observing peak currents on the ICF electrodes it is difficult to accurately calculate kinetic parameters using CV. As an alternative approach to obtaining kinetic parameters, fitting equivalent circuits to electrochemical impedance data of ICF electrodes can be carried out, and the from the results the behavior of a porous carbon felt electrode can be modelled.

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In situ Structural Determination of Underpotentially Deposited Pd Monolayer on Au(111) Surface during Oxygen Reduction Reaction

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Ultrathin metal films formed on foreign metal substrates often show unique electrocatalytic activities for various multi-electron transfer reactions such as oxygen reduction reaction (ORR), hydrogen evolution reaction (HER) and carbon dioxide reduction reaction. Underpotential deposition is a powerful technique to form thin metal films on a surface of single crystal electrodes with a well-defined atomic arrangement because several metals can deposit on the foreign metal substrate at potentials substantially more positive than the reversible potential of the bulk deposition of those metals.[1,2] For example, a Pd monolayer is underpotentially deposited on a Au(111) surface and it exhibits a catalytic activity for ORR much higher than bulk Au and Pd surfaces.[3] Here, in order to clarify the reaction mechanism, atomic arrangement and electronic structure of the Pd monolayer deposited on Au(111) surface during ORR has been investigated by in situ surface x-ray scattering (SXS)[4,5] and polarization-dependent total-reflection x-ray absorption fine structure (XAFS).[6,7]

Specular and non-specular rod profiles obtained by crystal truncation rod (CTR) measurements show that Pd atoms occupy the three-fold hollow sites. According to the EXAFS oscillation at the Pd K-edge measured at s-polarization, distance of Pd-Pd bonds is estimated to be 2.88 Å which is longer than that of bulk Pd, 2.76 Å, but in good agreement with that of bulk Au, 2.88 Å. Thus, the pseudo-morphic deposition of the Pd monolayer on Au(111) surface was confirmed by in situ structural analysis of SXS and XAFS.

Interestingly, not only Pd-Au bonds but also a small contribution of Pd-O bonds were observed in the EXAFS oscillation at the Pd K-edge measured at p-polarization, suggesting the adsorption of oxygenated species such as water, hydroxide groups, oxygen or intermediate species of ORR. A peak corresponding to the super-structure was observed in the surface x-ray diffraction (SXRD) measurements. A similar peak was also observed at the Pt(111) surface during ORR and its intensity is indeed proportional to the cathodic current for ORR. Such substantial correlation between the peak intensity and current density suggests that the super-structure is attributed to ORR.

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Solid oxide electrochemical cells supported on the air electrode with large straight open pores and catalyst-coated surfaces

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This study was aimed to improve the electrochemical performance of the air electrode-supported solid oxide electrochemical cells by optimizing the pore structure and surface composition of the electrode. The $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (LSM)–8mol%Y_2O_3-stabilized ZrO_2 (YSZ) substrate with finger-like large pores and thickness of ~700 μm was formed by the phase inversion tape-casting method. The substrate was used as an air electrode support to fabricate a solid oxide electrochemical cell comprising a 13 μm thick YSZ electrolyte layer and a 12 μm thick Ni-YSZ as fuel electrode (Fig. 1). The inner surface of the LSM-YSZ electrode was coated with $Sm_{0.2}Ce_{0.8}O_{1.95-\delta}$(SDC) nanoparticles of ~40 nm in size using the impregnation method. The maximum power densities of the single cell with the SDC-modified air electrode were 286, 442 and 652 mW cm^{-2} at 700, 750 and 800°C in the fuel cell mode, respectively, while the corresponding values for the single cell with the un-modified air electrode were 71, 126 and 211 mW cm^{-2} (Fig. 2). The CO_2 electrolysis performance of the two cells was measured as well at 800°C. The modified cell showed a current density of 0.88 A cm^{-2} and a CO production rate of 6.1 mL(STP) $cm^{-2}min^{-1}$ at 1.4 V and 67 vol. % CO_2, while the corresponding values for the unmodified cell were 0.32A cm^{-2} and 2.2 mL cm^{-2} min^{-1}. The much better electrochemical performance for the modified cell is attributed to the impregnated SDC nanoparticles which effectively increased the length of the three-phase-boundaries of the air electrode and thus significantly reduced the activation polarization. It is concluded that the air electrode support formed by the phase inversion method contains large straight open pores, allowing for easy surface modification of the electrode and thereby promoting the electrochemical performance.

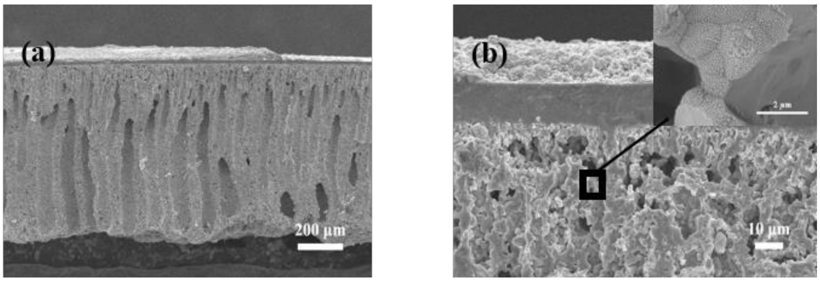

Fig. 1. (a) The cross-sectional image of the single cell supported on LSM-YSZ electrode; (b) The cross-section of the electrode-electrolyte interface, The inset shows the high-magnification SEM image of the deep region after impregnation with 15wt% SDC loading

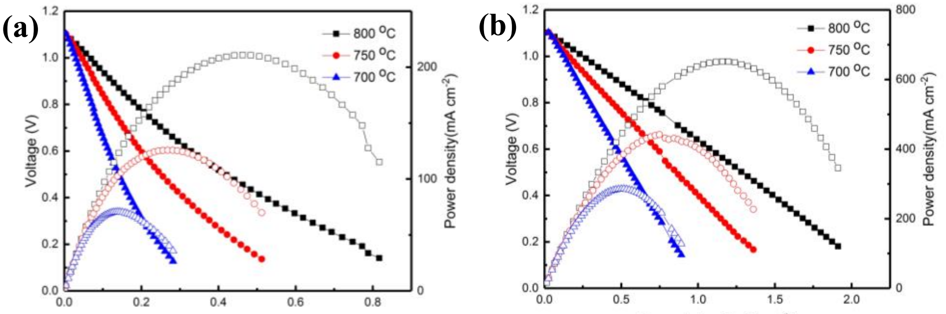

Fig. 2. Current-voltage curves of solid oxide electrochemical cell supported by LSM-YSZ electrode. *i-V* curves and corresponding powder densities of the fuel cells measured with humidified hydrogen as fuel at 800,750, and 700°C, (a) with un-modified air electrode, (b) with the SDC modified air electrode .

Acknowledgment

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Corrosion inhibition of pure aluminium by quinoline derivatives: Electrochemical and DFT approaches

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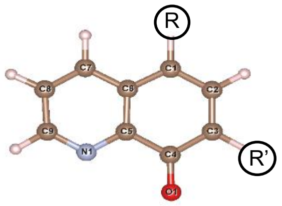
Since the beginning of the 1990s, the high toxicity associated with chromates has imposed restrictions on their use in the aeronautic industry. As a consequence, intense research efforts are being undertaken to find new environmentally friendly compounds as corrosion inhibitors of aluminium and aluminium alloys. It was shown that 8-HQ acts as an effective corrosion inhibitor for aluminium [1-3]. In a recent work [4, 5], density functional theory (DFT)-based concepts have been used to investigate the interaction mechanisms of the 8-HQ molecule, in its native form or as 8-HQ species present in solution, *i.e.* tautomer, dehydrogenated and hydrogenated species, on the Al(111) for different surface coverages. It was concluded that the native 8-HQ molecule is physisorbed and chemisorbed on the aluminium surface with similar adsorption energy. The binding of the dehydrogenated species is the strongest, followed by the tautomer molecule and the hydrogenated molecule with weaker binding. The 8-HQ and its derivatives showed covalent bonds with the Al surface and significant contribution of van der Waals interactions both at the molecule/substrate interface and between the molecules in the adsorbed organic layer.

On the other hand, it has been shown that some quinoline derivatives, such as 8-HQBr or 8-HQS are not efficient for the corrosion protection of aluminum [2, 6]. Fig. 1 shows the chemical structure of dehydrogenated quinoline derivatives.



8-HQ: R = H; R' = H
8-HQBr: R = Br; R' = Br
8-HQS: R = SO_3; R' = H

Fig. 1: Molecular structure of quinoline derivatives

The aim of the present work is to investigate, at atomic scale, the action mechanisms of quinoline derivatives on pure aluminium surfaces by using *ab initio* calculation in order to understand why the 8-HQ is an inhibitor and why the 8-HQBr and 8-HQS molecules are rather corrosion accelerators. The final goal is to correlate the theoretical approach to experimental ones (electrochemical data) in order to extract the factors which are favourable to the inhibition processes or in other words to find descriptors correlated to the inhibitor efficiency. A better understanding of the corrosion inhibition mechanisms will help to rationalize the search of new species that could provide corrosion protection close to that afforded by the chromates. Electrochemical measurements (polarisation curves and electrochemical impedance) were performed on pure aluminium (99.9999 wt. %) during immersion in aqueous solutions in the presence of the different quinoline derivatives to determine their corrosion efficiencies.

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Electrocatalytic Behavior of Single Walled Carbon Nanotubes With Alkylthio-substituted Cobalt Binuclear Phthalocyanines Towards Oxidation of 4-chlorophenols

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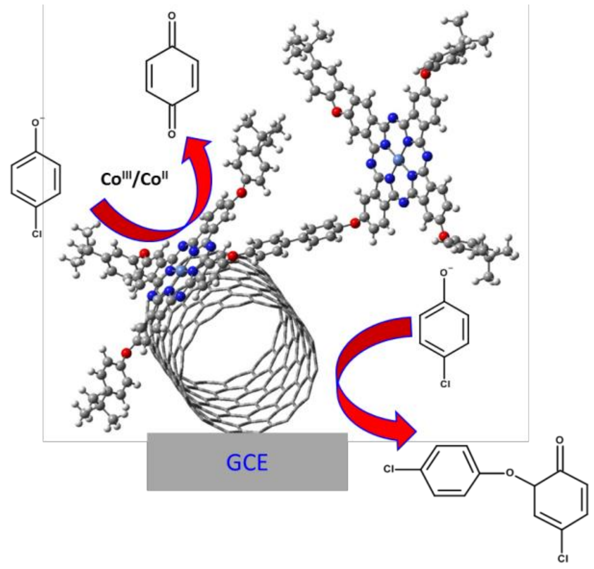
This work describes the adsorption of synthesized cobalt mono (CoPc) and binuclear phthalocyanines (CoBiPc) with single walled carbon nanotubes (SWCNT) to form SWCNT-CoPc or SWCNT-CoBiPc as non-covalent conjugates onto glassy carbon electrodes (GCE). The cobalt complexes and their SWCNT-conjugate-modified electrodes were studied for their electrocatalytic oxidation towards 4-chlorophenol. All modified electrodes showed improved catalytic current and stability towards the detection of 4-chlorophenol. The best activity was observed for the SWCNT-CoBiPc2 system in terms of current response and the SWCNT-CoBiPc1 system in terms of resistance to electrode fouling.



Electrocatalytic oxidation of 4-chlorophenol on SWCNT-CoBiPc in basic media

Artificial Enantiopure Inherently Chiral Membranes: Enantiodiscrimination Trough a New "Ion-Selective Like" Setup

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High-efficiency resolution technology is fundamental for scaling-up the separation of enantiomerically pure substances. Membrane technology fulfils this requisite, in fact it is characterized by *i)* high efficiency, *ii)* low energy usage, *iii)* simplicity, *iv)* convenience for up- and/or down-scaling, and *v)* continuous operability. Membrane-based chiral resolution can be achieved using either enantioselective or non-enantioselective membranes. Enantioselective membranes can be used for chiral separation of enantiomers because they contain chiral recognition sites. In this frame we have discovered that the electrooligomerization, in acetonitrile as solvent, for 108 deposition cycles, on an ITO (indium-tin oxide) electrode support, of our inherently chiral benchmark monomer constituted by an atropisomeric core (a bibenzothiophene, Figure 1), leads to self-standing racemic or enantiopure membranes. These ones were obtained by simply peeling off the solid deposit from the ITO immersed in water after the electrodeposition in acetonitrile.

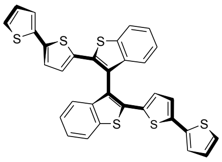

Figure 1

We have then characterized the inherently chiral membranes by a multivariate technique approach by means of EIS (electrochemical impedance spectroscopy used for conductivity measurements), SEM (scanning electron microscopy), BET (pore size distribution), AFM (atomic force microscopy for morphology, roughness and thickness) and TGA (chemical-physical properties) comparing the racemic *vs* enantiopure deposit properties. Considering *i)* the outstanding enantioselection ability achieved with our both inherently chiral electrode surfaces and media [1-2] and *ii)* the perfectly specular CD spectra displayed by the two membrane enantiomers, we have decided to implement enantiopure inherently chiral membranes in a "ion-selective like" set-up in order to study their enantiorecognition capability (Figure 2).

Figure 2

First of all, we have verified the potential difference was read correctly through the membrane, in fact a necessary precondition for developing an ion-selective electrode method is that the setup and, as a consequence, artificial chiral membranes allow correct determinations of transmembrane potential. After that we have tested enantiopure membranes in the presence of chiral charged species (in all configurations for both membranes and internal/external electrode solutions) for determining their enantioselective capability. Preliminary results are very promising and encourage us to perform the scaling up of the membrane electrosynthesis to be used for industrial scopes and to extend the study to other probe useful in the analytical and pharmaceutical field.

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Anion Exchange Membrane Fuel Cells: Enhanced alkaline hydrogen oxidation activity of platinum-free catalysts

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Anion exchange membrane fuel cells (AEMFCs) offer several important advantages with respect to proton exchange membrane fuel cells (PEMFCs), which can contribute to overcoming the high cost of fuel cell systems that has largely slowed large-scale implementation. The poor kinetics of the hydrogen oxidation reaction (HOR) and other limitations in performance such as the instability of membranes have stalled AEMFC development. Replacing Pt at the anode with a cheaper catalyst that has also enhanced activity for the HOR is a key objective for those working in the field of AMFCs. We recently reported a new class of HOR catalyst based on Pd nanoparticles supported on carbon and CeO_2 that allowed us to achieve 0.5 W cm^{-2} peak power density in a Pt-free AEMFC.[1,2] In this presentation, we report further enhanced HOR kinetics due to a maximized Pd-CeO_2 contact between these two phases on the nanoscale. To date, this is the only alternative non Pt HOR catalyst yet reported that matches state of the art fuel cell performances (> 1 W cm^{-2}). We present here a reproducible synthesis (on the gram scale) that consists of the addition of CeO_2 to carbon using an organometallic precursor followed by Pd deposition. With this catalyst more than 2 W cm^{-2} peak power density in fuel cell testing is achieved (Figure 1).

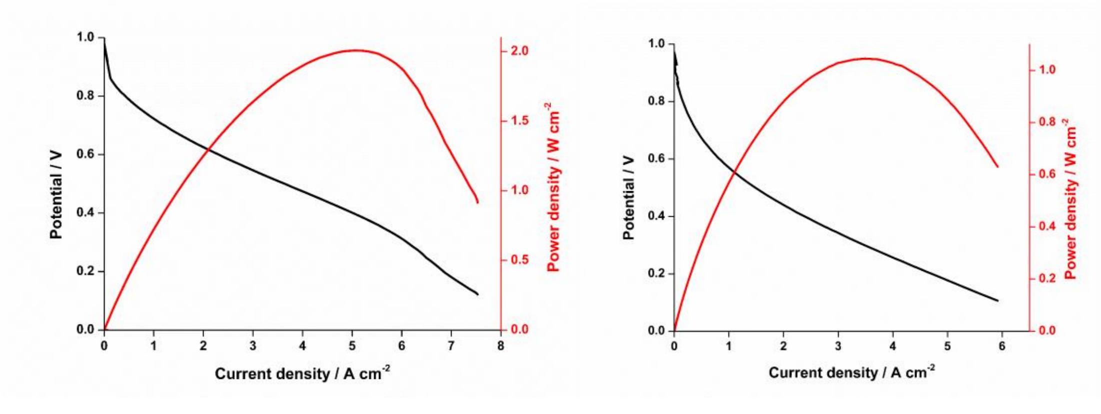

Figure 1: Power curves of AEMFCs equipped with a Pd/C-CeO_2 anode (0.3 mg cm^{-2}). (left) With a Pt/C cathode and (right) an Ag/C cathode.

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Eletrochemiluminescence Immunosensor for Heart Disease Biomarker Copeptin Based on Luminescent Immuno-Gold Nanoassemblies

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Acute myocardial infarction (AMI) is one of the most vital disease. Although great effort has been increasingly deployed in the region of AMI diagnosis and therapy, death rate has not significantly decreased yet. Thus, early diagnosis of AMI is greatly needed to ensure patients receive immediate and effective treatment. Recently, copeptin was found to be a stable and sensitive surrogate marker for early diagnosis and rule-out of AMI. However, to date, the detection of copeptin mainly depends on immunoassays based on labeling technique, such as enzyme-linked immunosorbent assay, chemiluminescence (CL) sandwich immunoassays. These methods need complicated labeling and purification steps, which are tedious and time-consuming. Herein, a coreactant-free and label-free eletrochemiluminescence (ECL) immunosensor was established for the determination of copeptin based on luminescent immuno-gold nanoassemblies consisting of Cu^{2+}/cysteine complexes and N-(aminobutyl)-N-(ethylisoluminol) (ABEI) functionalized gold nanoparticles combined with chitosan and immuno-gold nanoparticles prepared by connecting copeptin antibody with trisodium citrate stabilized gold nanoparticles. The luminescent immuno-gold nanoassemblies on the surface of an ITO electrode exhibited excellent ECL property without any coreactant. In the presence of copeptin, the ECL signal decreased due to inhibition of the electron transfer by peptides. According to the decreased ECL intensity, the concentration of copeptin could be determined in range of 2.0×10^{-14}-1.0×10^{-11} mol/L with extremely low detection limit of 5.18×10^{-15} mol/L, which was 2-3 orders of magnitude lower than that of obtained by commercial ELISA kit and CL sandwich immunosensor. Moreover, the proposed immunosensor does not need any coreactant, and avoids complicated labeling and purification procedure. Besides, the ECL immunosensor is rapid, specific and low-cost, which can be used for the determination of copeptin in human serum samples. This work reveals that the proposed luminescent immuno-gold nanoassemblies are ideal nanointerfaces for coreactant-free 1and label-free immunoassays. The proposed strategy may be used for the determination of other antigens if corresponding antibodies are available.

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PdCu Alloy Nanoparticles Supported on CeO_2 Nanorods: Enhanced Electrocatalytic Activity by Synergy of PdO and Oxygen Vacancy

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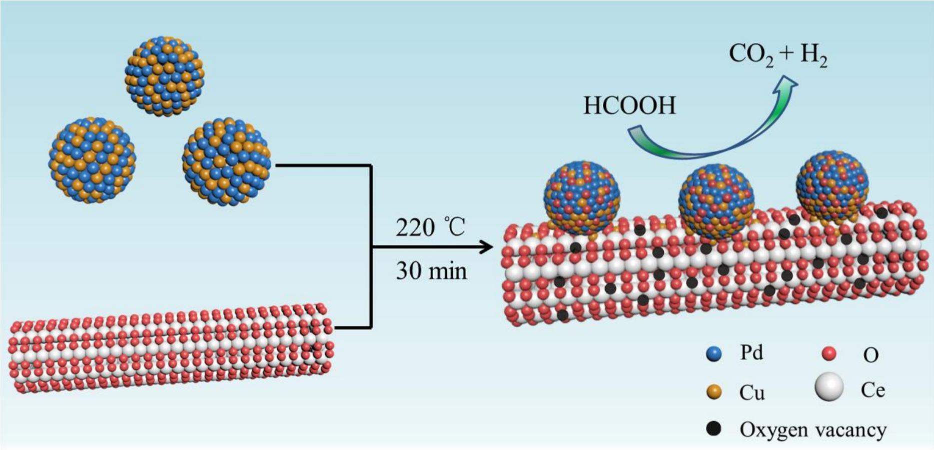
Metal oxides have been widely studied as promoter of catalytic performance of metal catalysts through the strong metal-support interactions, while the mechanism behind which is still debating. [1] Here we prepared a series of PdCu nanoparticles of different sizes and further loaded on CeO_2 nanorods. The interaction between PdCu and CeO_2 nanorods is discussed in terms of lattice strain, electronic structure, PdO, CO adsorption energy and surface defects, which are characterized by HRTEM, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and electrochemical CO stripping. It is observed that coupling of PdCu alloy nanoparticles with CeO_2 nanorods induces compressive strain, down-shift of the *d*-band center, reduced CO binding energy and augmentation of PdO content for PdCu nanoparticles. In addition, the smaller PdCu nanoparticles even induce more oxygen vacancy on CeO_2 nanorods. Based on comprehensive analyses, it is concluded that the synergy of enhanced PdO and oxygen vacancy remarkably promotes the catalytic performance of PdCu towards electrooxidation of formic acid, while electrooxidation of methanol on PdCu is promoted only by the oxygen vacancy.



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The influence of electrolyte phase transition on the thermal runaway in lithium ion batteries

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The omnipresence of lithium ion batteries in mobile devices and electric vehicles also gave rise to concerns regarding their safety. A well-known safety hazard is the thermal runaway, a cascade of exothermic reactions, which already led to high-profile images of burning electric cars in the media. Coupling of experiments and mathematical battery models allows insight into the underlying chemical processes. Due to the complexity and variety of the processes in the thermal runaway it was not yet possible to include all occurring effects in one model. The majority of existing models focuses on the propagation of heat through the battery or battery stack. But the influence of phase transitions of the electrolyte on the thermal runaway is often neglected or modeled via substitute reactions [1].

For the sake of thermodynamic consistency a new model was developed that incorporates phase equilibrium relations for the electrolyte components into a basis system. The model focuses on mass balances, reaction kinetics and the thermodynamic behavior of battery components while neglecting the spatial distribution of heat and concentrations throughout the cell. This focus allowed to rise the complexity in respect to occurring reactions and participating species. Thus, the consecutive and parallel nature of the underlying reaction network, see Fig. 1a), could be investigated. The necessity of modeling the phase transitions in respect to the thermal runaway could be shown by simulating an Accelerated Rate Calorimetry (ARC) measurement with and without considering the phase transition. Exemplary results are shown in Fig. 1b). The developed model further allows the analysis of the influence of different electrolyte compositions on the thermal runaway of lithium ion batteries as well as in depth insight into the immanent chemical processes.

To conclude, a model was developed which focuses on the mass balances and thermodynamic behavior of different species within a battery cell and phase transitions of the electrolyte. This novel model is the first of its kinds which is able to reproduce an ARC measurement thermodynamically consistent.

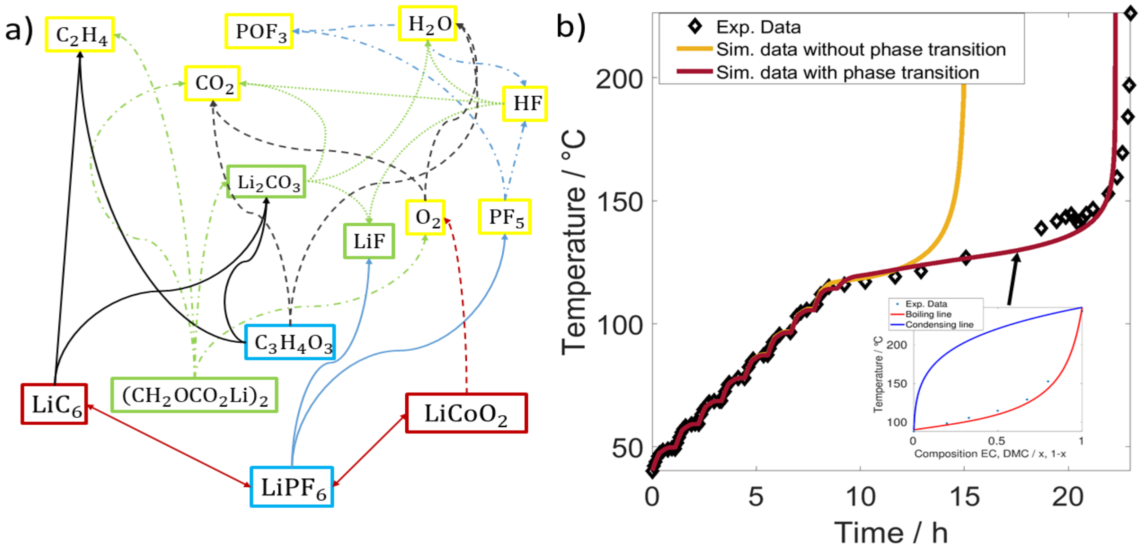

Figure 1: a) Modeled reaction network. b) Simulated ARC measurements with and without consideration of the phase transition model. Experimental data was taken from [2, 3].

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Voltammetry of Imino-β-diketones

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β-diketones ($R^1COCHC(OH)R^2$), are bidentate ligands with two O donor atoms (O,O-BID), that can coordinate to many metals such as Cr,[1] Mn,[2] Fe[3] and Rh.[4] This coordination property is used in analytical chemistry in the solvent extraction of metals.[5] The various groups R^1 and R^2 substituted on the bidentate, chelating β-diketonato ligand, influence the activity and effectiveness of the β-diketone towards metal coordination. Cyclic voltammetry is an experimental tool to determine the reactivity of different ligands towards oxidation and reduction. The reduction potential of a large series of β-diketones from literature, ranges from -1.05 – 2.14 V *vs* FcH/FcH^+.[6] By changing one O donor atom in this series of β-diketone $R^1COCHC(OH)R^2$ ligands to N (N,O-BID), we found that the reduction potential of the resulting imino-β-diketones $R^1COCHC(NHR)R^2$ was lowered substantially, to as low as -3.10 V *vs* FcH/FcH^+.[7] In this study, the electrochemical properties of a series of imino-β-diketones of the type $R^1COCHC(NHR)R^2$, are presented, as measured both by cyclic voltammetry and calculated by density functional theory (DFT) methods. Results show that the reduction potential is influenced by both the amino substituent R, as well as by the type of substituents R^1 and R^2, see Figure 1 (a). Reduction potential generally increases with an increasing amount of phenyl groups substituted on these ligands. The results also indicate that compounds containing more electron withdrawing groups on the R^2 or R position, tend to have a higher reduction potential. Calculated DFT energies, such as the energy of the lowest unoccupied orbital (E_{LUMO}) and the electron affinity (EA) of the ligands, relate linearly to the experimental reduction potential, see Figure 1 (b).

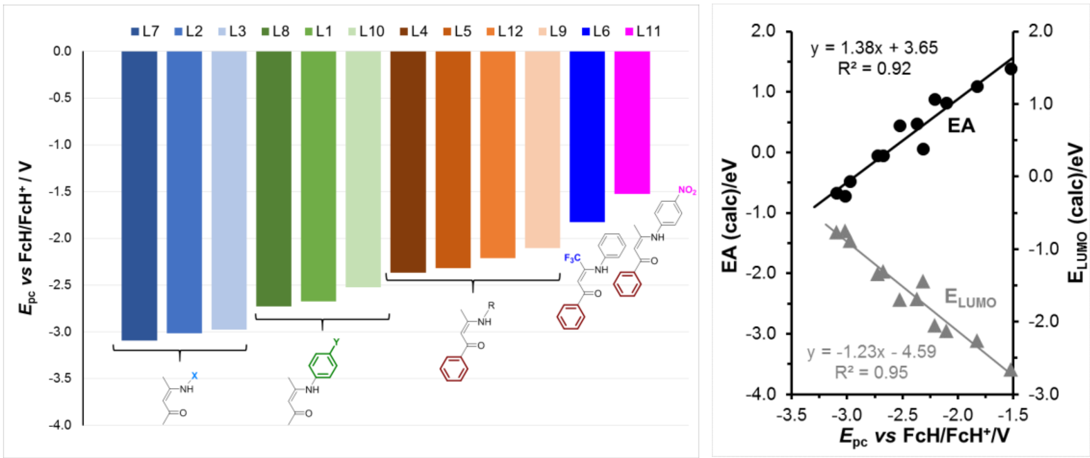

Figure 1. (a) Graph showing the increase (to less negative values) from left to right, in the reduction potential (E_{pc} shown on the y-axis) of substituted imino-β-diketones, due to the increasing amount of phenyl groups attached to the ligand. X = H (L2), CH_2Ph (L3), $CH(CH_3)_2$ (L7), Y = H (L1), CF_3 (L10), ^{t}Bu (L8), R = H (L5), Ph (L4), 3,5-di-Cl-Ph (L12), 2-CF_3-4-Cl-Ph (L9). (b) Linear relationships obtained between the DFT calculated energy of the lowest unoccupied orbital (E_{LUMO}) as well as the electron affinity (EA) of the ligands, and the experimental reduction potential (E_{pc}).

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Enhancing bioremediation efficiency and power generation in Microbial Fuel Cells through exogenous addition of biological and chemical surfactants.

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Microbial Fuel cells (MFCs) represent an energy-neutral means of treating wastewaters. However, common contaminants such as surfactants, which are found widely throughout various waste streams, have been reported to significantly influence MFC performance (Wen *et al*., 2011; Liu *et al*., 2012). The antimicrobial activities of surfactants might prevent biodegradation efficiency of these devices, preventing reuse and recycling of water containing these substances (Van Hamme *et al*., 2006; and Singh *et al*., 2007).

The current study aimed to investigate the influence of exogenous addition of various types of common surfactant classes to MFCs on power generation, and bioremediation efficiencies. The aim was to identify surfactants that enhance bioremediation and those that could function as a substrate / feedstock for MFCs.

An MFC inoculated with *Enterobacter cloacae* was constructed (Mshoperi *et al.*, 2014). The influence of varying concentrations of non-ionic, anionic and cationic surfactants on power generation at MFCs and subsequent bioremediation was investigated by operating the MFCs with surfactants added to the anode chamber. Furthermore, their influence on bacterial growth, chemical oxygen demand (COD), nutrient usage efficiency, MFC coulombic efficiency (CE) and voltammetric profile of bacteria-cultured electrodes was also investigated.

The electrochemical results demonstrated that, relative to the control, non-ionic surfactants generally increased the peak power densities at concentrations higher than or equal to the surfactants' critical micelle concentration (CMC). Furthermore, both the anionic and cationic surfactants, at concentrations lower than the surfactants' CMC, increased the peak power densities. Non-ionic surfactants increased bacterial proliferation and both anionic and cationic surfactants decreased bacterial proliferation, indicating that a concentration-dependent balance between bacterial proliferation and power generation enhancement may still benefit MFCs for these surfactant classes.

This study paves the way towards understanding and mitigating the toxic effects to the anodic biofilm caused by this class of common wastewater pollutants, to improve the application of MFCs in wastewater treatment.

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TEMPO and RTILs for the sustainable development of TEMPO-mediated Alcohol Electrooxidation

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Carbonyl compounds are fundamentally important in organic synthesis, due to the wide range of applications of these products as building blocks for many pharmaceuticals and fine-chemicals. Traditional methods for alcohol oxidations involve the use of stoichiometric inorganic or organic oxidants and hazardous reagents, resulting in atom-inefficient and unsustainable processes [1]. 2,2,6,6,-tetramethylpiperidine-1-oxyl (TEMPO) is a metal-free, sustainable alternative to traditional reagent for the oxidation of primary and secondary alcohols to carbonyl compounds. The catalytically-active oxoammonium species (TEMPO$^+$) can be formed using stoichiometric or catalytic amounts of secondary oxidants, or electrochemically [2]. The electrochemical route is attractive as it replaces reagents with electric current, where reagent waste along with difficult work-up and separation processes can be eliminated [3].

However, difficulties associated with the use of volatile organic solvent or water combined with the necessity of adding supporting electrolytes are the most frequently cited reasons for the general lack of interest in commercial-scale bulk electrosynthesis. Organic solvents are electrochemically unstable posing risks of explosions and generating toxic gases and are rarely recycled, while the supporting electrolytes present difficult separation and recovery processes [4].

In the context of these challenges, we have used Room Temperature Ionic Liquids (RTILs) which are used as both the solvent and electrolyte in the electrochemical TEMPO-mediated alcohol oxidations. In addition to the advantages of using RTILs in electrosynthetic processes due to their inherent conductivity, non-volatility and electrochemical stability, we have observed through voltammetry studies that the reactivity and selectivity of TEMPO in the electrooxidation of alcohols can be tuned via the design of the RTIL media, providing a facile approach for boosting the oxidation performance of TEMPO. In this talk we also report the use of novel bi-redox RTILs, which introduces paired electrosynthesis and eliminates the need for a proton sink in the TEMPO-mediated alcohol electrooxidations, see figure 1.

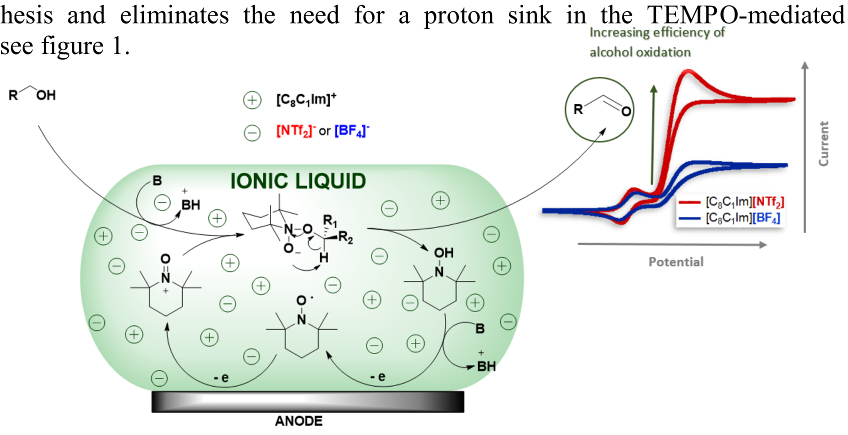

Figure 1: Comparing two RTILs for the TEMPO-mediated alcohol electro-oxidations, where $[NTf_2]^-$ based RTILs promotes faster reaction kinetics than $[BF_4]^-$ based RTILs.

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Multi-principal element high-entropy alloys as universal and tailorable electrocatalysts – Fundamentals and application

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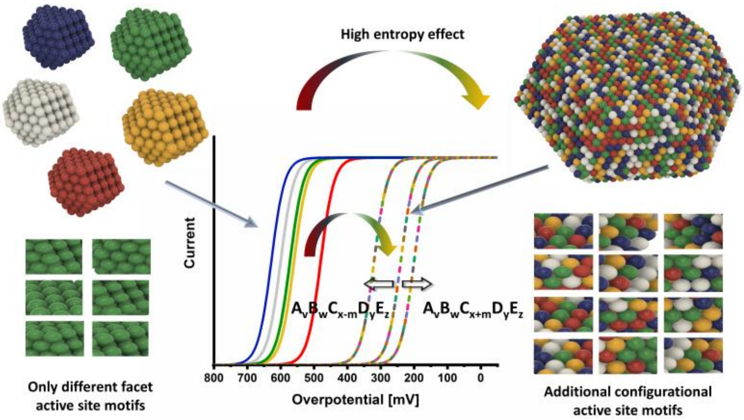

The activity of an electrocatalyst is assumed to be correlated with its position in Sabatier principle type volcano plots, which is mainly governed by the principal element. While the design of highly active catalysts often requires noble metals, we pursued a new strategy to replace scarce materials by abundant transition metals via utilization of multi-principal-element-alloy (MPEA) catalysts. For alloying more than 4 elements, an unusual thermodynamically stable state in a high-entropy-effect induced single solid solution phase was discovered. This state was already shown to be the basis for special mechanical properties.[1] In our studies regarding their electrocatalytic activity towards the electrochemical oxygen reduction reaction (ORR), we observed that the homogeneous distribution within these MPEAs leads to unique interactions of multiple elements to form previously unknown highly active catalytic sites. These are not defined and limited by the properties of the single elements any more. Exploiting that particular feature at the nanoscale with isolated single NPs, we discovered a noble-metal free system consisting of CrMnFeCoNi, which shows intrinsic activity for the ORR in alkaline solution comparable to the benchmark catalyst Pt.[2] Tailoring of its composition led to further activity enhancement, which indicates the enormous potential in fine-tuning of properties by directed optimization of both, configuration and composition.

Furthermore, we explored the general fundamental concepts accompanying this novel catalyst class such as discussing potentials, which are enabled by the presence of many different active sites next to each other and rationalize the uncommon electrochemical behavior.

In this contribution, we provide conceptual information about the unique capabilities and limitations of this catalyst class as well as experimental proof of the concepts in an applied reaction utilizing the ORR as a highly important model system.

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Nanoscale Studies Solve Macroscopic Problems: De - and Reactivation of Oxygen Depolarized Cathodes Under Process Conditions

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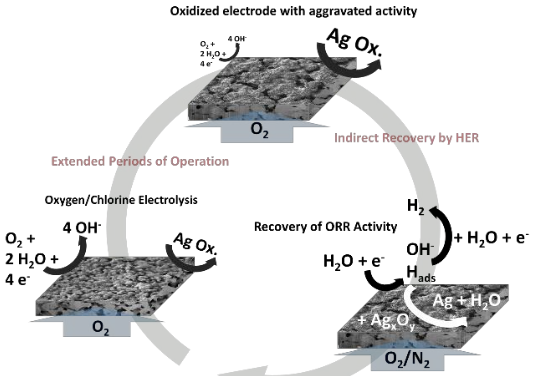

Figure 1: Proposed recycling of an ODC with diminished electrocatalytic activity.

Recent efforts to minimize energy consumption in the modern chlor-alkali process include the utilization of gas diffusion electrodes (GDE), the so-called oxygen depolarized cathodes (ODC). Conventionally, chlorine production is realized by electrolysis of brine in membrane-separated alkaline electrolyzers under anodic evolution of Cl_2 and cathodic generation of H_2, respectively. Exploiting the oxygen reduction reaction (ORR) by using ODCs as a substitute for the cathodic hydrogen evolution reaction (HER) enables electrical energy savings of up to 30%. Industrial ODC-ORR catalysis is mediated by a microporous Ag nanoparticle (AgNP)/PTFE structure operating in 10 M NaOH at temperatures above 80 °C. The availability of O_2 can be enhanced by dosage of gaseous O_2 to the backside of the GDE, increasing achievable current densities. The reaction is believed to proceed in significant rates only at the triple-phase boundary between solid catalyst, liquid electrolyte and gaseous O_2.

However, single AgNP experiments revealed a loss of catalytic activity towards the ORR upon a single O_2 dosage to the AgNP under study.[1] We rationalized the activity deterioration with the formation of surface oxides (Ag_2O) and furthermore explored conditions to recover the catalysts initial activity, seemingly due to indirect involvement of the HER. A similar loss of activity occurs in industrially applicable ODCs and hence we transferred the basic concept of catalyst regeneration from the nanoscale to macro-scaled ODCs (cm^2). That allowed for the identification of the species formed on the surface and in the pores during deactivation utilizing a variety of analytical tools such as X-ray photoelectron spectroscopy (XPS), Raman spectroscopy as well as scanning electron microscopy (SEM) combined with focused ion beam milling (FIB). The recovery is presumably achieved by a combination of the highly reductive potentials as well as the formed "nascent" hydrogen, accounting for additional reductive driving force in the system. This study represents an example, in which knowledge obtained in nanometric experiments facilitates solving industrial challenges.[2]

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Formation of $Ni_xP@NiO_x$ Core-Shell Heterostructures on Nickel Phosphide Particles for Oxygen Evolution Reaction – a Welcome Blessing or an Unavoidable Curse?

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Enhancement of electrocatalytic water splitting efficiency requires the design of novel catalyst materials that do not only provide high activity and stability but are also ideally composed of earth-abundant, inexpensive elements. In this context, targeted catalyst development can only be based on critical reassessment of existing catalysts, precise understanding of their activity's origin and consequent knowledge transfer to novel systems.

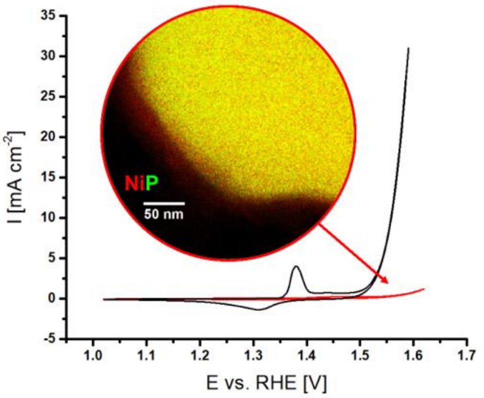

Figure 1. Electrocatalytic performance of pristine NiP sample (black) and $Ni_xP@NiO_X$ core-shell structure after 168h in 0.1 M KOH at 80 °C (red) and corresponding EDX map.

In recent years, nickel phosphides have received broad attention due to their tremendous performance as Janus-type particles for overall water splitting.[1] To date, the exact role of the guest atom within these materials remains disputable. We hypothesise, that guest-atom-induced changes of lattice parameters are a crucial factor for enhanced activity. Yet, the formation of a $Ni_xP@NiO_x$ core-shell structure upon electrochemical catalyst activation is widely considered a major contributor to their outstanding oxygen evolution performance.[2] The present study contributes to the understanding of the underlying mechanism for these structural changes and elucidates the role of phosphorous against the background of nickel phosphide's enhanced activity. For this purpose, nickel phosphide was subjected to highly alkaline conditions (1 M KOH) at industrially relevant temperatures (80 °C) for different durations (1 h to 168 h) without the presence of electrical bias.

Implementing X-ray photoelectron spectroscopy (XPS), inductively coupled plasma mass spectrometry (ICP-MS) as well as scanning and transmission electron microscopy (SEM and TEM), we observe continuous chemical depletion of phosphorous from the particles' shell via soluble phosphate species. Simultaneously a nickel oxide shell is formed, which ultimately leads to analogous core-shell structures without the influence of any electrical bias. Surprisingly, correlation with electrocatalytic performance reveals, that the activity of these heterostructures is drastically diminished in spite of the structural transformations. These observations strongly suggest that the formation of a $Ni_xP@NiO_x$ core-shell structure cannot be the sole reason for nickel phosphide's remarkable catalytic performance. In turn, these results emphasize the role of phosphorous' presence and imply that a complex interplay of competing processes forms the basis for nickel phosphide's excellent performance.

Furthermore, we also demonstrate how the obtained knowledge can be used in order to develop future strategies for the improvement and design of novel catalyst systems.

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The Specific Detection of Histamine by an Impedimetric Aptasensor

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Oligonucleotide aptamers, laboratory-generated binding biomolecules, are extensively studied for their role as biorecognition agents in biosensors. The biogenic amine histamine presents a unique opportunity to study the generation of novel aptamers and their subsequent sensing applications. Though the molecule is responsible for a multitude of health complications, its direct detection by spectrophotometric [1] or electrochemical [2,3] means is severely limited. Even the most commonly-reported method for histamine assaying, derivatization using *ortho*-phthalaldehyde and subsequent fluorimetry [4], requires sample pretreatment and is prone to nonspecific signal generation by other amine compounds. Consequently, an alternative means of detecting histamine is sought after in biomedical, pharmaceutical, and food industries.

In this work, the conditioning and selection of DNA aptamers through the Systematic Evolution of Ligands by Exponential Enrichment (SELEX) yielded prospective candidates with high specificity towards histamine. SELEX resulted in an enrichment of thymine-rich candidates and, in certain group exemplars, promising common motifs were found within the stem and loops of the aptamer secondary structures.

EIS has been identified as having several beneficial characteristics towards the development of a deployable small molecule aptasensor [6, 7]. The low reagent use and cost, high sensitivity, and rapid analysis made it a promising method by which the novel aptamers were screened and their binding ability to the target molecule compared. Additionally, as EIS is able to determine the electrostatic changes on the surface of the electrode caused by conformational change of the aptamer during binding, it was not limited by the minimal molecular mass of the target.

After screening of the sequences, a suitable aptamer was identified. A layer-by layer characterization of the prototype aptasensors was conducted and the target specificity of the aptasensor was determined against histamine and other small molecule analogues. Preliminary results indicated that the impedimetric aptasensor was highly specific towards histamine and could detect the unmodified target under physiological conditions at concentrations greater than 5 mM.

The use of an impedimetric-based aptasensor demonstrated a favourable perspective for the specific detection of histamine under physiological conditions, without the need for further chemical modification of the target.

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Up-scaled, Single-Chambered, Photosynthetic Microbial Fuel Cells for *In Situ* Nutrient and Metal Remediation in Waste Water Streams

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The development of sustainable methods of wastewater treatment is of paramount importance, especially under adverse conditions. These conditions are frequently partnered with heavy metal pollution, which increases treatment complexity.

The aim of the study was to develop a pilot-scale, single-chambered microbial fuel cell (scMFC), capable of generating usable power through various bioelectrochemical pathways. The pathways involved were specifically aimed at nutrient remediation and heavy metal reclamation in niche microbial environments.

The reactor was manufactured by modifying various glass apparatus, yielding a novel 3 L volume scMFC. The reactor was comprised of a single activated carbon (AC) anode and two separate AC cathodes, with adjusted modifications according to Mshoperi *et al.,* 2014. The reactor was operated in both continuous flow and batch mode using heavy metal doped synthetic wastewater (SWW), and it was inoculated with both bacteria and microalgae.

Preliminary analyses highlighted the application of algae for the removal of silver metal salts. Operation at industrially-relevant concentrations of $AgNO_3$ (10 mg/L) resulted in toxicity to the algae, decreasing the cell density from $6.35 \pm 3.07 \times 10^5$ to $3.85 \pm 1.89 \times 10^5$ cells/mL. SEM analyses indicated biosorption of metal into algal cell walls. Voltammetric analyses of electrodes confirmed cathodic deposition of metals onto the electrode surface caused by operation conditions produced within the scMFCs.

The ability of microalgae to act as both dioxygen producers and as electron acceptors make them viable cathodic biocatalysts; this is coupled with their ability for both biosorption and bioaccumulation of heavy metals. Microalgae functioning in conjunction with bacteria in photosynthetic MFCs can remove nutrients and metals from waste water while producing power generating conditions. The research highlights the feasibility of multifunctional tools for sustainable development in water treatment, renewable resources and energy.

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Electroporation Effects on Mediated Amperometry at Yeast-Modified Electrodes

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Budding yeast (*Saccharomyces cerevisiae*) is one of the most well-studied and understood eukaryotic organisms. Yeast cells could be used for whole-cell bioprocesses such as biocatalysis and recombinant protein fermentation, but natural barrier functions of the cell wall and cell membrane often retards entry of substrates and release of products. One of the possible techniques which could be used to improve permeability for target molecules is pulsed electric field (PEF), yet there is still a lack of sufficient data related to the effects of PEF on yeast cells especially in combination with whole-cell bioprocesses.

In this study we modified electrodes with whole yeast cells to detect electroporation effects. For the analysis, PEF-treated cells were immobilized on carbon paste electrodes which were then immersed into solution with potassium ferricyanide or menadione acting as mediators and producing measurable currents through oxidizing at electrode surface. Menadione-mediated amperometry was used for measurement of redox activity inside the yeast cells, while ferricyanide currents from amperometric sensor for lactic acid reflected membrane permeability (Fig 1.). Viability of cells was evaluated by counting colony-forming units. Leakage of intracellular compounds was evaluated by measuring fluorescence of supernatant or staining it with Ellman's reagent. Cells were exposed to single square shaped electric field pulses with pulse duration τ = 300 µs and electric field strengths (E) up to 16 kV/cm.

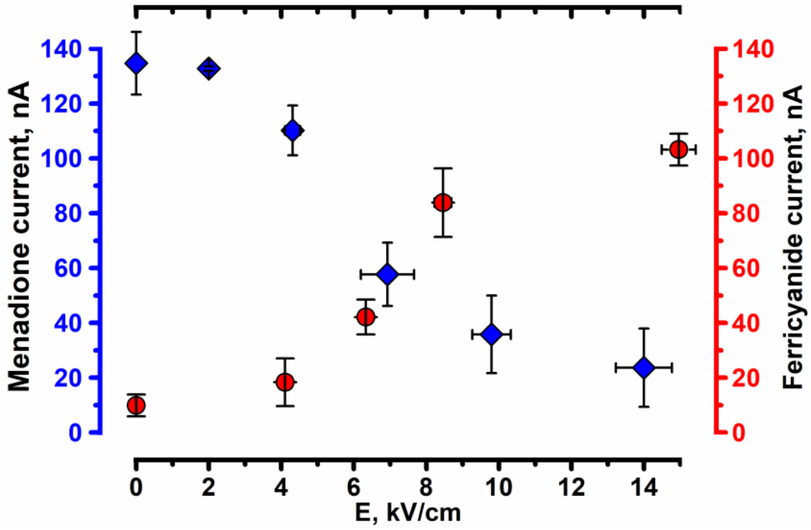

Fig 1. Effect of electric field strength on current responses of yeast-modified electrode. 67 µM menadione at an operating potential 0.3 V in phosphate buffer at pH 6.5. 0.2 mM lactic acid at yeast-modified electrodes at an operating potential 0.3 V in phosphate buffer at pH 7.3 containing 0.5 mM mediator $K_3[Fe(CN)_6]$.

We showed that after exposure to PEF, permeability of cell membrane/wall increased while viability decreased. Yeast-modified electrode responses to lactic acid and menadione were dependent on PEF exposure. Currents obtained from amperometric biosensor with treated cells increased from 9.9 ± 4 nA (E = 0 kV/cm) up to 103.2 ± 5.8 nA (E = 15 ± 0.5 kV/cm). PEF treated yeast cells also showed lower redox activity which decreased (from 135 ± 11 nA to 24 ± 14 nA) with raise in electric field strength (0 kV/cm up to 14 ± 0.8 kV/cm). Decrease of menadione-mediated current showed similar pattern with viability. Viability of yeast cells decreased (from 100 % up to 1.5 ± 0.5 %) with raise in electric field strength (E = 9.6 kV/cm). We conclude that amperometric measurements can be effectively used for investigation of various cellular responses after PEF treatment.

In situ Infrared and DFT Studies on Adsorption and Reactivity Processes at Metal Electrodes

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In situ vibrational spectroscopies have proved to be useful tools for the characterization of processes at metal electrode surfaces [1]. Among these techniques, infrared spectroscopy has been extensively used for the study of potential-dependent adsorption/desorption processes as well as that of faradaic reactions. Whereas external-reflection experiments (IRRAS, InfraRed Reflection Absorption Spectroscopy) have allowed the spectroscopic monitoring of electrode processes at well-defined (single crystal) metal surfaces, the use of nanostructured metal thin films in internal-reflection experiments (ATR-SEIRAS, Surface Enhanced Infrared Reflection Absorption Spectroscopy under Attenuated Total Reflection conditions) provides enhanced sensitivity and additional information on metal-solvent and adsorbate-solvent interactions [2]. Moreover, the use of nanostructured surfaces allows in some cases the recording of complementary ATR-SEIRAS and SERS (Surface Enhanced Raman Spectroscopy) spectra for a given metal/solution interface [3]. In this contribution, we present recent IRRAS and ATR-SEIRAS results on adsorption and reactivity processes at metal electrodes, including, as model processes, the adsorption of cyanate anion at gold [4a] and silver electrodes, its surface isomerization to cyanuric acid [4b,c] as well as the adsorption of oxocarbons (squaric [5] and croconic acids) at gold electrodes. These results, interpreted on the basis of DFT (Density Functional Theory) calculations for the obtention of optimized geometries and assignment of observed bands in the experimental infrared spectra, have shed some more light on some topics as the roles of adsorption site geometries, the molecular structure of adsorbates and the effect of coverage on the frequencies of collective vibrational modes.

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Synthesis of Nanostructured Materials for Sustainable Energy Storage

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Abstract. The *true* costs of fossil fuels to each of us individually or to the whole society aren't represented in their market price; i.e. money paid out of pocket for gasoline, natural gas, and oil. Because of the serious impacts of fossil fuels to our health and natural environment, technological advancement in the efficient storage of the energy obtained from renewable sources has become an essential need. In this presentation, I will sum up the steps that my research group has taken over the past few years toward the development of new approaches for supercapacitive energy storage. In one approach, we prepared highly interconnected three-dimensional graphene architectures by laser-scribing[1] and flash-conversion[2] methods, and fabricated high-performance and flexible graphene-based supercapacitors. Inspired from solid-state pseudocapacitive materials, we utilized solution-phase redox-active species to supply extra-energy[3]. Furthermore, we utilized a regenerative mechanism via a catalytic interaction at the electrode-electrolyte interface, as a new paradigm to fabricate a high-performance energy storage device[4]. In another approach, we grafted redox active species on the reduced graphene oxide surface via non-covalent π-π stacking interaction to mitigate self-discharge of the supercapacitors and facilitate progress toward a sustainable energy future[5]. We also have worked on storing the energy harvested from sun in both chemical (water splitting) and electrochemical (supercapacitor) form[6]. More recently, we attempted to stablish standard performance metrics for electrochemical energy storage systems to realize the true promise as well as the limitations of these fast-moving technologies[7]. I wish our activities will contribute to addressing our global energy challenge and provide glimmers of hope towards a more sustainable energy future.

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Influence of additives on the dye regeneration in ZnO-based dye-sensitized solar cells (DSSCs) investigated with scanning electrochemical microscopy (SECM)

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In the last decades, dye-sensitized solar cells (DSSCs) gained attention as a complement to other common green energy sources. This inexpensive solar-to-electrical energy conversion technology involves a redox shuttle as regenerator of the photo-oxidized dye adsorbed on the photoanode. The earth abundant wide band gap semiconductor ZnO is currently under evaluation as an alternative to the commonly used TiO_2, but is known to have a lower recombination resistance than other metal oxides [1]. The contribution of this work is the evaluation of the effect of electrolyte additives such as lithium cations and the alkaline 4-*tert*-butylpiridine (TBP) on the efficiency of the dye-regeneration in ZnO-based DSSCs by means of scanning electrochemical microscopy (SECM) [2]. For these investigations, electrodeposited porous ZnO photoanodes with different thickness, ranging from 0.02 to 7 µm, are sensitized with all-organic indoline dyes such as DN216. As shuttle for the SECM, the cobalt complex $[Co(bpy)_3]^{3+/2+}$ [3] is selected since it has a favorable match between its redox potential and the HOMO-LUMO system of the dye, which allows to reach higher open circuit photovoltages (V_{oc}).

Lithium cations and TBP adsorb on the surface of the semiconductor and modify the surface charge, shift the energy levels of the dye and the metal oxide, thus altering the behavior of the photoanode-dye-electrolyte system under different photon fluxes (J_{hv}). One of the effects is the control of the electron recombination from the conduction band of the semiconductor to the oxidized form of the mediator. Among the loss processes in DSSCs, the hindrance of mass transport of the sterically demanding mediator in the mesoporous network plays a relevant role in the dye regeneration efficiency and depends on the porosity and thickness of the sensitized photoanodes. The local regeneration of the photo-oxidized dye is studied by SECM analysis in the feedback mode using a combination of different electrolytes (mediator only, single additive plus mediator, mixture of additives plus mediator). The final outcome is a rate constant k_{ox} describing the overall dye regeneration, its dependence on the internal structure of the porous photoanode and the influence of electrolyte additives. These insights into structure-function relationships pave the way for further optimization of the overall device efficiency.

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Gold zeolitic imidazolate organic framework composite biosensor for detection of epidermal growth factor

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Zeolitic imidazolate metal organic frameworks (MOFs application in sensors is extensively studied due to its tenable structure and chemical stability. A gold zeolitic imidazolate framework composite (CTAB/Au/ZIF-8) biosensor was fabricated via drop coating of glassy carbon electrode, for the determination of epidermal growth factor (EGF). In the biosensors the ZIF-8's role is to provide the large surface area, excellent biocompatibility to the antibody while the Gold improves conductivity, accelerates signal transduction and amplifies biorecognittion. X-ray diffraction (TEM) and scanning electron microscope (SEM) were utilised for the surface morphology and structure elucidation of the modified electrode. Electrochemical properties were investigated by cyclic voltammetry (CV) and differential pulse (DPV). Apparent charge transfer rate constant (Ks), electron transfer coefficient (α), diffusion coefficient (D) of the transducer were found to be 0.048 s^{-1}, 0.035 and 5.200 x 10^{-4} cm^2 s^{-1} respectively. Under optimum conditions in 0.01M phosphate buffer, linearity was from 2 to 100 nM with a limit of detection of 0.58 nM. They was no observable interference from the tested possible interments and the biosensor efficiency was tested in saliva and urine.

Selected Inorganic and Organic Electrode Materials for Rechargeable Batteries

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This report focuses on selected inorganic transition-metal oxides and organic carbonyl compounds as high-performance electrode materials for rechargeable batteries. The main points are summarized below. First, several inorganic Ni-rich ternary layered oxides and Li-rich oxides have been successfully prepared and applied as cathode materials for Li-ion batteries, exhibiting high energy density (300 W h kg^{-1}) and long cycling life (over 300 cycles). The superior performance is attractive for practical applications in Li-ion batteries. Second, we synthesized several inorganic spinel oxides such as $CoMn_2O_4$ and carbon composites through facile room-temperature method (reduction/oxidation–phase conversion). The prepared spinel/carbon composites showed high catalytic activity in Li–air (Li–O_2) batteries with high energy density of about 500 W h kg^{-1}. Finally, owing to their environmental friendliness, structural designability, high capacity, and wide abundance, we proposed a series of well-designed organic carbonyl compounds as electrode materials for rechargeable lithium batteries. In general, organic carbonyl electrode materials suffer from high solubility in electrolyte and poor electronic conductivity, leading to serious capacity decay during cycles and inferior rate performance. To solve these problems, we developed several strategies from four aspects (molecular engineering, electrode design, electrolyte optimization, and separator modification) to construct high-performance metal–organic batteries. In summary, the well-designed electrode materials and proposed strategies in our work would promote further development of Li-ion batteries and other rechargeable batteries.

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Study of the interfacial mechanical degradation in all-solid-state lithium batteries

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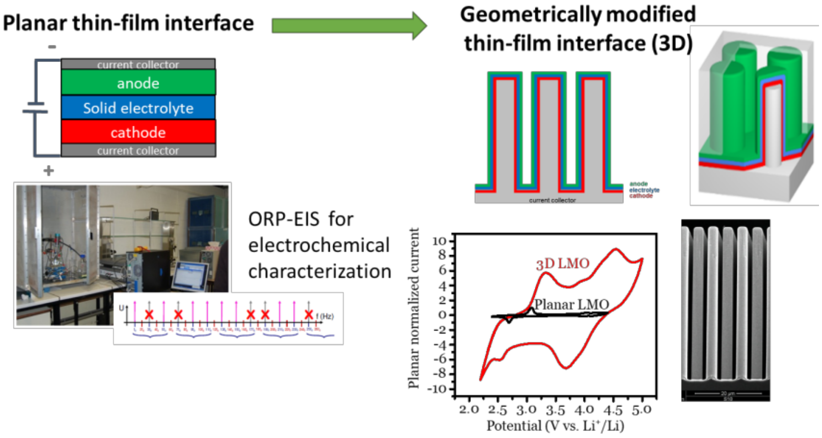
Lithium-ion batteries have become a key technology in our everyday lives, and great interest has grown during the past decade towards new materials and new configurations of the cells. Solid state lithium batteries (SSBs) allow having higher energy density without compromising power and capacity, while assuring high safety at variable temperatures and good cycle stability. However, during the charge and discharge of these batteries there are significant volume changes in the electrodes that produce stress and strain effects on the solid materials. These effects can make layers separate and cracks to form in the battery materials, which reduces the potentially improved performance of these batteries. The present study investigates the causes of the mechanical degradation and aging in Solid State Batteries using tool that allows to determine under which operation conditions a SSB can operate without suffering these undesirable effects. This tool consists on a physics-based FEM model of a complete thin-film battery that would simulate volume expansion of the positive electrode material during cycling of the batteries and predict local stress/strain failure as a function of the state of charge of the cell. The model follows a built-in approach in which the interface geometry increases in complexity gradually in three main steps (planar thin film, 3D pillar-array thin film [2], and irregular-interface porous-type cell), and it is validated experimentally at each step. In the first step, planar thin films (Li metal / LiPON / LMO) are constructed in collaboration with IMEC Research Center. Electrochemical characterization of these planar thin films is performed using the in-house developed Odd Random Phase Electrochemical Impedance Spectroscopy setup (ORP-EIS) [3] in order to define the model input parameters. Further dilatation measurements are performed on the planar thin films in order to quantify volume changes in the cells during charge and discharge and validate the model results. In further steps, the simulation of volume changes during charge and discharge is performed in geometrically modified thin-film interfaces to determine the relation between interface geometry and stress formation in the solid materials during charge and discharge.



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(Spectro)-Electrochemical Investigations of Water Splitting Enzymes, Bio-inspired Catalysts and Metal Oxides on the Electrode Surface

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Recent work from our lab investigating hydrogenases, molecular catalysts and metal oxides using electrochemistry, with special focus on our latest work on operando X-ray spectroelectrochemistry will be presented here.

Hydrogenases are very efficient enzymes for hydrogen oxidation or production.[1] The use of such enzymes in devices, such as fuel cells, is limited by its extreme sensitivity towards oxidative inactivation. We have shown how a redox hydrogel can be used to protect standard O_2 sensitive [NiFe]-hydrogenases,[2] as well as the extremely O_2 sensitive [FeFe] hydrogenase from *Chlamydomonas reinhardtii*[3] during fuel cell operation. Another advantage of this approach is that increased protein loading on the electrode surface allows for the direct observation of the enzyme active site using X-ray or EPR spectroscopies under potential control.

In the second part of this lecture, I will show very recent results combining electrochemistry with X-ray spectroscopy to gain insight into a bio-inspired $Ni[P_2N_2]_2$ type of catalysts on the electrode surface.[4, 5] These synthetic catalysts are also O_2 sensitive under electrocatalytic H_2 oxidizing conditions, while when the complex is in solution and H_2 reduced, it is able to reduce O_2. This gave us the idea to design a redox-silent polymer that allows the Ni complex to undergo two different catalytic reactions depending on its location inside the polymer film and its redox connectivity with the electrode, resulting in dramatic stabilization of the catalyst.[6] X-ray spectroelectrochemical experiments confirm that the catalyst maintains its molecular structure upon immobilization on the electrode surface or in the polymer.

Operando X-ray spectroelectrochemistry is often used to observe heterogeneous water oxidation catalysts. Nickel oxides are among the most efficient catalysts for water oxidation. At this point, the nature of the catalytically phase in Ni-oxide based OER catalysts is an ongoing subject of controversy. We have also used a combination of Ni L-edge X-ray absorption spectroscopy (XAS) and 2p3d resonant inelastic X-ray scattering (RIXS) in order to obtain detailed insights into a novel graphene supported Ni_3MnO_4 catalyst under operating conditions. These experiments provide clear evidence for the presence of a γ-NiOOH phase at the onset of electrocatalysis.

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Violating Coulomb's Law: An apparent attraction between Li$^+$ ions mediated by carbon nanotubes

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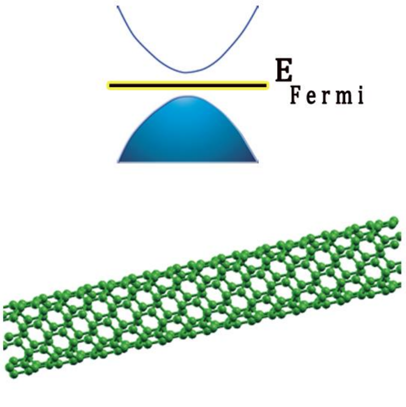
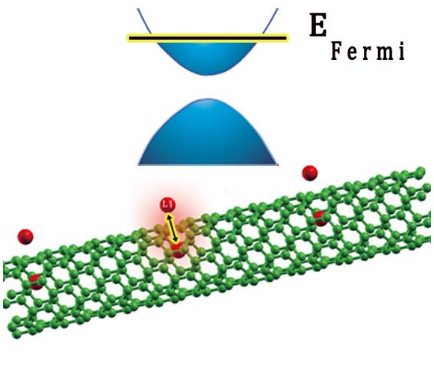
Normally ions with the same charge repel each other, but in very rare cases an intervening medium can produce an apparent attraction, superconductivity and the formation of Cooper pairs being the best example [1]. We have studied the adsorption of Li-ions on semiconducting (8,0) carbon nanotubes (CNT) by density functional theory, one ion being inside, the other outside. The tube shields the direct Coulomb interaction between the ions, but the presence of the ion inside facilitates the adsorption of the ion outside, thus producing an apparent attraction.

We repeated the calculations for the conducting (5,5) CNT. The attraction persists, but it is weaker than on the (8,0) CNT. In addition, the magnitude of the effect depends on the position of the Li-ion inside.

We offer a semi-quantitative explanation based on the unique band structure of CNTs. Let's consider the case of the semiconducting (8,0) tube [2]. The presence of the Li-ion inside induces a polarization or image charge, which makes the tube locally conductive – see picture. This transformation costs a certain amount of energy. When the second ion is adsorbed in the vicinity, the tube is already conducting, and the energy required for the second polarization charge is lower. This argument can by supported by explicit formulae. In the case of the already conducting (5,5) charge the adsorption of the first ion enhances the electronic density of state at the Fermi level, which also favors the adsorption of the second ion. But since the tube is already conducting, the effect is smaller.

The adsorption of halide ions inside or outside the tube is complicated by the formation of a chemical bond. Our first results suggest, that a Li-ion inside the tube enhances the adsorption of a Cl-ion outside.





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Polyacrylonitrile fibres as efficient electrode materials for the detection of *Vibrio cholera* toxins in samples

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Cholera constitutes a key public health challenge. It is caused by a bacterium called *Vibrio cholerae*. which causes a diarrheal disease that affects mostly the populations of developing countries. It is usually transmitted by consumption of contaminated food or water. The Centre for Disease Control and Prevention (CDC, cholera Africa) declares that Sub-Saharan Africa bears the greatest burden of the disease, mainly due to less developed countries, characterized by lack of safe drinking water, poor sanitary infrastructure, limited access to healthcare facilities, economically disadvantaged citizenry. There is a need for rapid diagnosis of cholera in order to expedite treatment of affected individuals (1).

Early detection of cholera outbreak still remains a challenge, the lack of reliable, sensitive and rapid test to successfully detect *Vibrio cholerae* in patients hampers efforts to effectively deal with the health problems posed by cholera in many African countries. The shortening of the turnaround times and decreasing cost will likely result in overall public health saving within the country (2).

This work is aimed at using polyacrylonitrile fibres (PAN) as viable electrode platforms for the development of simple and highly sensitive immunosensors for *Vibrio cholerae* toxin detection. PAN has high surface area, high thermal stability, high mechanical properties and porosity. In this presentation, we will discuss how the PAN based electrochemical sensor was used to determine cholera using cyclic voltammetry (CV), square wave voltammetry (SWV) and electrochemical impedance spectroscopy (EIS).

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Electrochemical Detection of Arsenite with chemically deposited gold nanoparticles and vapor deposited film electrodes

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Concentrations of Arsenic oxyanions above 10 μg/L in drinking water are considered dangerous by the World Health Organization [1]. Levels above this in daily drinking can lead to renal toxicity and a condition known as Arsenicosis, which produces lesions on the skin of the person consuming the water. The electrochemical method of linear stripping voltammetry (LSV) can be used on a gold electrode to detect trace concentrations of Arsenite, As (III) [2]. These electrodes and analysis systems can be designed to be light and small enough for in-situ analysis of As. Investigation of low cost and facile electrodes for detection of As can aid in production of sensors for accurate and repeatable in-field determinations.

LSV was applied to two gold (Au) nanoelectrodes to investigate detection of trace Arsenite, As (III), in a synthesized water matrix. A solution of chloroauric acid ($HAuCl_4$) and polyvinyl alcohol (PVA) generated colloidal nanoparticles, which were reduced and deposited onto Vulcan XC72 R as a carbon support. Nanoparticles, ranged from 3 to 8 nm in diameter, and the nanoparticle mixture was painted as a Nafion ink onto Sigracet 29AA carbon paper to make an electrode. Cyclic voltammetry of the nanoparticle electrode indicated a large capacitive current from the high surface area of the carbon support which therefore limited the ability to resolve low concentrations of As (III) and were therefor not investigated for their ability to detect As at trace concentrations. As an alternative to nanoparticles, a thin porous film, 27 nm thick, of Au was vapor deposited by sputtering directly onto Sigracet 29AA. The Au film electrode was held at -0.7 V and swept from -0.4 to 0.4 V at a scan rate of 100 mV/s. The reference electrode was mercury-mercury sulfate and the electrolyte solution was 18 MΩ deionized water adjusted to ca. pH 3 with sulfuric acid (H_2SO_4). LSV analysis was conducted before and after standard additions of 5, 10, 25, 50 and 75 μg/L As (III). The resulting oxidation peaks had a high peak to background ratio and the peak area showed a linear correlation to concentration. The results from this investigation indicate that vapor deposited film electrodes are a promising technology for electrochemical detection of As (III) in natural waters.

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Creating High-Performance Heterogeneous Catalysts through Surface Engineering

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Noble metal-based nanocrystals have played important roles in heterogeneous catalysis due to their high activity and chemical stability. Owing to the large surface to volume ratio at nanoscale slight changes in the surface structure of catalytic materials can have large impacts on the catalytic stability and activity. The composition, facet, and the topology of the top surface layers of a nanocatalyst eventually determine its performance in catalytic reactions. In this presentation, I will share our recent efforts on designing the surface compositions, structures and the overall morphology of noble metal catalysts to improve both catalytic activity and stability of nanocatalysts.

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Electrochemiluminescence Imaging: Latent Fingermarks, Cells and Multicolor Immunoassay

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Electrochemiluminescence (ECL), where a chemiluminescence is initiated and controlled by applying a potential, has grown significantly as a highly sensitive and selective analytical and diagnostic method in recent years. Since the light-emitting species are in situ generated close to electrode surfaces, ECL reflects the local surface reactivity, has a near zero background and allows temporal and spatial control over the reaction. These features make ECL very useful in imaging applications, e.g., for the examination of the functional areas of electrodes, the distribution of electrochemical active sites and the electron-transfer kinetics, for scanning sample surfaces with an ultramicroelectrode tip generating ECL as a light source, for building light-emitting and displaying devices and for detection in microarray sensors. In this presentation, imaging latent fingermarks on electrode surfaces by ECL will be introduced. The basic principle is based on the spatially selective control of ECL generation on the electrode surface, on which fingermarks function as a mask or template. The visualization of latent fingermarks can be enhanced by ECL generation either from the bare surface or from the labelled ridge details, yielding so called negative and positive images, respectively [1,2]. Moreover, the positive imaging mode also allows the dection of a variety of biological secretions/metabolites present in the ridge residues, providing additional evidence for personal identification [3]. In the second part of this presentation, the primary results on the surface adension of live cells and drug screening studied by ECL microscope will be presented [4]. This approach can reveal more precisely the surface adensition, morphology and lysis of live cells on electrode surface, in comparison with classical optical microscopes. Finally, ECL imaging as a tool to rationalize the emission from triple luminophores will be introduced, which have been ultized to build up a potential resolved multicolor system for simultaneous identification of multiple disease biomarkers in a single sample [5].

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Electrochemically Enabled Radical Reactions

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Organic electrochemistry, which employs electric current as the traceless oxidizing or reducing reagents, is attracting renewed interests in response to the ever-increasing demand for more efficient and sustainable organic synthesis. Because of its reagent-free feature and tunability, electrochemistry is powerful in the generation of radical and radical ion intermediates in a controllable fashion through clean single electron transfer (SET). In the presentation, our recent progress on electrochemical and photoelectrochemical generation of radical and radical ion intermediates and their synthetic applications in dehydrogenative bond-forming reactions will be discussed. In these oxidative transformations, the electrons collected at the anode from the substrates move to the cathode to combine with protons to produced hydrogen, obviating the need for oxidizing reagents.

Photoelectrochemical Etching for Preparing Ultrasmooth Gallium Nitride Surface in Acidic Electrolyte

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Due to its wide band gap and superior electronic characteristics, GaN has been widely used in various electronic and opto-electronic devices.[1] Nevertheless, the current technologies of chemical/electrochemical etching cannot be applied to the GaN wafer because of its high chemical inertness. In order to establish a new photoelectrochemical (PEC) etching method for preparing high-quality GaN surfaces, the depth-study of the interfacial reactions of n-type gallium nitride (GaN) photoanode was described in this work. The effects of photoanode potential on the photocurrent, the etching rates, the etching current efficiencies, and the surface morphologies were systemically investigated. Results show that in 2 mM H_2SO_4+0.1 M K_2SO_4 electrolyte, the PEC etching can generate a flat Ga polar GaN (0001) plane via a step-edge etching mechanism (Figure 1). The surface roughness (Ra) attains 3.51±0.46 nm and the etching rate reaches 10.78±0.87 nm/min. The present study confirms that the acidic PEC etching is a promising approach for preparing high-quality GaN surfaces in a high efficiency.

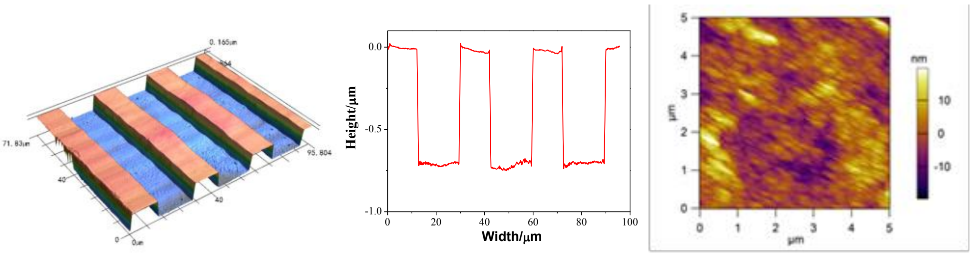

Fig.1 The optical picture (left) and the section analysis (middle) of the PEC etching GaN grooves and the AMF image (right) of the bottom surface of the groove.

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Electrochemical reduction of bis(β-diketonato)copper(II) compounds

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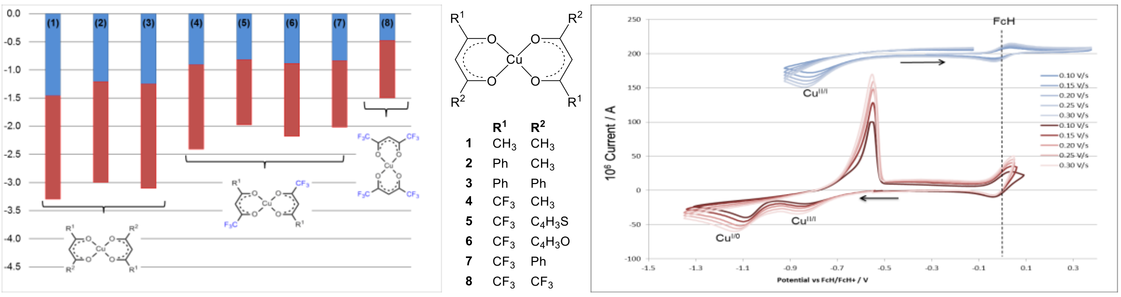
Bis(β-diketonato)copper(II) coordination compounds have widely been used as catalysts in industrial processes.[1] The effectiveness of a catalyst depends *inter alia* on its reactivity towards oxidation and reduction. The redox processes of both the uncoordinated β-diketone, $R^1COCHC(OH)R^2$,[2] as well as their corresponding metal-β-diketonato complexes[3], are generally dependant on the electronegativity of substituent groups R^1 and R^2 attached to the β-diketones. It therefore is imperative to investigate the redox processes of both the β-diketones and their bis(β-diketonato)copper(II) compounds, in order to understand and fine-tune the factors influencing the catalytic properties of these complexes.

In this contribution, the electrochemical behaviour is reported of a series of eight square-planar bis(β-diketonato)copper(II) complexes, with a variety of groups R^1 and R^2 substituted on the β-diketonato ligand $(R^1COCHCOR^2)^-$, each exhibiting different electron-donating and electron-withdrawing properties (see Figure 1 middle).[4] Two reduction processes were observed for each complex: the $Cu^{II} \rightarrow Cu^{I}$ reduction (between $E_{pc} = -1.458$ V and -0.473 V, *vs* FcH/FcH$^+$), and the $Cu^{I} \rightarrow Cu^{0}$ reduction (between $E_{pc} = -1.90$ V and -1.02 V, *vs* FcH/FcH$^+$), as well as the sharp anodic dissolution wave of deposited copper at *ca.* -0.5 V, see Figure 1 (right). The electronegativity of substituent groups R^1 and R^2 was found to greatly influence the experimentally measured reduction potentials (E_{pc}) of the bis(β-diketonato)copper(II) complexes **1**–**8** to such an extent, that E_{pc} varied over a large range of *ca.* 1.0 V. This large range of reduction potentials is especially due to the large variety of electronegativities of the R^1 and R^2 substituents. The effect from the electronegativities of groups R^1 and R^2 on the reduction potential is additive, since with increasing amount of electron withdrawing CF_3 groups in the bis(β-diketonato)copper(II) complexes (from none, to one, to two CF_3), the reduction potential shifts to higher (less negative) values, for both observed reduction processes (Figure 1 left, both blue and red bars).



	R^1	R^2
1	CH_3	CH_3
2	Ph	CH_3
3	Ph	Ph
4	CF_3	CH_3
5	CF_3	C_4H_3S
6	CF_3	C_4H_3O
7	CF_3	Ph
8	CF_3	CF_3

Fig. 1. Left: Illustration of the influence of the amount of CF_3 groups in the $[Cu^{II}(\beta\text{-diketonato})_2]$ complexes, on the reduction potential E_{pc} (V *vs* FcH/FcH$^+$ plotted on the y-axis), for the first $Cu^{II} \rightarrow Cu^{I}$ reduction (blue bars) and the second $Cu^{I} \rightarrow Cu^{0}$ reduction (red bars) of complexes **1**–**8**; structures with substituents shown in the **middle**. _**Right:** Cyclic voltammograms (V *vs* FcH/FcH$^+$) of the two complexes $[Cu^{II}(\text{trifluorobenzoylacetone})_2]$ complex **7** (bottom, red), and $[Cu^{II}(\text{trifluorothenoylacetylacetone})_2]$ complex **5** (top, blue). The FcH/FcH$^+$ redox couple of ferrocene, FcH, is used as internal standard.

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A Flexible CVD Graphene Platform Electrode Modified with L-Aspartic acid for the Simultaneous Determination of Acetaminophen, Epinephrine and Tyrosine

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Graphene (GN), a two-dimensional planar sheet of hexagonally configured sp^2 hybridized carbon atoms, has attracted growing scientific interest in fundamental researches as well as practical applications such as fuel cells, super capacitors, batteries and electrochemical sensors [1]. GN synthesized by chemical vapor deposition (CVD) is superior than chemically synthesized GN, due to its less planar defects, good reproducibility, and homogeneous coverage ability without restacking phenomenon, which leads to enhanced electron transport properties [2]. In this work, CVD graphene on Cu foil was transferred to flexible polyethylene terephthalate substrates with the aid of polymethyl-methacrylate to form a graphene platform electroe (GPE), L-Aspartic acid (L-Asp) were electrodeposited on GPE to form a L-Asp/GPE. The as-fabricated L-Asp/GPE sensor was investigated by detecting acetaminophen(AC), epinephrine (EP) and tyrosine(TY) in the solution of 0.1 M phosphate buffer solution (pH=7.0) by cyclic voltammetry. The separations between the neighboring peaks, about 213 mV and 283mV, respectively, were large enough for simultaneous determination of AC, EP and TY. As a result, a flexible L-Asp/GPE electrochemical sensor for the deterimnaiotn of AC, EP and TY was developed (Fig. 1). The detection limit of AC, EP and TY was presented by chronoamperometry, which were 0.011 μM, 0.006 μM and 0.32 μM (S/N = 3), respectively. In addition, the as-obtained sensor delivered good stability as well as high resistance to interference, and was successfully utilized in determining real samples.

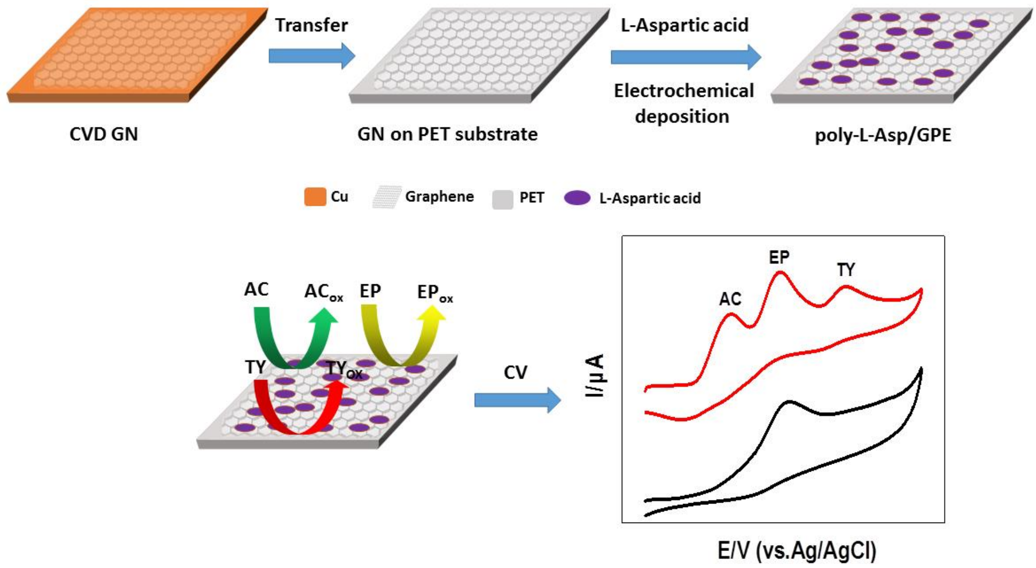

Fig. 1 Schematic illustration of the fabrication of GPE and L-Asp/GPE and the cyclic voltammetric responses of AC, EP and TY on GPE (black) and L-Asp/GPE (red).

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The Effects of CO_2 Contamination on Reaction Mechanism in Non-aqueous Na-air Batteries: A DFT Study

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Metal–air batteries become promising candidates for modern energy storage due to their high theoretical energy density in comparison to other energy storage devices. The low cost, low overpotential and abundance of Na compared with Li makes Na–air batteries more attractive. Here, we apply density functional theory (DFT) calculations to study the effect of CO_2 contamination on reaction mechanisms and resulting electrochemical overpotentials on stepped surfaces of NaO_2 and Na_2O_2, the discharge products at the cathode of rechargeable non-aqueous Na-air batteries (NASAB). Adsorption energies of CO_2 at various nucleation sites for both surfaces were determined and their corresponding binding energies show that CO_2 adsorbs strongly at various sites of the surfaces, it would preferentially bind at the step valley (-1.31 eV) and front step valley (-4.39 eV) sites of step (001) NaO_2 and $(1\bar{1}00)$ Na_2O_2 surfaces, respectively (see figure 1). We also investigate the reaction mechanisms with and without CO_2 on stepped surfaces of the NaO_2 and Na_2O_2 systems, result reveals significant increase in discharge overpotentials on NaO_2 surface, $\eta_{\mathrm{dis}} = 0.14$ V to 0.48 V. Similarly, the results of CO_2 contamination on Na_2O_2 surface also revealed remarkable increase in both discharge and charge overvoltages, 0.69 V to 1.26 V and 0.68 V to 0.92 V, respectively. Moreover, the equilibrium potential is decreased by 0.13 V in the presence of CO_2 on Na_2O_2 surface. In general, the DFT calculations show that in both cases, with and without CO_2, the cells that discharge with NaO_2 exhibit low overpotentials while the Na_2O_2 exhibit higher over potentials. The growth/depletion mechanisms are strongly influenced by CO_2 contamination, and exhibit increased overpotentials and hence affect the performance of the Na-air battery.

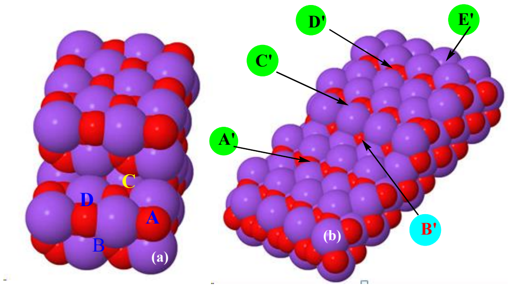

Figure 1: CO_2 adsorption at various sites of stepped (a) (001) NaO_2 and (b) $(1\bar{1}00)$ Na_2O_2 surface.

Key Words: NaO_2, Na_2O_2, Na–O_2 Batteries, DFT, CO_2 Contamination, Overpotential

Metal Organic Framework (MOF)-Derived Carbons as Bifunctional Electrocatalysts for Oxygen Reduction (ORR) and Evolution Reactions (OER)

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Renewable energy storage devices are one of the most promising technologies for sustainable and environmental-friendly energy sources. Amongst these devices, zinc-air batteries (ZABs) have drawn global attention because of their advantageous characteristics, which include high theoretical energy output and low-cost. Oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are essential parameters for the fabrication of zinc-air battery[1]. These reactions are well known for their extremely sluggish kinetics. Thus, effective and efficient electrocatalyst is necessary to drive these reactions. Platinum (Pt) has been the most common electrocatalyst for ORR and OER, but its poor stability, high cost and scarcity have limited the commercialization of the state-of-art zinc-air battery [2].

In recent years, metal organic frameworks (MOFs) have proven themselves as unique crystalline materials with characteristic high surface area, tunable pore size and redox active[3]. This on-going research attempts to explore these inherent unique properties of MOFs for the synthesis of low cost cobalt nanoparticles on MOF-derived carbons as bifunctional electrocatalysts for ORR and OER with comparative performance to Pt for the development of Zn-air battery.

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Monitoring the Electrochemical Capacitance by In Situ Impedance Spectroscopy as Indicator for Particle Degradation of Ni-Rich Cathode Active Materials

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Lithium-rich layered lithium nickel cobalt manganese oxides (NCMs) are more and more used as cathode active materials in current lithium-ion cell chemistries due to their high specific capacity; they are also expected to play a major role in future battery technologies, such as all-solid-state batteries. However, a reported failure mechanism of Li-rich NCMs are the volume-change induced breakage of NCM primary particles and secondary agglomerates upon repeated (de)lithiation, leading to a loss of electrical contact and enhanced side reactions caused by an increased surface area [1]. De Biasi et al. showed by in situ X-ray diffraction that the unit cell volume changes during cycling to a given upper cutoff potential increases with nickel content, leading to increasingly severe fracture of the secondary particle agglomerates and, therefore, to a substantial surface area increase during cycling [2].

In the present study, we develop a method to quantify the increase in the active materials' surface area upon cycling using electrochemical impedance spectroscopy (EIS). Hence, we make use of the direct correlation between the capacitance and the surface area of the electrode [3]. To monitor the impedance response of the cathode upon cycling in a full-cell, we perform EIS measurements with a micro-reference electrode [4].

To evaluate the capacitance rise and the correlated surface area increase of different active materials, the electrodes were cycled in full-cells against capacitively oversized pre-lithiated LTO electrodes for more than 200 cycles, applying different upper cutoff potentials. Impedance spectra of the cathode are recorded after each of the three formation cycles and, subsequently, after every 5th cycle. From the impedance spectra, the cathode capacitance is quantified and correlated to the NCM surface area as a function of cycle number and upper cutoff potential. To validate this approach, active materials with very low and relatively high volume change upon cycling were also examined (e.g., $LiFePO_4$ and $Li_4Ti_5O_{12}$). In addition, the electrodes were harvested to examine the breakage of the particles upon cycling by post-mortem FIB-SEM analysis. It will be shown that the measured capacitance increase indeed correlates with the given volume change of the investigated materials upon cycling. We also applied this method to determine the volume change induced surface area increase as a function of the degree of lithiation (i.e, the state of charge) in the first single charge/discharge cycle. Furthermore, this method enables to observe the degradation of Ni-rich NCMs upon oxygen release at high state of charge as well as to quantify the mechanical particle breakage due to compression of the electrodes.

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Electroless Plating of Silver Nanoparticle Films with Controlled Particle Size and Areal Density: Production of Plasmonic Transducers for DNA Biosensing

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Due to its simplicity, scalability, high deposit quality and excellent conformity, electroless plating represents a promising electrochemical reaction class for producing metal nanomaterials. Traditionally, it is focused on the deposition of compact, smooth films, which serve as protective or conductive coatings. To expand the utility of electroless plating to other application fields, new synthetic strategies are required to surpass its structural and compositional limitations. For instance, procedures for depositing isolated coinage metal nanoparticles are lacking, which display the basis for localized surface plasmon resonance-based sensing platforms. In this contribution, we show how electroless silver plating can be tailored to achieve this target morphology (Figure 1).[1]

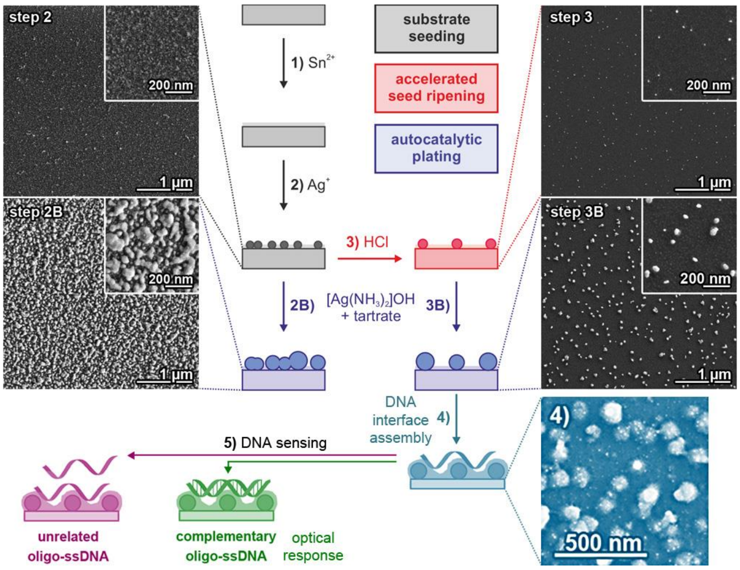

Figure 1. Sensor fabrication scheme, including electron micrographs of the respective reaction stages.

We realize spread-out silver nanoparticle films by complementing the classical two-step seeding based on Sn(II) sensitization and self-limited Ag(I) activation[2] with an accelerated seed aging step. The latter is achieved by briefly immersing activated samples in diluted hydrochloric acid, exploiting the high reactivity of silver nanostructures in the presence of chloride.[3] Mechanistically, the seed layer transformation is characterized by an almost instantaneous nanoparticle reshaping and Ostwald ripening, which is accompanied by continuous silver oxidation. The degree of modification can be controlled by the immersion time and acid concentration, allowing one to adjust the areal density of the nanoparticle seeds. Subsequently, the seeds are amplified with electroless plating until they reach a desired size. Our approach is fully wet-chemical, proceeds within minutes, only employs standard chemicals, is compatible with different substrate materials, and can be applied to curved surfaces and channels, making it compatible with fiber optic and lab-in-a-chip setups. We demonstrate how this synthetic toolkit can be utilized to fabricate transducers for single-use optical DNA biosensors based on the nanoparticles' localized surface plasmon resonance. To this end, a sensing interface is prepared by layer-by-layer buildup of polyelectrolytes, followed by adsorption and covalent immobilization of single-stranded DNA. The obtained transducers demonstrate robustness and selectivity in sensing experiments with binding complementary and unrelated DNA strands.

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Layered Sodium Manganese Oxide ($Na_2Mn_3O_7$) As a Versatile Battery Insertion Material

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Rechargeable Li-ion batteries plays a key role in propelling modern consumer electronics, electric automobiles along with stationary grid storage. Manganese-based layered oxide cathodes have been widely investigated for Li-ion batteries due to the elemental abundance, low cost, non-toxicity and multiple oxidation states (+II to +VII) associated with Mn. It has led to successful commercialization of cathodes like $LiMn_2O_4$ and $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$. Mn-based oxides can be put on anvil to develop high energy density cathodes by exploiting multiple electron transfer reaction. $Li_2Mn_3O_7$ forms one such material with high theoretical energy density. However, direct chemical synthesis of this layered Li-Mn-O ternary compound is cumbersome due to the feasible formation of thermodynamically stable spinels like $Li_xMn_2O_4$, $Li_2Mn_4O_9$ and $Li_4Mn_5O_{12}$. It can be prepared by indirect methods such as *chimie douce* type (soft chemistry) ion-exchange of pristine $Na_2Mn_3O_7$ by Li^+ ions. Also, these metastable phases (like $Li_2Mn_3O_7$) can be obtained by electrochemical ion-exchange/ ion-intercalation.

Inspired by this potential advantages and polymorphism associated with Mn-based systems, here, ternary layered Na-Mn-O based metal oxide ($Na_2Mn_3O_7$) was synthesized using different synthetic routes (solid-state, combustion synthesis, Pechini, hydrothermal etc.) to tune the size and morphology of $Na_2Mn_3O_7$ particles. The phase pure $Na_2Mn_3O_7$ crystallizes in triclinic layered structure (s.g. *P*-1). It consists of Mn in +IV oxidation state with electrochemically active Mn^{4+}/Mn^{3+} redox center. The as-synthesized black powder worked as a versatile cathode for the Li-ion, Na-ion, K-ion and Zn-ion batteries [1-5]. The systematic electrochemical studies were carried in both the aqueous and non-aqueous electrolytes. It delivered a reversible capacity of ~160, ~140, ~134 and ~330 mA h g^{-1} respectively with Li, Na, K and Zn metal as anode in half-cell architectures. Interestingly, Li-ion battery exhibited solid-solution type (de)intercalation upon the variation of Li-ion (A) concentration in $Na_2A_xMn_3O_7$, whereas Na-ion, K-ion and Zn-ion (de)intercalation involve two-phase redox reaction. The detailed (de)intercalation mechanism along with diffusional studies of the various alkali-ions (Li/Na/K) along with Zn-ion will be described to present $Na_2Mn_3O_7$ as a versatile cathode material.

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Wireless Synthesis of Thermoresponsive Nanostructured Janus Carbon Materials using Bipolar Electrochemistry

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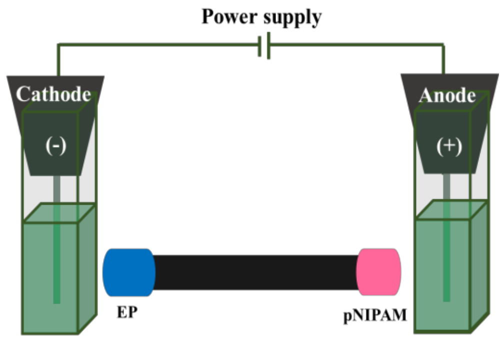
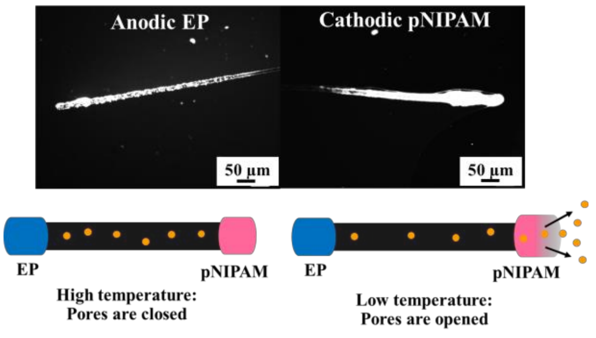
In this work, bipolar electrochemistry (BPE) is used to perform the electrodeposition of polymers on both sides of carbon objects without physical contact between the carbon objects and the electrodes [1]. In BPE a conducting object (the bipolar electrode) is positioned in an electrolyte solution between two feeder electrodes. When the electric field is applied oxidation and reduction reactions will occur simultaneously at the opposite sides of the bipolar electrode. As a proof-of-principle, we modified carbon fibers with a thermoresponsive poly(N-isopropylacrylamide) (pNIPAM) hydrogel layer on one side [2] and an inert polymer layer, electrophoretic paint (EP), on the opposite side. Other objects were prepared with pNIPAM-pNIPAM on both sides. The results show that the length and thickness of pNIPAM-EP and pNIPAM-pNIPAM can be controlled by varying the electric field and the deposition time. This concept was then generalized to nano-sized carbon tubes (CNTs). They were synthesized via chemical vapor deposition using anodic aluminum oxide (AAO) as template and acetylene (C_2H_2) as carbon source. CNTs modified with pNIPAM-EP and pNIPAM-pNIPAM were obtained by applying BPE to the CNTs embedded in the pores of an AAO membrane. The modified CNTs are recovered after AAO membrane dissolution. This technique opens up applications of these objects for example in the fields of drug delivery and storage.





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Gold and Silver Nanostructures Prepared Directly from Leaching Solutions by Electrodeposition-Redox Replacement

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Abstract: Currently industrial gold leaching is based on cyanidation, which is an inherently hazardous process and consequently there is a strong driving force for the development of more environmentally friendly routes for precious metal recovery. One interesting alternative is glycine, which offers a great potential for silver and gold leaching due its low unit price and non-toxicity[1]. Nevertheless, glycine dissolves also base metals such as copper and zinc, and consequently the concentration of precious metals in the pregnant leaching solution is considerably less when compared to that of the associated base metals. This can pose a challenge for the precious metal recovery. For example, energy consumption and selectivity are critical issues in direct extraction of precious metals by electrowinning or cementation. Recently, we have introduced electrodeposition - redox replacement (EDRR) as an alternative method for precious metal recovery from hydrometallurgical solutions that contain tens of g/L of base metals and only ppm or even ppb levels of precious metals [2,3]. Moreover, we have demonstrated the possibility to create Pt/Ni nanoparticles by EDRR from solutions mimicking industrial process streams[4].

In this presentation, the preparation of silver and gold nanostructures using EDRR from glycine based hydrometallurgical leaching solutions was investigated. The morphology and composition of the structures were controlled by EDRR parameters such as deposition potential, current or time, redox replacement time and the number of repeating EDRR cycles (**Fig 1.**). It was shown that the EDRR exhibits remarkable flexibility when tailoring functional surfaces with gold and silver-based nanostructures and this can be achieved directly from hydrometallurgical leaching solutions, even if they contain a complex matrix of metals. Moreover, these functional surfaces can be prepared without any additional chemicals, hence improving the environmental aspect of the process.

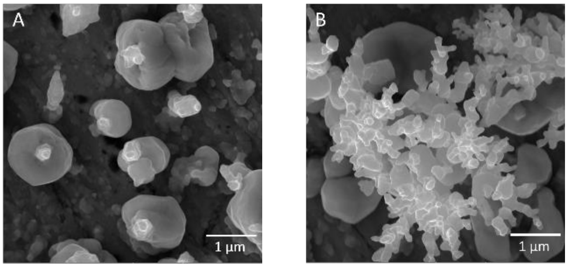

Figure 1. Nanostructures of precious metals obtained by EDRR.

Overall, this research clearly highlights the potential of the EDRR method for obtaining high value-added precious metal nanostructures in a controlled fashion directly from industrial leaching solutions, following circular economy principles.

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Functional separators for the batteries of the future

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Even if the separator has been considered so far an inactive component of a battery, its properties are of paramount importance for the operation and safety of batteries featuring liquid electrolyte. It avoids the contact of the electrodes and prevents electronic short circuits while enabling ion transport. Its mechanical, chemical and electrochemical stability assures long life to the device and its thermal stability may act as a switch to shut down the current flow in case of battery overheating. The thickness and the amount of soaked electrolyte affect the specific and volumetric device performance [1].

The increasing energy demand and the wide spread of renewable energy sources requiring large-size, safe and low-cost energy storage systems have focused the research efforts on the so-called post lithium-ion batteries that include Li-metal batteries, Li/S, metal/air and Na-ion batteries. These studies have been evincing the need of other functions of the separator: blocking O_2 and moisture in Li/air batteries, blocking lithium polysulfides in Li/S batteries, contributing to the formation of a smooth Li surface without dendrites in batteries with metal Li anode [2-5]. In addition, the demand of low-cost, environmentally friendly Na-ion batteries for the large-scale use of renewable energy requires an eco-efficient fabrication of sustainable separators [6].

Several strategies have been pursued to create new separators or to modify commercial ones in order to have a separator that actively contributes to the operation of the battery by adding carbonaceous particles, metal oxides, ionomers and polymers into the separator structure or by forming a surface layer [7-10].

Several approaches to modify commercial polyolefin separators, including the use of the electrospinning technique, for the application in Li-metal batteries will be here presented. The physical-chemical properties as well as the electrochemical performance of the separators will be investigated and discussed.

Acknowledgments
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The Authors would like to thank CAT Progetti S.R.L. for providing electrospinning equipment and P. Bertuzzi (CAT Progetti S.R.L.) for the helpful discussions.

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Complementary Insight into the Experimental Reduction Potentials of the Tris(β-Diketonato)Iron(III) Complexes Using the DFT Methods

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Different levels of density functional theory (DFT) were applied to gain better insight into the reported experimental reduction potentials of sixteen derivatives of tris(β-diketonato)iron(III) complexes, [Fe(RCOCHCOR′)$_3$] (Figure 1 left), with the R and R′ substituents in different combinations of CH_3, Ph, CF_3, C_4H_3S, C_4H_3O, H and ^{t}Bu,[1]. These computations were conducted in an effort to complement the existing experimental results (examples in Figure 1, middle) and to gain better understanding of the effects of the isomeric forms (*mer* or *fac*) on the iron(III/II) reduction. This study employed two free energy cycles, which are technically slightly different, in combination with the DFT methods M06, M062X and M06L, for calculating the theoretical reduction potential of these complexes.[2] The results from the computational approach show the same trend as observed in the experimental reduction potential values (Figure 1 middle), namely that the complexes with stronger electron withdrawing substituents R and R′ on the coordinating β-diketonato ligands (e.g. CF_3), resulted in higher (less negative) reduction potential. Also, the experimental results were reproduced to a significant level of accuracy, especially where the combination of the thermodynamic cycle and DFT method gave a mean absolute deviation (MAD) of 0.054. These theoretical methods provided more insight into the experimental results, since they enabled a clear distinction between the reduction potentials of the *mer* or *fac* isomers of the molecules, which was not feasible through the experimental results. These results proved the usefulness of the first principle quantum computational methods in reproducing and providing better insight into the experimental reduction potentials.

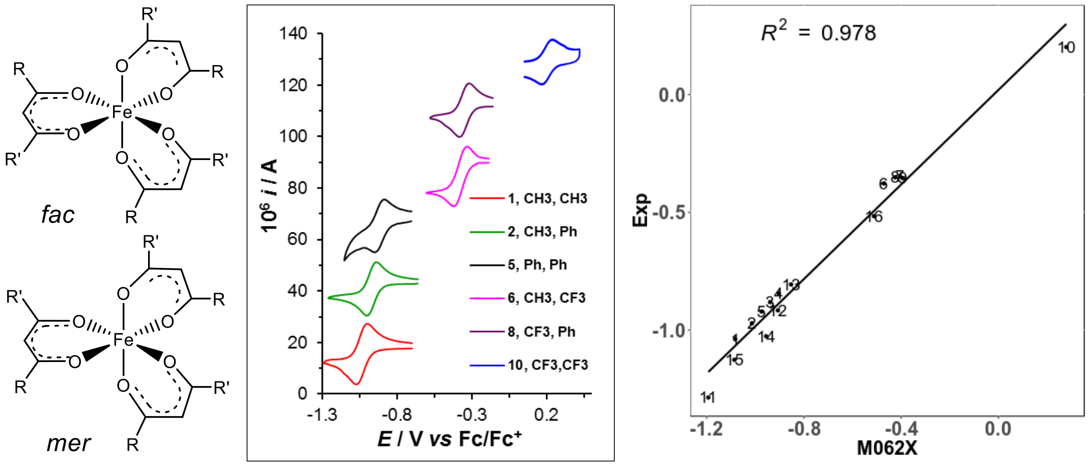

Figure 1: The correlation of the experimental reduction potentials (selected cyclic voltammograms given in the middle) of the [Fe(RCOCHCOR′)$_3$] complexes (left) to the computational reduction potentials from the M062X hybrid functional method of DFT (right).

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Characterization of Human Methaemoglobins Using Cyclic Voltammetric Studies on their Aquo-, Cyano-, Azido- and Fluoro Complexes.

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The ferric iron in aquo - methaemoglobin is bonded to four pyrrole groups, a protein moiety and a water molecule. This can be considered to be an analogue of the ferricyanide ion present in the Test solution used in cyclic voltammetry. In this study, the values of peak current and peak potential were determined for human aquo - methaemoglobins A, AC, AS and S at approximately similar concentrations. The range of cathodic peak potential in mV was characteristic for each aquo - methaemoglobin; 139-163, 181-192, 172-182 and 152-153 for methaemoglobin A, AC, AS and S respectively. The range for potassium ferricyanide was 160 – 177, though at fairly higher concentrations. The studies have been extended to some low spin complexes, cyano- and azido and high spin complexes, fluoro- of these methaemoglobins. The results on concentration dependence of the voltammetric parameters and the possible effects of the protein moiety and ligands on these parameters will be discussed.

The experiments were carried out in 0.2 M phosphate buffer, pH 6.2.

Voltammetric parameters were:

Initial and Final potential, 600 mV; Switching potential, 0 mV; Quiet time 2s; Scan rate, 100 mV/s; Current, 100 µA.

Working electrode, platinum; Counter electrode, platinum wire; Reference electrode, Ag/AgCl.

Printed Accumulators Based on Organic Electrodes for Printed Electronics Applications

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In last years, there is increasing interest about the organic material based electrodes for lithium based accumulators. In literature are described various types of organic materials which exhibit multi-electron transitions during charging/discharging cycles, enabling high specific capacity typically in the range 300-800 mA.h/g [1]. Although many organic cathodes exhibit high specific capacity in solid-state batteries, negative properties such as cycling instability, low electrical conductivity, or high solubility in the electrolyte are still present. The simplest quinone derivatives are usually represented by simple quinoid structures such as 1,4-benzoquinone, 9,10-phenanthroquinone [9,10] or 9,10-anthraquinone. The last one exhibits in cell with a specific capacity of 222 mA.h/g [2]. Higher stability in terms of cycling, exhibited sulfo-substituted materials or polymeric materials prepared by the Phillips method from 9,10-anthraquinone monomer by reaction with sodium sulphide [3]. The poly(anthraquinonyl sulfide) [3] shows a initial specific capacity of 198 mA.h/g (88% theoretical) and 178 mAh/g after 200 cycles.

The presented study is focused to development of printed electrodes where the commercial 9,10-anthraquinone (AQ) (DEZA a. s., CZ) and synthetized poly (1,5-anthraquinonyl sulfide) (PAQS) were used as a electrode materials. The PAQS were synthetized according Song work [3]. From both materials were prepared homogeneous ink formulations with viscosity related to screen/stencil printing. The electrodes were printed on Al and Cu foil with up to 14 mg of active material per cm^2. In the cells Li/AQ, Li/PAQS the organic electrodes on Al were used and for Cu collector based in the cells AQ/LMO, PAQS/LMO. In all cells the LiTFSI based electrolytes was used. The stencil printing was realized using semiautomatic screen printing machine Ekra E1. Assembling and characterization of the Li foil based cell was performed under inert condition using glovebox with Ar atmosphere. Because R&D activities for printed accumulators are also dedicated for small printed electronics devices as a Smart labels, or IoT device too, the assembling of selected accumulators were realized in ambient condition with relative humidity 20 %. For such type of applications the highest criteria's as a long term stability, high effective usage of electrode materials is not so important. Simplifying of production of printed electronics with printed accumulators have many benefits, because it is possible to fabricate whole device (Smart Labels, IoT device, etc.) at the same in printing production line. Given approach has production and economical advantages, connecting and assembling of high effective pouch cells is rather than problematic and final flexibility and thickness is mediocre too. Despite for lithium accumulators not typic assembling process conditions, the cell consisted from electrode pair PAQS/LMO deliver OCV 2.35 V with mid voltage plateau equal to 1.8 V. The specific capacity after first formation process was 63 mA.h/g. The specific capacity stability after 250 cycles with specific capacity 59 mA.h/g which related 93.6 % of initial capacity. The equivalent cells based on AQ electrodes exhibits lower OCV 2.1 V with mid voltage plateau equal to 1.7 V. The initial capacity was 55 mA.h/g and after 200 cycles at 0.5C 22 mA.h/g.

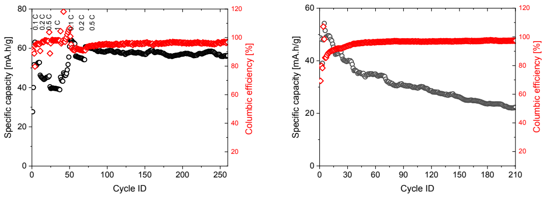

Figure 1: The specific capacity for cells PAQS/LMO and AQ/LMO.

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Unveiling and Artificially Increasing Purple Bacteria Salt-Tolerance: from Biological to Engineering Approaches

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Coupling of photosynthetic biomaterials with an electrode surface opens for the environmental friendly conversion of solar energy into electrical current in photobioelectrochemical systems.[1,2] These systems are of particular interest for specific applications, where the utilized biological entities confer unique properties compared to classical chemical systems. An example is the development of photobioelectrochemical sensors for online monitoring of herbicides,[3] or other toxic compounds, present in water samples. Application of such sensors would allow for the on-line monitoring of potentially contaminated areas after a natural or industrial disaster. Currently, expensive and ex-situ analyses are usually required (i.e., high-performance liquid chromatography), since an effective strategy for the on-line and on-site monitoring has yet to be developed.

Among different photosynthetic bacteria, purple bacteria are characterized by extremely versatile metabolisms, allowing them to grow in various conditions. Specifically, *Rhodobacter capsulatus* (*R. capsulatus*) has a simple photosynthetic process, with a very effective anaerobic photoheterotrophic metabolism. Our group has recently clarified the quinone-mediated extracellular electron transfer process between *R. capsulatus* cells and a carbon electrode,[4] opening for further applications of this bacterium in photobioelectrochemical sensors. We are currently aiming to develop sensors for the monitoring of toxic compounds in water samples characterized by a changing salinity. Accordingly, the capability of *R. capsulatus* to grow in saline environments makes it an excellent candidate for this purpose. Variations in salinity are common after natural or industrial disasters, i.e., flooded wastewater after a hurricane, or water ponds after the flood of industrial wastewater (i.e., from coal industry or tanning industry). We have recently shown how changes in salinity affect bioelectrocatalytic performance of *R. capsulatus*, with a critical decrease of the current output for salinities as low as 10 gL^{-1}. However, cell transfers and prolonged exposure to increasing salt concentrations allowed bacterial adaptation to the environment, improving performance up to 20 gL^{-1} NaCl.[5]

In order to artificially increase the salt tolerance of *R. capsulatus,* we aimed to understand the biological processes underlying of the adaptation, and their influence on bioelectrochemical performances. With this purpose, the influence of horizontal gene transfer, quorum sensing, and differential gene expression was investigated. Moreover, we explored the engineering of bacterial cells entrapment approaches, to unveil the possibility of enhancing salinity tolerance and bioelectrochemical performance without the time required for bacterial cell adaptation.

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Scale-up limitation of gas diffusion electrodes for CO_2 conversion

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Electrochemical CO_2 reduction has the potential of reducing greenhouse gas emissions and storing excess electricity from renewable energy sources in the form of hydrocarbons. In the last decade, researchers have demonstrated that delivering CO_2 in the gas phase can overcome mass transfer limitations associated with the limited solubility and diffusion in the liquid phase. Industrially relevant current densities of ≥ 300 mA/cm^2 have been reported in flow reactors incorporating macroporous gas diffusion electrodes at the centimeter scale.[1,2]

However, when increasing the dimension of a vertically oriented reactor, a noteworthy hydrostatic pressure gradient emerges only in the liquid phase making it challenging to maintain the separation of liquid and gas phase (Figure 1). Pressure gradients across the porous gas diffusion layer can lead to a performance decrease, loss of electrolyte, and intermixing of the gaseous product streams. The limited scale-up capability of this reactor design is an aspect that has not received much attention yet.

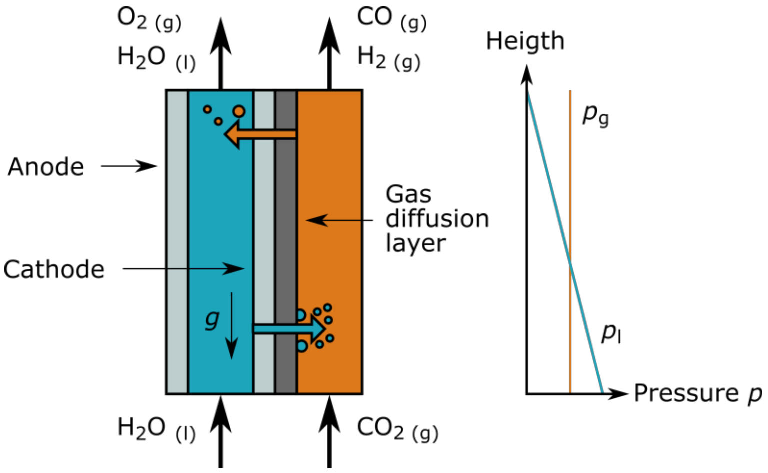

Figure 1: Hydrostatic pressure gradients can lead to an imbalance in pressure across the gas diffusion layer resulting in liquid and/or gas breakthrough.

We aim to quantify the scale-up limitation imposed by presence of a hydrostatic pressure gradient in the liquid phase. We emulate the conditions of a large scale system with a small scale setup using an electrochemical flow cell that controls the pressure gradient across the interface with downstream pressure regulators.

We observed gas permeation into the liquid phase at a pressure difference of -8 mbar for TGP-H-060 (5wt% PTFE). Liquid permeation occurred when the pressure gradient across the membrane exceeded 10 mbar. This pressure range corresponds to a maximum plate height of only about 18 cm.

We conclude that the design of a CO_2 electrolyzer at an industrial scale based solely on a macroporous gas diffusion layer would have considerable drawbacks. To overcome this limitation, we intend to implement additional microporous layers, gas diffusion layers with pore size gradients, or an ion-exchange membrane.

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Electrochemical determination of Caffeine at Electrodes modified with Polypyrrole and green synthesized bimetallic nanoparticles.

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Keywords: Caffeine, Screen printed carbon electrode, Glassy carbon electrode, Bimetallic nanoparticles, Polypyrrole, Cyclic voltammetry, Differential pulse voltammetry

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Abstract

Silver (Ag) and gold (Au) nanoparticles (NPs), as well as Ag/Au bimetallic nanoparticles (BMNPs) were synthesized using the extract of *citrus sinensis* (sweet orange) peels. The nanoparticles were used to form nanocomposite material supported on polypyrrole (PPY) for the modification of screen printed carbon electrode (SPCE) as well as glassy carbon electrode (GCE) and consequently for the trace detection of caffeine. The synthesized nanomaterials were characterized by fourier transform infrared spectroscopy (FT-IR), ultraviolet-visible (UV-Vis) spectrophotometry, x-ray diffraction (XRD) spectroscopy and scanning electron microscopy (SEM). Electrochemical characterization of the modified electrodes was conducted by cyclic voltammetry (CV) using the ferrocyanide/ferricyanide redox probe prepared in phosphate buffer saline (PBS). PPY-Ag/AuBMNP modified SPCE exhibited faster electron transport properties as well as enhanced catalytic current response as compared to bare-SPCE, SPCE-AgNPs, SPCE-AuNPs, SPCE-Ag/AuBMNP, SPCE-PPY, SPCE-PPY-AgNPs and SPCE-PPY-AuNPs. Characterization studies further demonstrated that PPY-Ag/AuBMNPs modified SPCE was stable with virtually no current decrease between the 1st and 20th scan by CV. By differential pulse voltammetry PPY-Ag/AuBMNPs sensor yielded a comparably low detection limit of 5.3 μM with sensitivity of 0.74 μA/μM in the caffeine concentration range of 9 μM to 82 μM.

An investigation of the nitrite electro-oxidation capabilities of flavone tetrasubstituted metallophthalocyanines and their carbon nanotube conjugates

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MPc-based electron-mediating films immobilized on working electrodes have illustrated promise for simultaneous multiple analyte detection which can be promoted by metal- and ligand-based redox processes [**1**]. Of growing interest is the nanofabrication of MPc-carbon nanotube conjugates which have shown to enhance the electrocatalytic activities of chemically-modified electrodes [**2**]. A new trend for this class of MPc-based electrochemical detectors entails the design of molecules that encompasses biologically active moieties that can improve selectivity [**3**].

In this research study, new tetrasubstituted MPcs, {M = Mn(OAc) or Fe} bearing flavone moieties in peripheral positions have been synthesized and characterized [**4**]. The mononuclear metal complexes exhibit redox properties associated with metal and Pc-based redox couples. Platinum working electrodes modified with the MPcs and their MWCNT nano-conjugates showed more sensitive responses towards nitrite electro-oxidation than the bare working electrode. The electrocatalytic behaviours of the MPc-flav-MWCNTs Pt electrodes show higher diffusion rate constants than those found in other reported studies and selectively detected nitrite in the presence of *bis*-phenol A (BPA) and paracetamol (PC) as interferents, see **Figure 1**. The rationale behind the design of MPcs bearing flavone moieties originates from the fact flavone and its derivatives have illustrated potent antioxidant capabilities towards nitrite and its corresponding radical species [**5**]. Consequently, the presence of the flavone substituents may promote the selective detection of nitrite for working electrodes modified with the MPcs and their carbon nanotube conjugates.

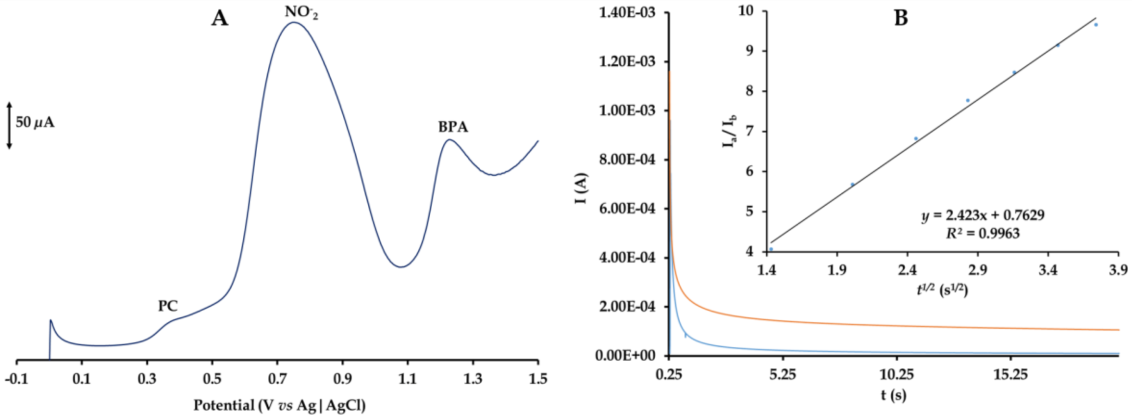

Figure 1 (A): *Chronoamperograms attained using the FePc-flav-MWCNTs Pt electrode. Inset: Plot of I_c/I_b against $t^{1/2}$.* (**B**): *SWV of a sample solution containing 1 mM nitrite, 1 mM PC and 1 mM BPA in PBS buffer using the FePc-flav-MWCNTs Pt electrode.*

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A technology for treating spent lubricants from wire drawing

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In metal industry, cooling lubricants play a very important role. Millions of tons are used worldwide. It is their task to lubricate contact surfaces and to dissipate heat in metal treating processes. Cooling lubricants can be divided into non-water and water-miscible systems, also into liquids representing emulsions or water-soluble systems. Exact composition and technology of preparation is often production secret. It is state of the art that most cooling lubricants are biodegradable when heavy metal ions, which may accumulate during the treatment process, are separated from the spent lubricants. Early publications [1, 2] deal with the electrochemical removal of copper ions from spent cooling lubricants in form of solutions and emulsions.

This paper escribes for the first time a technology that was worked out in co-operation with German Wire Drawing Industry to deposit copper from spent lubricant solution, which were used in chemical steel wire coating processes. These solutions contained mainly Cu^{2+} ions in the concentrations range between 5 and 12 g dm^{-3}, Fe^{2+} between 6 and 35 g dm^{-3}, Fe^{3+} between 0.5 and 3.5 g dm^{-3}, and H_2SO_4 until 85 g dm^{-3}. It was not the aim to remove the iron because the wire producer wished to use it for flocculation in the company-own waste water treatment plant. However, copper concentration should be removed down to mg dm^{-3} concentration level.

First experiments were carried out at room temperature (20-30°C) using a laboratory 5 dm^3 - parallel plate electrode cell with and without plastic separator and a undivided modified 28 dm^3 - commercial cell (*Hereaus*) equipped with steel plate cathodes and extended mesh anodes. The results did show that copper removal is possible until ca. 1 g dm^3. Dendritic powder formation was observed when depletion was continued to still lower concentrations.

As a consequence of all preliminary experiments, a decision was made to develop a 2-step technology for copper removal. For depositing copper until 1g dm^3 concentration level a special cell was designed (left cell in Fig. 1) having 10 plate cathodes, 11 extended mesh anodes, and a volume of 390 dm^3. For higher depletion down to lower mg dm^3 concentrations, a variant of the so called Vertically Moving Particle Bed reactor [3], developed and constructed in-house (*Dr. Rittel GmbH*), was used, able to work until a current load of 200 A (cell at the right in Fig. 1). This technology was transferred into practice.

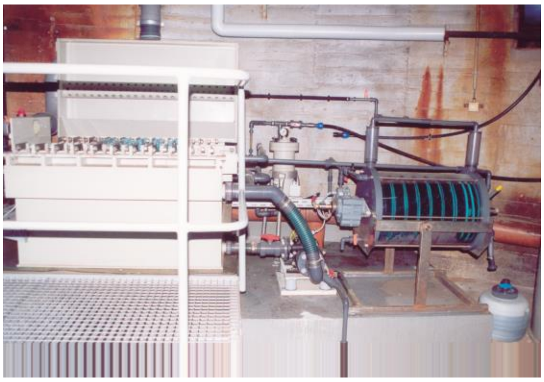

Fig. 1 The 2-cell technology under practical operation

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Micro-structured Pyramidal Arrays as a Rough Electrode Model for Validating Electrode Simulations

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The surface morphology of an electrode affects the electrochemically active surface area [1] and the redox species concentration gradient within the diffusion layer [2]. While several studies have been carried out to find a correlation between the electrode surface roughness and its electrochemical properties, the interfacial features of electrodes are often modeled as disordered fractals [3] which complicates direct comparison between the models and experiments. In this study, to quantify the electrode roughness effect on the electrode kinetic properties and mass transport behavior, an electrode containing a well-defined and regular pyramidal micro-array was used as a model rough electrode.

The micro-structured pyramidal arrays were fabricated over a glass substrate using nano-imprint lithography method and were coated by a 120 nm thick layer of Au. The pyramids fabricated in this work were found by SEM to be consistent in shape (Fig 1.a), with a tight size distribution of 5 micron in height. Cyclic voltammetry in sulfuric acid was used to calculate the electrocatalytically active surface area (EASA) of both gold electrodes, using the charge transferred during reduction in acidic electrolytes (Fig 1.b). The electrochemical responses of a patterned Au electrode was compared to a flat Au electrode coated onto a glass substrate for an iron redox couple (1.c), with a numerical simulation applied to elucidate the mass transport behavior of the redox species near the electrode surface.

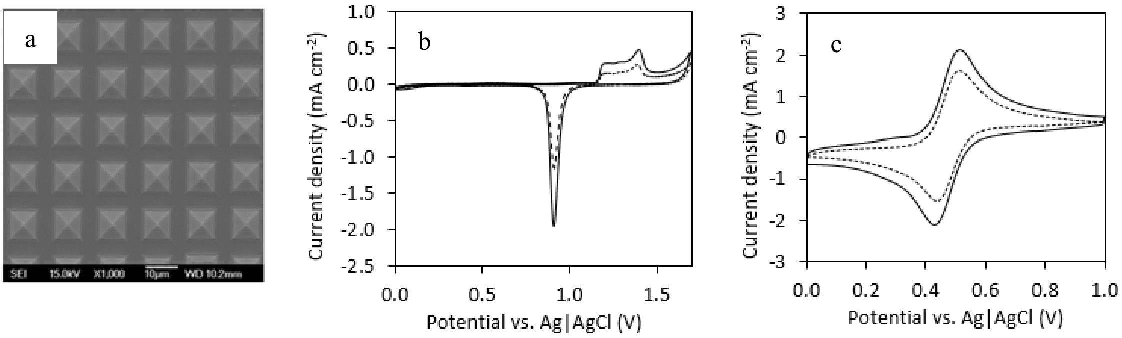

Figure 1: a. SEM micrograph at 1000 times magnification of patterned gold surface. b. Cyclic voltammetry of patterned gold (solid line) and flat gold (---), recorded at 100 mV s^{-1} in 0.5 M H_2SO_4. c. Cyclic voltammetry of patterned gold (solid line) and flat gold (---), recorded at 2 V s^{-1} in 1 mM Fe^{2+}/Fe^{3+} in 0.5 M H_2SO_4.

The SEM micrograph of a patterned gold electrode (Fig 1.a) shows a highly ordered pyramidal pattern of tunable height, highlighting the utility of the nano-imprint lithography method. The larger gold oxide reduction peak of the patterned Au electrode present at approximately 0.9 V in Fig 1.b was expected and is a result of increased electrochemically active surface area, provided by the micro-structure pyramidal arrays. The cyclic voltammogram of the gold electrodes at a scan rate of 2 V s^{-1} (Fig 1.c) indicate that the rough electrode leads to an increased current at all potentials at fast scan rates due to the increased mass transport to the surface.

Due to the fast scan speed, the diffusion layer thickness is relatively thin and therefore the difference in concentration profile along the pyramids is significant and increases mass transport to the surface. Computational modelling has been carried out to account for the pyramidal array morphology of the electrode and to evaluate the effect of scaling the geometric parameters and potential sweep rate. Understanding the effect of the surface roughness will allow for intelligent design of electrodes that maximize the kinetics and mass transport behavior of a redox system.

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Covalently grafted Aryl Layers on Tin(IV) Oxide: Tuning the Surface Conductivity

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SnO_2 is a member of an interesting class of materials that are both simultaneously transparent and conducting. At the surface of these materials the valence and conduction bands bend downward to form a quantised potential well and an electron accumulation layer. For SnO_2 this effect arises from the adsorption of H adatoms giving a hydroxyl-terminated surface. As an earth-abundant, low toxicity material, SnO2 has promise for devices such as transparent thin-film transistors, however for such applications, the surface conductivity must be removed.

Our work aims to tune the surface bending of SnO_2 and similar materials by grafting thin organic layers to the surface. Aryldiazonium salts are well-known as highly versatile reagents for surface modification and several studies using metal oxide substrates have provided evidence for metal-O-aryl bonding. We have investigated spontaneous and electrochemical grafting of aryl derivatives to epitaxially grown thin films of SnO_2(101) and have characterized the resulting materials using atomic force microscopy (AFM) and highly surface-sensitive synchrotron-based X-ray photoelectron spectroscopy (XPS). Aryldiazonium salts with electron-withdrawing and electron-donating substituents were selected with the expectation that the electron accumulation layer (and surface band bending) could be tuned according to the molecular dipole. XPS data confirm that aryl groups are covalently bonded to the surface and valence band spectra reveal that all grafted layers change the surface band bending. However for some derivatives the magnitude and direction of band bending changes were unexpected and computational studies are underway to provide further insight into our experimental findings.

Short-Time Electrodeposition of Ni/CoNi Hydroxides on GaAs under Growth-Inhibition Condition for Photoelectrochemical Water Splitting

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Photoelectrochemical (PEC) cells enable the direct storage of solar energy into the chemical bonds of hydrogen or light hydrocarbons, potentially overcoming the discontinuous solar energy output due to its intermittent availability.[1] n-GaAs is a promising photoanode as it provides a suitable bandgap (1.43 eV) to absorb energy from the solar spectrum (<867 nm) and a more negative photocurrent onset compared to silicon.[2] Bare GaAs, however, suffers from photocorrosion under water oxidation conditions, leading to insulating oxide layer formation or dissolution. Efforts to overcome the instability of GaAs include the addition of protective layers, such as noble metal films, polymer coatings, or atomic layer deposition of TiO_2. These approaches nonetheless require expensive materials and/or complicated deposition techniques, limiting scalability. Additionally, the Fermi-level pinning caused by the formation of large Schottky barrier due to a continuous metallic layer, leads to a reduced photovoltage. In this scenario, a simple and cheap approach to form ultra-thin protective GaAs films with optimal junction behavior is desirable.

Herein, inhibited electrodeposition is carried out to form fine Ni or CoNi hydroxide layer/particles on GaAs substrates. Self-limiting growth is evidenced by XPS, showing that the deposition time is independent of the layer thickness of ~10 nm for both Ni and CoNi deposition. Short-time deposition ($t \leq 1.0s$) is investigated to achieve the optimum compromise between the formation of a sufficiently protective layer while simultaneously minimizing the reduction of incident light absorption by the particles/layer. Compared with pure Ni deposition, alloying with Co leads to a slower growth rate of the hydroxides, probably implying that the grain size for CoNi hydroxides is smaller than that for Ni hydroxides. Both Ni and CoNi deposition lead to a high photoresponse (9.4 mA cm^{-2} for 0.2s-deposited Ni; 8.9 mA cm^{-2} for 0.5s-deposited CoNi) and slow photocorrosion in an aqueous solution containing $K_3Fe(CN)_6/K_4Fe(CN)_6$ under 1.5G AM solar illumination. The photocurrent decreases when deposition time is above 1s, probably due to the reduced absorption of photons and changes in the junction barrier height as a continuous layer is formed. The CoNi deposited on GaAs exhibits improved photoresponse and stability compared to Ni deposited on GaAs at an applied potential of 1.23V vs. RHE under light for 300s, attributed to a finer particle size and an increased catalytic property of CoNi vs. Ni.

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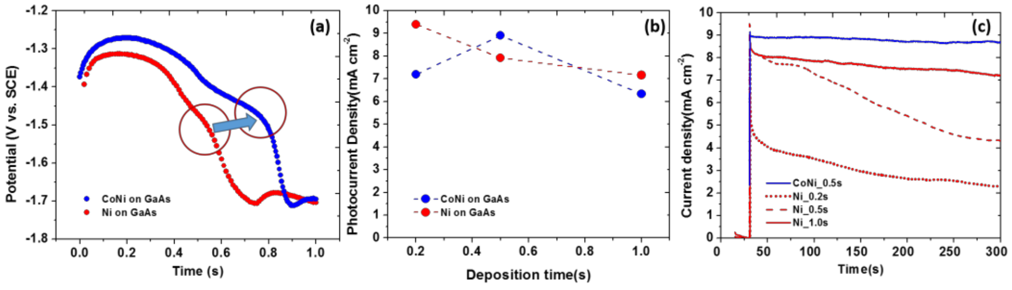
Figure 1. (a) Potential transients during a galvanostatic deposition for Ni and CoNi on GaAs substrate. The potential changes marked in red circles are an indicator for the growth-inhibited nucleation.[3] For CoNi deposition, this process is delayed compared with Ni deposition, probably due to a slower formation of hydroxides. (b) Photocurrent density at 1.23V vs. RHE under AM 1.5G solar illumination for Ni-deposited and CoNi-deposited GaAs with different deposition times. (c) Photocurrent density at 1.23V vs. RHE measured in the first 300s in the same condition as (b), where the 0.5s-CoNi deposited GaAs exhibits optimum photoresponse and stability.



Atomically Precise Gold Clusters for Electrocatalytic CO_2 Reduction

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Electrocatalytic reduction of CO_2 into fuels has the potential to "revolutionize green energy technologies" [1], although there are significant challenges that must be overcome before this technology is viable [2]. In particular, it is critical to find a material that can catalyse the reaction both efficiently and selectively. Gold electrocatalysts can fulfill these requirements as they can exhibit high CO selectivity at relatively low overpotentials [3, 4].

In order to tailor the electrocatalytic properties of gold-containing cathodes, atomically precise ligand-protected gold clusters (Au_6, Au_9, Au_{13} and Au_{101}) have been chemically synthesized and adsorbed onto carbon paper substrates. These cluster-coated electrodes were then used for CO_2 reduction in aqueous $KHCO_3$ electrolytes, and have shown very high Faradaic efficiency towards CO (80 - 90 %) at -1.5 V *vs.* AgAgCl, using relatively low gold loadings (90 μg/cm^2). Importantly, while these gold clusters do undergo partial aggregation during the CO_2 reduction reaction, the clusters maintain high selectivity over 4 h of electrolysis, with both cyclic voltammetry and XPS analysis suggesting that these cathodes still exhibit some cluster specific properties. While all four clusters (Au_6, Au_9, Au_{13} and Au_{101}) have almost identical selectively towards CO, when the cluster-coated electrodes are calcined at 200 °C, the selectivity towards CO decreases, with this loss in selectively greatest for the smaller clusters. This is accompanied by a clear shift in the Au 4f binding energies towards values typical for bulk gold (as measured by XPS), suggesting that the high selectively is due to active sites unique to the gold clusters.

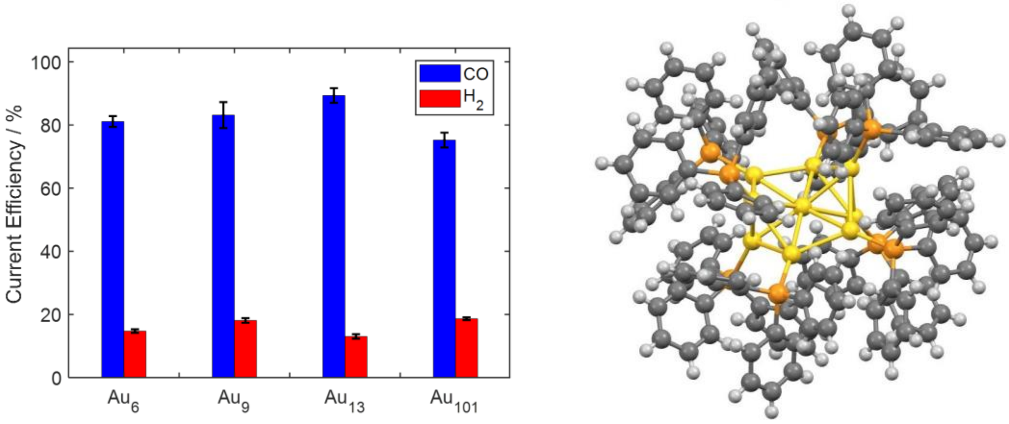

Figure 1: (left) Current efficiency of gold clusters at -1.5 V *vs.* Ag|AgCl for CO_2 reduction in 0.2 mol L^{-1} $KHCO_3$ saturated with CO_2. (right) "ball-and-stick" plot of the crystal structure of phosphine-protected Au_9 cluster (Au – yellow; P – orange; C – grey; H – white; counter-ions are omitted for clarity).

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Potential-Dependent Adsorbed Structures of Oxygen Species on Pt(111) Single-Crystal Electrode during Oxygen Reduction Reaction Investigated by *In situ* Surface X-ray Scattering

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Platinum is one of the most important electrocatalysts, especially for the oxygen reduction reaction (ORR) which is a key reaction of the polymer electrolyte membrane fuel cell (PEMFC), and therefore the potential-dependent structures at the Pt(111) single-crystal electrode/electrolyte solution interfaces have been extensively studied as a model system for the Pt electro-catalysts using various surface techniques [1-6]. Because of the lack of a suitable *in situ* technique to detect the oxygen species, which is adsorbed on the electrode surface as a reaction intermediate during the ORR, however, quantitative elucidation of the ORR mechanism has not been reached yet. Thus, the clarification of the adsorbed structure of the oxygen species on the Pt electrocatalyst surface is a considerable progress in elucidation of the ORR mechanism.

Using the *in situ* surface x-ray scattering (SXS) technique with the spectro-electrochemical cell in the thin-layer configuration [7], we have determined the detailed structures of various electrochemical interfaces in a static state, such as three-dimensional arrangements of deposited metal atoms and adsorbed molecular/ionic species on the single-crystal metal surfaces [8-12]. Here, we have successfully determined the structure of the intermediated oxygen species during the ORR. The potential-dependent structure of the Pt(111) single-crystal electrode/oxygen saturated perchloric acid solution interface was investigated by *in situ* SXS. In the potential region where the ORR takes place, the $(2.255\times2.255)R3.67°$ super-structure on the Pt(111)-(1×1) surface was observed based on the results of the crystal truncation rod (CTR) and surface x-ray diffraction (SXRD). Because such a super-structure is not observed in the oxygen-free electrolyte solution and the SXRD intensity due to such a super-structure indeed correlates with the cathodic current for the ORR, we concluded that the super-structure of the adsorbed oxygen species is formed as an intermediate state of the ORR. Because the SXRD intensity due to the (1×1) structure of the surface hydroxyl group adsorbed at the atop site showed totally opposite potential dependence behaviors, moreover, it was suggested that its adsorption controls the ORR [13,14].

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Combination of Solid-Oxide Pellet and Gel Polymer as Electrolyte for Quasi-Solid Lithium-Ion Batteries

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Typical lithium ion batteries (LIBs) contain organic liquid electrolytes; those liquid electrolytes can be replaced with ceramic solid-oxide electrolytes (SEs) to remedy various safety problems. SEs offer a wide electrochemical potential range and open the gateway for the use of high-voltage cathodes. However, the poor ionic mobility at the cathode–SE interface has yet to be resolved. This study reports quasi-solid LIBs with outstanding performance. These LIBs were assembled using a garnet-type $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$ (LLZTO) electrolyte pellet and a high Li^+ transference gel polymer electrolyte (GPE) to interface the LLZTO pellet and cathode.

We propose a high Li^+ transference GPE as an interlayer to comply with the unity Li^+-transference number in SEs. In comparison with an LE, the GPE localizes PF_6^- anions and thus minimizes ion-solvent clusters in the electrolytes to facilitate effective Li^+-ion motion. The proposed GPE exhibits a high Li^+ transference number of 0.67, which suppresses polarization in the interface caused by PF_6^- accumulation.

When assembled using a thin Al component and the aforementioned GPE as the anode–LLZTO and cathode–LLZTO interlayers, respectively, an Li|(Al/LLZTO/GPE)|$LiFePO_4$ battery delivers discharge capacities of 156 and 121 mAh g^{-1} (based on $LiFePO_4$) at 0.1 and 2 C-rate, respectively, at 25 °C. Benefitting from its high Li^+ transference, this quasi-solid battery exhibits high electrochemical stability, achieving 94% capacity retention after 100 continuous charge−discharge cycles at 0.1 C.

The combination of the LLZTO and GPE regulates the transport of Li^+ ions for even plating or stripping of a Li-metal electrode. This advantage enables the GPE to replace the Al component as the interlayer between the LLZTO pellet and Li-metal anode.

Importance of molecular orientation for direct electron transfer and (photo)electrochemical sensors

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Orientation and conformation of molecules on electrode surfaces play important roles in determining direct electron transfer (DET) and performance of (photo)electrochemical sensors. We used surface enhanced infrared absorption spectroscopy (SEIRAS) and electrochemical techniques to study the influence of surface properties (charges and wettability) on the orientation and conformation and related DET of immobilized proteins, and the influence of molecular orientation on the performance of (photo) electrochemical sensors. It is found that the surface charges modulate the orientation and direct electron transfer of the immobilized proteins (e.g., cytochrome C). Negatively charged surface will not change the DET rate, but decrease the amount of electroactive proteins via electrostatic repulsion. On the contrast, positively charged surface significantly decreases the DET rate via conformation change. In addition, the surface wettability affects the orientation of proteins as well. Cytochrome C on hydrophilic surface takes right orientation and its DET can easily occur; while on hydrophobic surface, the DET is completely inhibited which is confirmed by assembled porphyrin with defined orientation at electrode surface. Based on the above understanding, a high performance photoelectrochemical sensor has been established with porphyrin plane parallel to the electrode surface.

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Electrochemical Study of the Corrosion Resistance of Rheo HPDC Al–Si Alloys and New Conversion Coatings

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Corrosion properties of two Al–Si alloys processed by Rheo-high pressure die cast (HPDC) method were examined using polarization and electrochemical impedance spectroscopy (EIS) techniques on as-cast and ground surfaces. The effects of the silicon content, transverse and longitudinal macrosegregation on the corrosion resistance of the alloys were determined.

Microstructural studies revealed that samples from different positions contain different fractions of solid and liquid parts of the initial slurry. Electrochemical behavior of as-cast, ground surface, and bulk material was shown to be different due to the presence of a segregated skin layer and surface quality.
Cerium-based conversion coatings were afterwards deposited on high pressure die cast (HPDC) Al-Si alloys using an immersion method. Hydrogen peroxide and sodium chloride were added to the conversion solution to accelerate the coating formation and to understand its formation mechanism.

These studies showed that the deposition of cerium hydroxide/oxide conversion layer starts from iron-rich intermetallic particles, which are located inside the eutectic region and then the coating growth continues to cover the entire alloy surface. This phenomenon passivates the active interfaces between iron-rich intermetallic particles and/or the eutectic silicon phase and the aluminum matrix, which are prone to localized corrosion in chloride ions containing environments. Accordingly, values of the total impedance in EIS measurements significantly increased for the treated substrates.

Morphologies of the conversion coatings and the oxidation state of cerium compounds were found to be dependent on the composition of the solution and the presence of chloride ions and/or hydrogen peroxide. Aluminum alloy with higher silicon content showed a more active surface during immersion in the conversion solution. This makes it more difficult to be treated using aggressive conversion solutions.

Acknowledgments

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Characterization and Analysis of Toluene Direct Electro-hydrogenation Electrolyzer for Hydrogen Energy Carrier Synthesis

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Introduction

For the hydrogen energy-based society, the effective introduction and utilization of renewable energy has been the prime task to reduce carbon dioxide emission. Hence, the large-scale transport and storage system of hydrogen has been considered as the important technology. We have studied the high-efficient electrolytic direct-hydrogenation of toluene with water decomposition for the organic hydride system.[1] The electrolytic method has the advantages of small theoretical decomposition voltage and no exothermic heat loss compare with the conventional 2-step hydrogenation with the water electrolysis. In this study, we investigated the effect of electrochemical property with low toluene concentration for the toluene electrohydrogenation electrolyzer, and analyzed the void fraction ($0 \leq s\text{-}1 \leq 1$, s: liquid saturation) in diffusion layer and the mass transfer overpotential with diffusion limiting current.

Experimental

A DSE® electrode for the oxygen evolution (De Nora Permelec ltd), a carbon paper (29BC or 10BC, SGL carbon ltd.) applied 0.5 $\text{mg}_{\text{-PtRu}}$ cm^{-2} of PtRu/C (TEC61E54, TKK) catalyst with ionomer, and Nafion 117® (Du Pont) were used for the anode, the cathode, and the proton exchange membrane (PEM), respectively. The carbon paper as the diffusion layer was loaded 0.02 $\text{mg}_{\text{-Pt}}$ cm^{-2} of Pt particles by the impregnation method for the chemical-hydrogenation catalyst.[2] The cathode was hot-pressed on the PEM at 120 $^{\circ}$C and 0.1 MPa for 3 min to fabricate a membrane cathode assembly. During the operation of the electrolyzer at 60°C, the anode and cathode compartments were circulated 1 mol dm^{-3} H_2SO_4 at 10 ml min^{-1} and 100, 10, 5, 1 or 0% toluene diluted by methylcyclohexane or pure water at 10 ml min^{-1}, respectively. The electrochemical measurements were conducted for the linear sweep voltammetry (LSV), the electrochemical impedance spectroscopy (EIS), chronoamperometry (CA) the current efficiency measurements. Furthermore, the pressure loss measurement performed for the cathode side of electrolyzer during operation.

Results and discussion

Figure 1 shows the current density dependence of void fraction in cathode diffusion layer for toluene direct electro-hydrogenation electrolyzer. These curves simulated using the equations of the relationships of capillary pressure and *Leverett*'s function and the permeability of porous from pressure loss measurement. The void fraction in the cathode catalyst layer increased with decrease of toluene concentration. For toluene direct electro-hydrogenation electrolyzer, when the shortage of toluene supply to the cathode catalyst occurs, hydrogen gas generates by the proton. Hence, this tendency for the decrease of toluene concentration represented in Figure 1. Above 0.25 A cm^{-2}, the void fraction showed the saturation or the decrease except for water. This tendency was strong to low toluene concentration. This reason was considered the accumulation of the water in the catalyst and diffusion layers through the PEM from anode.

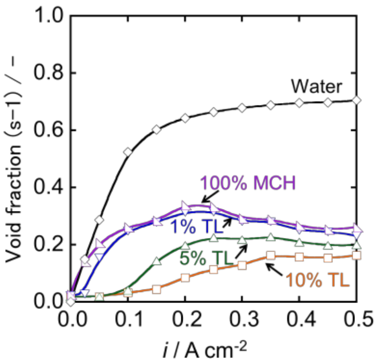

Figure 1. Current density dependence of void fraction in cathode diffusion layer for toluene direct electro-hydrogenation electrolyzer.

Acknowledgements

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Tris (2,2′-bipyridyl) ruthenium(II) Electrochemiluminescence of Some Oxygen-Containing Organic Additives in Food and Cosmetic

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Electrochemiluminescence (ECL) is a light-emitting phenomenon resulting from electrochemical reaction. It plays important roles in *in vitro* diagnosis (IVD), light-emitting devices, mechanism study, and so on [1]. Tris(2,2′ -bipyridyl)ruthenium(II) ECL have been the most studied because of their outstanding properties, such as high ECL efficiency, good stability, and broad applications. Co-reactants are often involved in $Ru(bpy)_3^{2+}$ ECL for analytical applications. Typical coreactants include aliphatic amines, oxalate, and $S_2O_8^{2-}$ [2－9]. The $Ru(bpy)_3^{2+}$ ECL of these coreactants has been extensively studied. In contrast, the $Ru(bpy)_3^{2+}$ ECL of oxygen-containing organic compounds, such as esters, ketones, aldehydes, alcohols, is seldom studied and are unpredictable.

Oxygen-containing organic compounds are frequently used as additives in food and cosmetic. Their detection is quite important. However, most detection methods require derivitization or costly instruments. We present here our recent study of $Ru(bpy)_3^{2+}$ ECL of several commonly-used oxygen-containing organic additives, such as ethyl formate, 1,3-dihydroxyacetone, and sodium dehydroacetate. These additives exhibit intense ECL, enabling their direct detection by $Ru(bpy)_3^{2+}$ ECL without any derivitization. These results promote the study of electrochemistry of oxygen-containing organic compounds and the applications of $Ru(bpy)_3^{2+}$ ECL in the detection of oxygen-containing organic compounds

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Imaging Oxygen Evolution Reaction Activity on Au$_{poly}$ Electrodes

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Heterogeneous water-based fuel cell chemistry underpins a future hydrogen economy without net CO_2 emission. A better understanding of the underlying processes is needed to improve the economically not yet viable catalysts for such chemistry. For any catalytic reaction, a fraction of the available sites, i.e. the *active sites*, are considered to be responsible for the entire reactivity [1]. The investigation of active sites in heterogeneous catalysis is typically done on model systems in ultrahigh vacuum [2]. However, transfer of knowledge obtained in this fashion to real world catalysts, particularly to heterogeneous chemistry at solid/liquid interfaces, is generally not possible [3].

Here we present an approach to investigating active sites, or areas, of more complex catalysts under conditions close to application: the Oxygen Evolution Reaction (OER), the oxidation side of water electrolysis, on a polycrystalline gold foil in 0.5 M Na_2HPO_4 (pH = 9). To explore the dependence of OER activity on surface structure, we performed voltammetric and amperometric experiments, while monitoring the surface with Second Harmonic Generation (SHG) microscopy at $\lambda_{fundamental}$=1030 nm. As shown below, SHG microscopy makes it possible to monitor where O_2 bubbles nucleate, grow and detach during the OER. SHG microscopy was preferred over linear microscopy due to better contrast and shorter acquisition times.

Above 2 V vs. the Reversible Hydrogen Electrode (RHE), we observed evolution of O_2 bubbles to be constrained to small (10s of µm), but highly active, areas. The current related to O_2 formation in these areas is qualitatively the same as the measured electrochemical current as a function of potential. We conclude from this correlation, that the measured electrochemical current is dominated by the OER at active spots covering 1-8 % of the surface. The formation and/or stabilization of these active areas results from the combination of a structural defect penetrating to the bulk and a sufficiently thick layer of oxide. The former ensures that the active area is stable with respect to surface reconstruction during electrochemical cleaning, while the latter is apparent in the images collected at potentials cathodic of bubble generation. Surprisingly, formation of O_2 bubbles was also observed below 2 V RHE on what we argue are highly active surface defects, that are not stable with respect to surface reconstruction. Finally, we discuss the relationship of surface heterogeneity and reactivity and the implication of our results for the design of future catalysts.

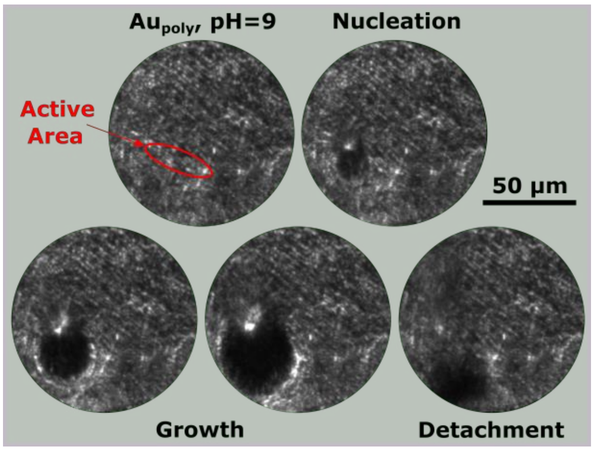

Figure: SHG micrograph of a polycrystalline gold surface in 0.5 M Na_2HPO_4 (pH = 9) at 2.1 V vs. RHE. The diameter of the field of view is ~100 µm. The top left shows the active area exclusively from which O_2 bubbles emerged encircled in red. Top right to bottom shows nucleation, growth and detachment of a single O_2 bubble over the

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Molecular Electrocatalytic Reaction at the Electrode/Electrolyte Interface by In-situ Scanning Tunneling Microscopy

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The electrode/electrolyte interface plays a critical role in the performance of electrochemical energy storage and conversion devices. Understanding the structure and reaction processes at solid/liquid interface is of great importance in surface science and electrochemistry. Metalloporphyrins, a model system of the metal-organic catalysts for different electrocatalytic processes, have attracted considerable attention for the advantages of high efficiency and low cost. Understanding the catalytic role of the active sites in molecular catalysts facilitates the design of high performance metal-organic catalysts. Electrochemical scanning tunneling microscopy (ECSTM) is a powerful technique for investigating electrocatalytic reaction at solid/liquid interface at the molecular scale. In this presentation, we discuss the application of the high resolution ECSTM to study the interfacial electrochemical reactions by molecular catalysts at molecular level. The time evolution of molecular metalloporphyrins and metallophthalocyanines in several important electrocatalytic processes, such as oxygen reduction reaction, oxygen evolution reaction, can be resolved at the different potential and different electrolyte environment.

Bubble Formation at Porous Electrodes

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Porous electrodes for PEM electrolyser and fuel cell technologies are optimized primarily to provide a high specific surface area for the desired electrochemical reactions. However, the increase in surface area comes at the cost of increased voltage losses due to the transport of reactant and product species through the porous medium. In gas evolving porous electrodes, the formation and transport of gas bubbles plays an important role: on the one hand, gas in the pores replaces the electrolyte phase, thus hindering ion transport and reducing the effective ionic conductivity in the porous electrode; on the other hand, gas bubbles cover and deactivate a portion of the catalyst surface area.

Gas formation and removal must be accounted for in the design of electrolyzer electrodes. The presented work strives to unravel the fundamental relationships between structure, properties and performance of porous gas-evolving electrodes. The approach combines a macro-scale performance model of the electrode with a micro-scale model of gas evolution. At the macro-scale, a classic porous electrode model describes the transport of ions, electrons and oxygen using concepts of statistical physics of random composite media and accounting for the gas phase volume and distribution.

The micro-scale model describes the formation and growth of gas bubbles based on chemical energy considerations. It can explain the experimentally found high oversaturation that is necessary to nucleate bubbles [1]. Additionally, the size of the bubble nucleus in the experiment was estimated.

The model rationalizes the influence of structural parameters on the operation of porous electrodes and yields guidelines for electrode design [2]. The transport regime of the dissolved gas, which is controlled either by diffusion or transfer at the liquid-gas interface, determines the bubble growth law. The model was used to explore the idea of placing preferential nucleation sites onto the electrode surface, as illustrated in Figure 1. This structural modification results in a significant performance enhancement. Since it is energetically favourable for dissolved gas to transfer into an existing bubble formed at a nucleation site, the nucleation of new bubbles in its neighbourhood will be suppressed. This effect allows optimizing the performance of gas-evolving electrodes by controlling the placement of nucleation sites.

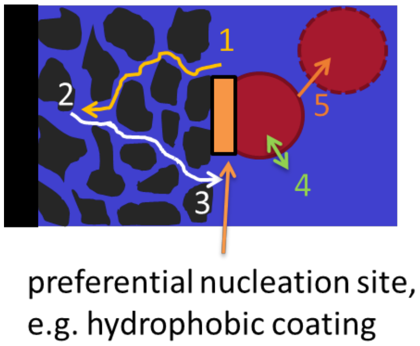

Figure 1: Bubble growth on a preferential nucleation site on a porous electrode. 1 ion transport; 2 electrochemical reaction; 3 dissolved gas transport; 4 gas transfer into the bubble; 5 bubble detachment.

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Negative electrodes for Na-ion batteries and solid-state batteries

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This presentation will discuss negative electrodes for sodium-ion batteries (SIBs) and solid-state batteries (SSBs). Firstly, we discuss an unconventional route for utilizing graphite as electrode for SIBs. We discuss an electrode reaction based on intercalating solvated sodium ions rather than naked ions.[1-2] We show that this process is highly reversible and the redox potential can be tuned by the type of solvent and that the family of solvent suitable for this process can be enriched by slight temperature increase. This mechanism leads to large volume expansion yet excellent cycle life is found. The excellent cycle life can be better understood using in situ electrochemical dilatometry. At the same time, the reaction works without a SEI which is a highly unusual case. Secondly, we discuss the use of Sn supported by graphene nanoplatelets for sodium storage and report on a memory effect for Sn when cycling at different currents. Thirdly, we will discuss the use of alloys for solid-state batteries using the Li-In electrode as example. The phase behavior is discussed using coulometric titration and the stability in contact with Li_3PS_4 as solid electrolyte is discussed in relation to the different Li-In intermetallic phases. Finally, a so-far overlooked phenomenon called *sulfur spillover* will be introduced that may have a large impact on metal-sulfur batteries.

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Redox Behaviour of [Ru(β-diketonato)$_3$] Complexes

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The [Ru(acac)$_3$] (Hacac = acetylacetone) complex has been known since 1914,[1] and has been investigated amongst others for use as catalyst[2] and as electrolyte in nonaqueous redox flow batteries.[3] The redox behaviour of several [Ru(β-diketonato)$_3$] complexes has previously been reported (β-diketonato = (RCOCHCOR′)$^-$, with groups R and R′ in different combinations of CH_3, Ph, CF_3, C_4H_3S, C_4H_3O and ^{t}Bu). It was found to be related to the sum of the Hammett constants of the R and R′ substituents on the β-diketonato ligands.[4] The Ru(III)/Ru(II) redox couples of these complexes have been used to construct the Lever ligand electrochemical parameter, E_L(L).[5] The Ru(III)/Ru(II) and Ru(III)/Ru(IV) redox couples of complex [Ru(acac)$_3$] were used to illustrate that ferrocene can be used as an internal standard for electrochemical measurements, irrespective of the reference electrode.[6] Although computational chemistry can confirm the locus of the redox processes and can be used to calculate and predict redox potentials, virtually no combined electrochemical and computational chemistry study has been performed on a series of these [Ru(β-diketonato)$_3$] complexes.

In this contribution, a relationship was found between the experimentally measured redox potentials of both redox processes observed, and the following calculated electronic properties: the DFT calculated energies of the molecular orbitals involved in the observed redox processes, as well as electron affinity, ionization potential, electrophilicity index,[7] Mulliken electronegativity[8] and molecular electrostatic potential of the Ru metal, see Figure 1 as example. An analysis of the electronic structure and molecular orbitals of these complexes shed further light on these results.

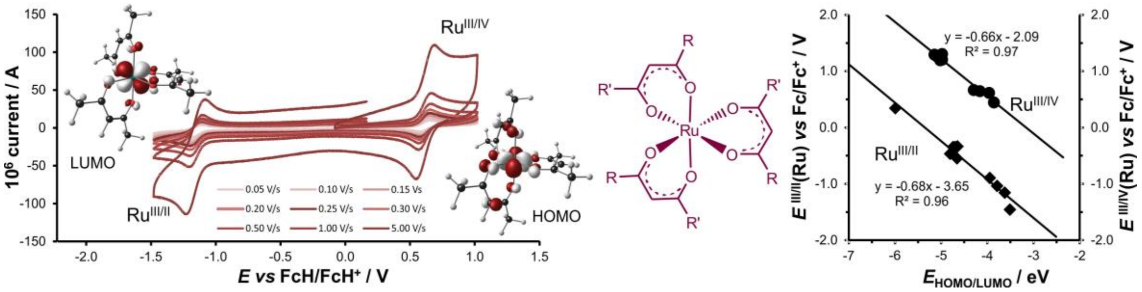

Figure 1. Left: Cyclic voltammograms of a 0.001 mol dm^{-3} solution of complex [Ru^{III}(acetylacetonato)$_2$] at the indicated nine scan rates, in 0.100 mol dm^{-3} TBAPF$_6$/CH$_3$CN, including the molecular orbitals involved in the observed redox processes. Right: Relationship between the experimental redox potential of the Ru$^{III/II}$ (y-axis left) and Ru$^{III/IV}$ (y-axis right) redox couples, *versus* the DFT calculated energy of the LUMO and HOMO respectively, for a series of [Ru(RCOCHCOR′)$_3$] complexes (structure in middle).

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Atomistic insights on the electrode material CuDEPP: Combining the advantages of batteries and super capacitors

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Devices for electrical energy storage need to provide high energy yields as well as output power while at the same time guaranteeing safety, low costs and long operation times. The porphyrin CuDEPP [5,15-bis(ethynyl)-10,20-diphenylporphinato]copper(II) is a promising electrode material for various battery systems both as anode or cathode. In contrast to the slow discharge/charge processes in traditional lithium-ion batteries, the CuDEPP electrode features a fast redox conversion in which up to four electrons are transferred. CuDEPP combines the positive properties of lithium ion batteries (high energy density) with those of a supercapacitor (fast electron release and absorption). While its functionality has been demonstrated experimentally,[1] there had been no atomistic information as to why CuDEPP expresses these interesting properties or how the incorporation of ions affects its structure.

To answer these questions, we have investigated CuDEPP using density functional theory (DFT). Starting with the smallest possible unit (*i.e.* a single molecule) we successively increased the spatial dimensionality of the structure by studying: a) di- and trimers, b) molecular stacking in a 1D chain, c) extending these chains to planar CuDEPP sheets and finally c) a three-dimensional extended polymer structure. Combining the individual results of the molecule, the chain, the plane and the extended polymer lead to a comprehensive and consecutive understanding of the CuDEPP system.

Having thoroughly investigated the isolated properties of the CuDEPP material itself, afterwards the insertion (or intercalation) of different ions (including Li, Mg and Na) has been studied, in order to understand the energetics, diffusion barriers and structural changes (*e.g.* volume expansion) within the CuDEPP host material. Based on the optimal ion intercalation structure, discharge voltage curves have been calculated. The thus-obtained cell voltages can be directly compared to experimental measurements.

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An in-situ formed carbon-based anode system for water splitting

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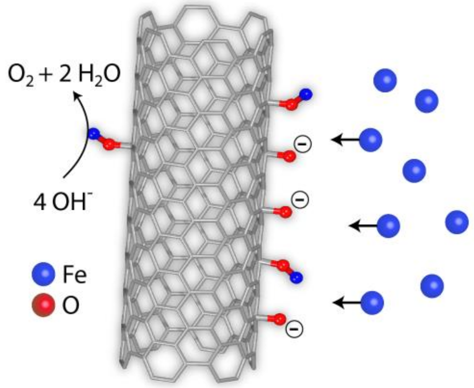
The energy challenge has been considered as a major challenge for today's society and future generations. The conversion of electricity into chemical energy is a critical process in the network of chemical energy conversions.[1] Electrolytic water splitting is of high relevance, and the most difficult elementary step is in oxygen evolution reaction (OER). Noble metal oxides such as IrOx are highly active and show relatively good chemical stability as OER catalysts, but their supply is not scalable, which limits their application. Although some of the first-row transition metal oxides and their hybrids exhibit appreciable reactivity, the stability is still far from satisfactory.[2] The intrinsically insufficient conductivity is another issue for transition metal oxides. Carbon materials, such as graphene and multi-walled carbon nanotubes (CNTs) are used as supports to provide efficient charge transport. Due to the environmental acceptability, high surface area and excellent electron transfer ability, carbon materials especially heteroatom doped ones are also being used as low cost metal-free catalysts for OER. However, no matter as supports or as catalysts, the influence from the carbon surface functional groups and defects are almost inevitable, which also leads to controversial conclusions, despite strong statements in the literature. We find that a functionalized carbon nanotube, by in-situ trapping trace iron in electrolyte, can form a highly effective catalytic system for water splitting. This in-situ formed anode system exhibits surprisingly high activity and stability. Oxygen functional groups on the carbon surface are confirmed to play the key role to form the catalytically active C–O–Fe species. No valence change happens for the carbon materials during the catalytic process, thus endowing a remarkably improved stability as compared to the traditional metal-based anodes. This unprecedented finding provides a methodology to develop scalable and high performance carbon-based electrode systems for electrolysis.



Scheme. The designed anode system. The functional groups on the CNT surface adsorb the iron species to form the real active sites for the oxygen evolution. The iron and oxygen represent their relative species.

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How can DFT and vibrational spectroscopies work synergistically to reveal electrochemical reactions and interfacial structures

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Spectroelectrochemistry can obtain the molecular fingerprint information in real time under electrochemical conditions, and to reveal the electrochemical processes at the molecular level. However, so far most *in-situ* vibrational spectroscopic (mainly Raman and IR) studies have been carried out on surface adsorption. It's a great challenge to move forward to study surface reaction especially to identify reaction intermediates and thus reveal the true reaction mechanism. This is mainly because that the surface reaction intermediates have short life time and are hard to be mimicked by the solution species. For achieving this goal, *in-situ* spectroscopies must combine with theoretical and EC methods for identifying unknown intermediates.

We'll discuss the SERS-DFT study on the electrocatalytic reduction of benzyl chloride on Ag by combing experiments and DFT calculations. The detailed analysis on the results indicate that the strong and broad Raman band can be assigned as two reaction intermediates. In light of the consistent EC-SERS observations and DFT simulations on the spectra, the details of the electrocatalysis regarding the binding energy and the activation energy of reactants and intermediates can be provided.

Recently we have also developed a methodology by integrating the surface charged method, the implicit solvation model, and the finite difference method to precisely reproduce the measured potential-dependent IR and Raman spectra with not only frequencies but also intensities. The later has been very difficult to be realized so far. Some preliminary results show that the as-developed method could be affective to deeply reveal the EC interfaces and processes.

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Investigation of cell microenvironment effect on cell behaviors using electrochemical scanning probe microscopy

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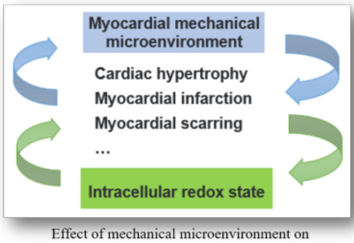
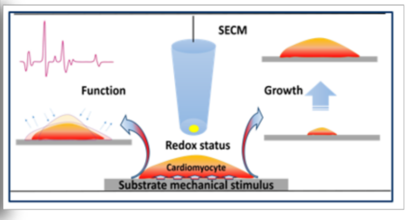
Cell microenvironment (chemical, mechanical, electric) directly effects cell functions and behaviors (biology, mechanics, electrophysiology). Study of cell microenvironment effect on cell functions and behaviors is important for understanding the pathological mechanism of diseases (heart disease, cancer). Different kinds of hydrogels, which is an ideal material to mimic 3D extracellular matrix (ECM) of cell, have been developed and used to construct 3D cell microenvironment in vitro. To understand the effect of cell microenvironment constructed by hydrogels on cell behaviors, the technique which can characterize both the property of hydrogels and the topography and multi-behaviors of cells at μm/nm scale in an in-situ, non-damage way is needed. Scanning electrochemical microscopy (SECM) and scanning ion conductance microscopy (SICM) are two kinds of electrochemical scanning probe microscopy with the capability of providing morphology and performing chemical analyses of cells in an in situ, reversible and non-destructive way.

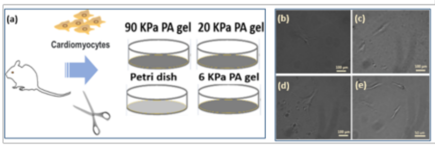
In our work, we firstly constructed cell microenvironment based on three kinds of functional hydrogels (i.e., self-healing hydrogels, magnetic hydrogels and hydrogel microwell arrays). Then SECM was applied to in-situ track the self-healing process of hydrogel, the H_2O_2 consumption across magnetic hydrogel nanocomposites and the oxygen permeability across hydrogel microwell arrays. The effect of mechanical microenvironment on the redox state of cardiomyocytes and cardiac fibroblasts was also characterized by SECM. To further characterize the cell morphology at nm-scale, we also home built our SICM system and used it to characterize the cell morphology and cell volume on hydrogels with different stuffiness.



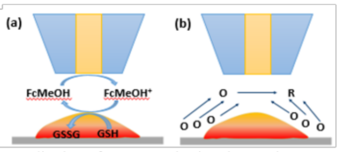
Effect of mechanical microenvironment on cell functions and behaviors



Application of SECM to *in-situ* characterize the effect substrate stiffness on redox state of cardiac cells



Culture cardiomyocytes on hydrogels with different stiffness



Application of SECM to in-situ characterize GSH concentration of cardiomyocytes on hydrogels with different stiffness

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Interfacial architecture of graphene – potential applications in an electrochemical environment

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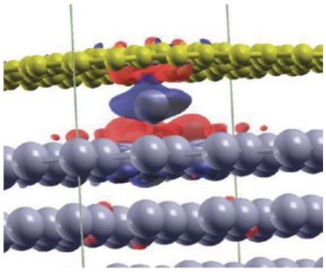
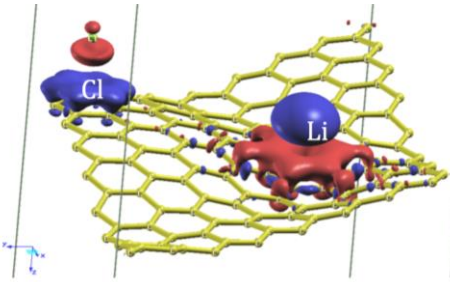
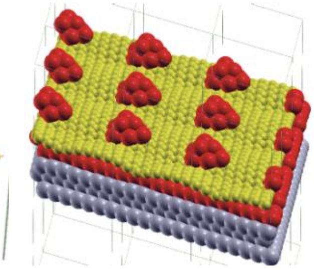
Graphene supported on crystalline metal substrates [1, 2] has recently attracted much attentian. Due to lattice mismatch a well-defined periodic Moiré pattern is formed between graphene and the metal substrate [3, 4]. Both the graphene overlayer and the underlying substrate are locally strained leading to quasi-periodic overlayer buckling and local lateral distortions. This feature provides a natural periodically-templated substrate for self-assembled nanostructures: adatoms, metallic clusters, adsorbed ions. Deposited atoms can nucleate at specific preferred sites and aggregate at these locations, forming a periodic array, which shows different electrocatalytic properties. The presence of topological defects or foreign atoms acts as doping and induces mid gap states. In the framework of a quantum mechanical theory of electron transfer and based on simple analytical models, we found intriguing features in the electron transfer kinetics for the graphene/electrolyte interface as compared with a metal electrode. We have also explored the electron transfer process when mid-gap states are present, and analyzed the effects according to their positions relative to the Fermi level.



Li ion inserted between graphene and Pt(111).



coadsorption of Li and chloride ions at corrugated graphene



Nano-cluster of Rh on Graphene supported on RhML/ Pt(111).

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The impact of a global constraint on electrochemical many particle systems with coexisting states

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Bistability, i.e. the coexistence of different states at identical external parameters, is a frequently encountered phenomenon in electrode reactions. Under a global constraint, such as a constant current in a galvanostatic experiment, the electrode may split spontaneously in a patterned state in which the two states coexist stably on the electrode surface. Moreover, in an array of electrodes, the global constraint might lead to a multitude of phenomena, most importantly sequential activation resulting in a heterogeneous distribution of the two states on the individual electrodes of the array, or to oscillations, as observed during CO oxidation on an array of Pt electrodes (1,2). In some respects, these intrinsically nonequilibirum systems are similar to systems exhibiting first order phase transitions. In electrochemistry, insertion batteries are an important example of the latter, where the two phases are associated with charged and discharged particles of the insertion material. Hence, a battery under charging / discharging conditions can be classified as a many particle phase transition system under a global constraint. Thermodynamic analysis showed that peculiar hysteretic behavior seen in experiments can be understood by a 'sequential particle by particle charging/discharging mechanism' (3). In the talk, I will consider bistable electrode reactions and insertion batteries with phase transition under a common framework, and I will demonstrate that in both classes of systems the diverse heterogeneous states originate from the same instabilities.

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Investigating the impact of onion-like carbons on the supercapacitance of Ti_2CT_X MXene

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Increasing energy demands in contemporary society have driven research in energy storage to create devices which emphasize both energy density and power density. The supercapacitor is a key example of such a device. It is a broad category of devices that occupies the middle ground between batteries and capacitors. The purpose of this work is to present a detailed understanding of supercapacitors via an investigation into a class of 2D materials called MXenes as an active electrode material for supercapacitor applications. The bulk of research in MXenes focuses on the MXene Ti_3C_2, which was what the first published study by Gogotsi et al (2011)[1] was focused on. In this study a different titanium carbide MXene, Ti_2C, was investigated as a supercapacitor active material, as well as the influence of another nanomaterial, carbon onions or onion-like carbons (OLCs). This work was partly motivated by the promising results obtained by Melchior et al (2018)[2] on the same titanium carbide MXene and the use of Carbon Nanospheres (CNS) to increase the electrochemical performance. The materials prepared in this work were characterised by a number of physical techniques; including X-ray Diffraction (XRD), Raman Spectroscopy, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-ray Photoelectron Spectroscopy (XPS), and Brunauer-Emmett-Teller surface area analysis (BET). The materials were also characterised using electrochemical techniques such as Cyclic Voltammetry, Constant Current Charge/Discharge, and Electrochemical Impedance Spectroscopy. It was found that the introduction of OLCs into the layered MXene structure increases the long term cycling stability of the material from 80% to > 95% when used in 5% and 10% weight percentages. It was also found to increase the supercapacitance of the MXene in the 5% quantity from 104 F/g to 148 F/g, but decreased the supercapacitance in the 10% quantity from 104 F/g to 92 F/g. The power and energy density also improved in the 5% OLC doped sample compared to the pristine sample for current densities between 0.5 A/g and 5 A/g. Overall, this study showcased the ability of OLCs to improve electrochemical performance of a Ti_2C based supercapacitor.

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Electrochemical determination of tramadol at sulphonic acid-functionalized single-walled carbon nanotube electrode platforms

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In the ever-changing dynamics in society towards just in time, it is important that faster and more cost-effective techniques are developed towards detection of drugs of abuse such as Tramadol to foster and promote public health and enhance societal security and safety as most of these substances are illicitly used in the commission of crimes.

It is noteworthy that literature is awash with different techniques of sensitive detection of Tramadol, such as UV-vis spectrophotometry and HPLC. However, electrochemical methods have been shown to be accurate, more sensitive, selective and more cost-effective, and easy to be miniaturized for portable applications.

Unlike many other drugs, electrochemical detection of tramadol has not been studied. In the last couple of years, only few reports have emerged focussing on gold nanoparticles [1], the use of electrode platforms such as amorphous carbon [2], and graphene oxide-modified multi-walled carbon nanotubes (GO-MWCNTs) [3]. To solve some of the identified challenges such as high oxidation potential and high detection limit, there is a need for continued search for low-cost electrode platforms. In this work, the use of polyaminobenzene sulfonate-functionalized single-walled carbon nanotube (SWCNT-PABS) has been proposed. This presentation will discuss our recent findings in the use of glassy carbon electrodes modified with SWCNT-PABS for the sensitive detection of tramadol at a significantly reduced detection potential. This sensor promises to offer a more cost-effective alternative for potential application in the prevention of drug abuse in public health promotion and management, prevention of crimes in law enforcement, quality control and assurance in pharmaceuticals; and clinical analyses.

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Pt/C Catalyst Degradation in Relation to High Temperature PEM Fuel Cell Operation

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Fuel cells with proton-exchange membrane (PEM FCs), utilising H_2 as a fuel and Pt/C catalyst on the electrodes, represent progressive way of chemical energy conversion to electricity. However, limited availability of highly pure H_2 limits widespread fuel cell application. Utilisation of H_2 contaminated with CO, produced from fossil fuels and biomass, represents a convenient transient state. One of the options of how to reduce negative effect of CO on Pt catalyst is operating the PEM FC within temperature range of 120 to 160 °C. In addition, higher temperature makes the heat recuperation feasible. Due to the low relative humidity of the reacting gases, membranes based on polybenzimidazole or pyridine polymers doped with H_3PO_4 are used. Presence of concentrated H_3PO_4 at elevated temperature has, however, profound negative effect on Pt catalyst stability.

Degradation of Pt catalyst mainly results in the increase of average nanoparticle size. This is caused by several degradation processes, including agglomeration and sintering of nanoparticles, and, more importantly, Ostwald ripening. During Ostwald ripening, smaller nanoparticles electrochemically dissolve while produced Pt^{2+} ions reductively redeposit on larger nanoparticles. Dissolution of Pt is a rate determining step of this degradation mechanism and can be summarised by three Pt surface reactions: electrochemical Pt oxidation to Pt^{2+} (Eq. 1), electrochemical Pt oxidation to PtO (Eq. 2) and chemical dissolution of PtO to Pt^{2+} (Eq. 3).

$$Pt^{2+} + 2e^- \rightleftharpoons Pt \qquad \text{(Eq. 1)}$$
$$PtO + 2H^+ + 2e^- \rightleftharpoons Pt + H_2O \qquad \text{(Eq. 2)}$$
$$PtO + 2H^+ \rightleftharpoons Pt^{2+} + H_2O \qquad \text{(Eq. 3)}$$

Although critical for optimisation of PEM FC operation regime and estimation of its lifetime, kinetics of Pt surface reactions in concentrated H_3PO_4 at elevated temperatures are practically completely missing in literature. That is due to extremely corrosive properties of H_3PO_4 and adsorption of $H_2PO_4^-$ on Pt surface, making representative experimental determination of kinetic constants complicated. Mathematical modelling in combination with voltammetric experiments can enable estimation of kinetics of all involved reactions. Correspondingly, the goal of this work was to combine well-defined voltammetric experiments with mathematical model in order to determine Pt dissolution kinetics in detail at conditions relevant to high temperature PEM FC operation. Experiments were performed by cyclic voltammetry in 99 wt.% H_3PO_4 electrolyte saturated with N_2 within temperature range of 120 to 160 °C, either on a bulk Pt electrode or using in-house made gas diffusion electrodes with deposited Pt/C catalyst. Evaluation of experimental data provided input parameters for mathematical model and enabled its validation. Mathematical model reported in previous works [1, 2] modified accordingly to studied system was used for this purpose. Mathematical modelling part of the study proceeded in two phases. First, experimental cyclic voltammograms on a bulk Pt electrode were simulated by 0D mathematical model of Pt surface reactions. Secondly, 1D model of degradation of gas diffusion electrode in potentiostatic mode was defined using kinetic constants determined from both the experimental data and from the 0D model. Developed models are able to predict extent of Pt dissolution and Pt catalyst degradation at conditions corresponding to high temperature PEM FC operation, enabling further optimisation of its operational regime.

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Bandgap design by application: a case study of graphitic carbon nitride

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Electrocatalyst enhanced photoelectrochemistry is a promising route to improve photoelectrochemical reactions that have large thermodynamic barriers. The search for a semiconductor with improved solar spectrum compatibility and electrocatalysts that are tailor made for a specific reaction is the Holy-Grail of photoelectrocatalysis. Semiconductors with adjustable electronic structure and electrocatalysts adapted for a specific electrochemical reactions are needed to surpass traditional technologies.

Carbon nitrides have received increasing attention for photoelectrochemical applications since the seminal work by Domen et. al [1]. Graphitic carbon nitride is a polymer semiconductor with no carbon-carbon bonds. It is believed that graphitic carbon nitride's structure is bases on the triazine or tri-s-triazine repeating units. Such a structure can be modified with ease to become a p- or n-semiconductor. The versatility of such a structure makes graphitic carbon nitride an ideal semiconductor to study reactions that are energetically hindered (carbon dioxide reduction and oxygen evolution reaction). Herein we report a method that improves the solar spectrum compatibility and that can be used to adjust the position of the valence and conduction band, respectively. The obtained materials are extensively characterized by UV-Vis, FT-IR, XPS, XRD and electron microscopy. Mott-Schottky experiments were used to characterize the band structure. Photoelectrochemical experiments were carried out in a custom made electrochemical cell adapted for photo-applications. We provide experimental evidence for an enhanced photoelectrochemical activity by low level doping of graphitic carbon nitride.

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Application of wide field surface plasmon microscopy for analysis of initial stages of electrochemical nucleation

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An analysis of initial stages of electrochemical nucleation is crucial to understand the mechanism of this process and is of importance for the design and electrochemical synthesis of new materials. Here we suggest an application of the Wide Field Surface Plasmon Microscopy (WF-SPRM) to trace electrochemical nucleation of copper at low overpotentials. The WF-SPRM was initially developed for real-time detection of single nanoparticles of natural (viruses, exosomes) or technical origin [1-4]. A large monitored surface area of the sensor surface allows us to detect many hundreds of particles in each frame or totally up to a million particles on the sensor surface. An application of WF-SPRM for analysis of electrochemical nucleation provides a non-intrusive monitoring of formation and grow of each single nucleus independently (starting from the size of ~40 nm) on the macroscopic (~1 sq. mm) electrode surface. An analysis of the WF-SPRM records gives growth kinetics of each nucleus independently, time dependence of their surface density and their mutual localization. The nuclei sizes were calculated using calibration with adsorbing nanoparticles. The current transients, calculated from the analysis of optical data, correspond quantitatively to the independently measured experimental current-time dependences. The data obtained can be used for analysis of mechanisms of electrochemical nucleation.

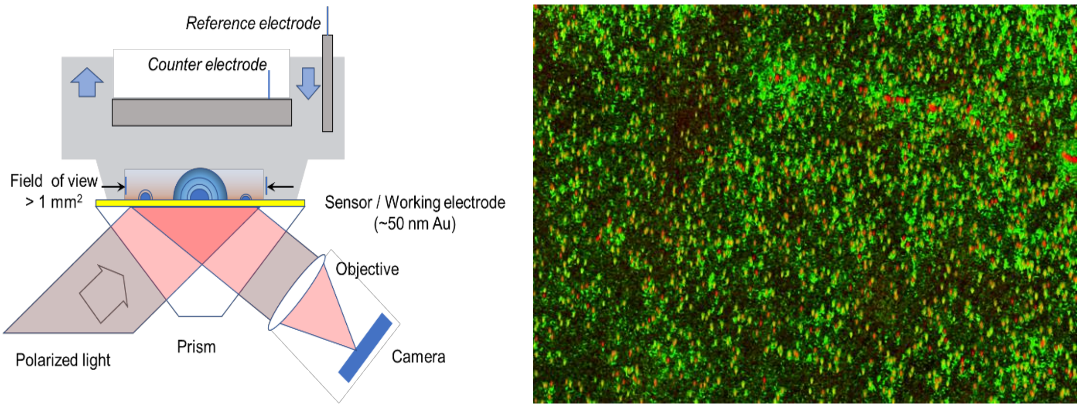

Fig. 1. Schematic view of wide field surface plasmon microscopy setup (left) and the map of the nuclei growth (right) where the time of nuclei appearance is indicated by shades of green and the average growth rate is indicated by the shades of red.

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Flame Fusion Nickel Single Crystal Growth: Unravelling Decades of Impossibility

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Since the introduction of the "flame annealing" methodology by Clavilier in 1980 for growing poly-oriented spherical single crystals (POSSCs), it has been assumed that the approach is only applicable to noble metals, such as Pt, Au, etc. Here, we report on the first ever growth of non-noble transition metal POSSCs – namely nickel (Ni) – using a hydrogen-rich flame. We discuss the challenges associated with the growth of spherical single crystals of non-noble transition metals, particularly the effect of heat-induced oxidation that has been an obstacle for researchers over several decades. Furthermore, we present simple modifications that need to be introduced to the already established step-by-step methodology and associated instrumentation to successfully grow spherical Ni single crystals. These changes in combination with our newly developed approach result in high quality Ni POSSCs, as verified by Laue X-ray back-scattering and scanning electron microscopy (Figure 1).

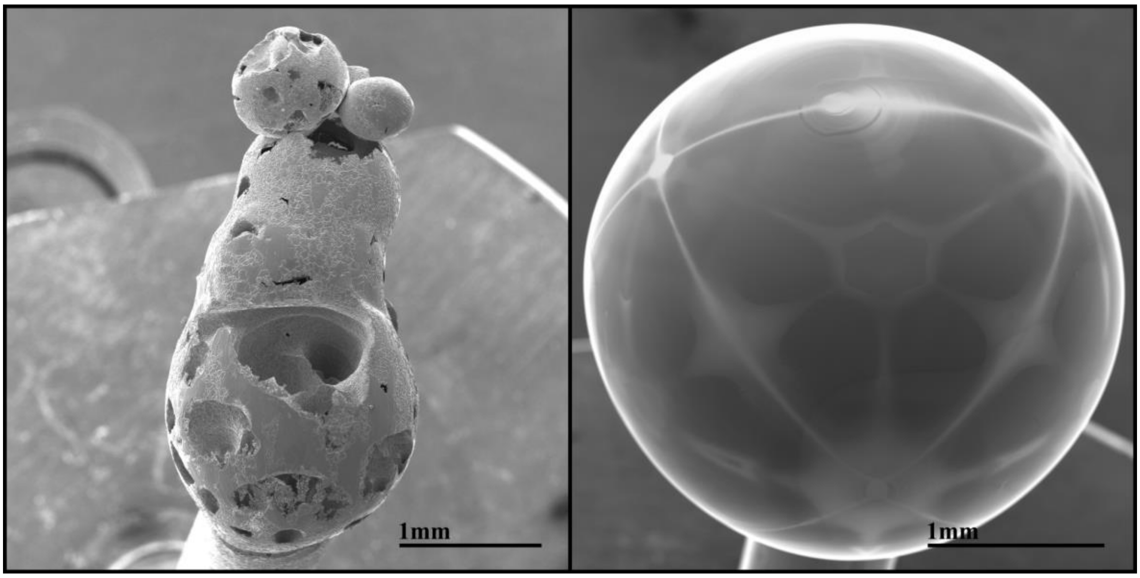

Figure 1: Grown Ni beads using an unmodified (left) and modified (right) experimental set-up.

In order to gain more insight into the expected shape of real Ni POSSCs, we modelled spherical Ni single crystals using a "Wulff construction" model with surface energies of twenty-nine (29) Ni surface facets determined by density functional theory (DFT) as input. Following the crystal growth and orientation cyclic voltammetry measurements in aqueous NaOH solution were conducted using Ni(100), Ni(111) and Ni(110) electrodes. These measurements revealed features unique to their surface geometry. Those highly original results reveal only a glimpse of the vast number of possibilities facilitated by this novel method for single crystal growth and electrochemistry.

Flame Fusion Single Crystal Growth of Non-Noble fcc, hcp and bcc Metals Using the Example of Copper, Cobalt and Iron

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The growth of non-noble metallic single crystals builds on our development of an experimental methodology for preparing Ni single crystals *via* the flame fusion approach. It also benefits from the early invention of Clavilier in 1980, who successfully employed the "flame annealing" technique for growing poly-oriented spherical single crystals (POSSCs) of Pt. Since we were able to successfully prepare Ni-POSSCs, we explored the possibility of applying our unique set-up to grow single crystals of other non-noble transition metals, especially those that adopt the bcc and hcp structures upon solidification. Herein, we report on the successful growth of Cu, Co and Fe spherical single crystals for electrochemistry and electrocatalysis research. We focused our initial attention on Cu due to its application in CO_2 electro-reduction, Co due to its catalytic properties and usage as an alloying element, and Fe due to its enormous and omnipresent application in steels.
Our results confirm the successful preparation of Cu, Co and even Fe POSSCs, with their quality being verified by Laue X-ray back-scattering (Figure 1) and scanning electron microscopy. Additionally, the properties of such prepared POSSCs were characterized by electrochemical techniques.

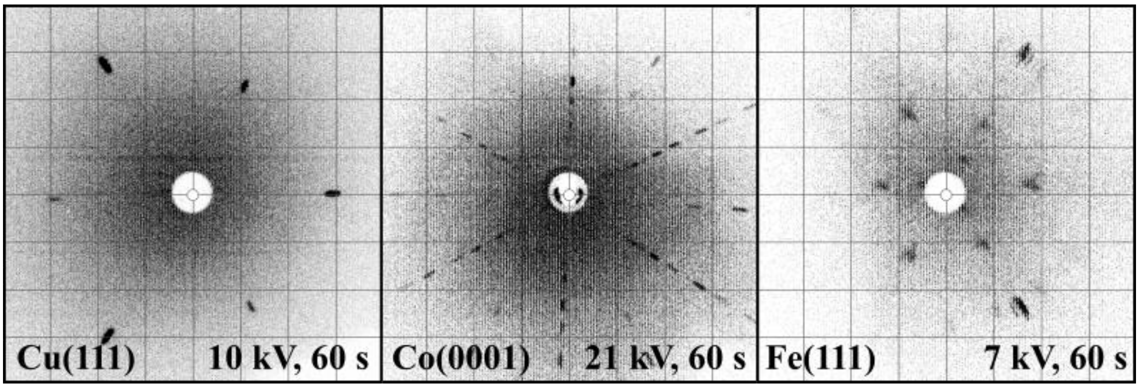

Figure 1: Laue backscattering patterns of grown Cu, Co and Fe spherical bead. Depicted are the patterns of basal planes, namely Cu(111), Co(0001) and Fe(111).

The modified flame-fusion approach now provides an inexpensive and relatively simple method for preparing high-quality POSSCs of various transition metals. While electrochemical studies on many of these metals have so far been limited to polycrystalline or structurally poorly-defined materials, our approach opens up a new avenue for exploring single crystal-based fundamental research that has not been possible so far.

Corrosion stability of aluminum in aqueous solutions and deep eutectic solvents: advantages and disadvantages

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Deep eutectic solvents (DES) have emerged as a green type of ionic liquids that are easy to prepare, of low cost, with good conductivity and high metal solvation. Due to the absence, or limited water content, they could be utilized in a wider voltage range of applications compared to aqueous solutions. During their application in electroplating, biodiesel production, energy storage and metal extraction, the metallic parts, such as wires, pipes, tanks and reactors are exposed to DESs. Therefore, the DES corrosivity is of growing importance and interest. Although DES application has been thoroughly analyzed there are still not many studies on the metal passivation and degradation in DESs.

The broad knowledge on aluminum corrosion in aqueous environment will be combined in this study with quite modest knowledge on its corrosion in DES accumulated until now. The aim of the research is elucidating to which extent the well-known models of aluminum corrosion and passivation in aqueous environment may be applied in DES. Research will be carried out in reline, DES based on choline-chloride and urea, as non-aqueous media, and compared to its behavior in aqueous electrolyte containing chloride ions of the same conductivity as reline. As a case study, the corrosion of AA2024 and AA6065 in reline will be analyzed. These alloys differ in intermetallics (IMPs) content, mostly on copper -rich ones. As intermetallics are the points of the corrosion onset and pit formation, it is important to determine the interactions of different aluminum electrodes and DES, and consequently, the extent of aluminum degradation in this media. The Volta potential difference, as a driving force for particular aluminum alloy corrosion, will be tested by Scanning Kelvin Probe. This study will indicate the role of the intermetallic particles type and content on the aluminum alloy stability in reline vs. aqueous solution.

One of the DESs benefits is the lower concentration of corrosive species (water, oxygen) than in aqueous solutions and given the disadvantage of the high DES viscosity, the diffusion of corrosive ions to, and metal ions from electrode, may result in different susceptibility to corrosion in these two media. Deeper insight of the much slower aluminum corrosion in reline than in aqueous chloride solution, determined by electrochemical impedance spectroscopy, will be explained by various characterization techniques. The current density maps on both alloys will be followed by Scanning Vibrating technique in two corrosive media. Owing to the high hydroscopic nature of DESs the water pick-up during time in an open electrochemical cell will be followed. Simultaneously, the amount of metal dissolved into the reline, as well as aqueous solution, as a consequence of aluminum corrosion, will be determined by Inductively Coupled Plasma Emission Spectrometry. Both carbamide and choline cation, present in reline, are known to be corrosion inhibitors, due to their strong adsorption at metal surface. Besides, chloride concentration in reline is very high and this is expected to affect metal speciation and growth of passive layer. Consequently, a passive layer formed in DES and aqueous solution could be substantially different and, in turn, vary in stability. A localized breakdown of the passive oxide layer on two aluminum alloys, followed by pit formation, will be determined in different corrosive media by potentiodynamic measurements, and all the results will be compared and discussed.

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Physico-chemistry of cobalt-enriched and cobalt-starved metal organic framework (MOF)-derived electrode platforms for the detection of dopamine

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Metal organic frameworks (MOFs) have been used as precursors for the development of carbon-based materials for a plethora of application (1,2). Microwave-assisted synthesis (MAS) has been used for economic and energy-efficient processing methods for several electrode materials, including for the preparation of excellent phase purity and high yield MOF crystals (3). In this work, MAS has been used to prepare cobalt oxide rich- and starved-MOF-derived porous carbons (i.e., R-Co_3O_4@MOFDC and its metal-starved product, S-Co_3O_4@MOFDC). Both R-Co_3O_4@MOFDC and S-Co_3O_4@MOFDC were thoroughly characterized using UV-vis spectroscopy, X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The electrochemical properties of the catalysts were firstly studied with 3 mM ferricyanide $[Fe(CN_6)]^{3-}$ / ferrocyanide $[Fe(CN_6)]^{4-}$ in 0.1 M KCl solution using cyclic voltammetry and electrochemical impedance spectroscopy (EIS). R-Co_3O_4@MOFDC demonstrated higher electron transfer kinetics.

These materials were investigated for the electrochemical determination of dopamine (DA) in the presence of uric acid (UA) and ascorbic acid (AA). When the redox response of DA, in phosphate buffer solution (PBS) of pH 7 was measured with both cyclic voltammetry (CA) and square wave voltammetry (SWV), no interference from AA and UA were observed. The results show that the R-Co_3O_4@MOFDC modified electrode exhibit excellent electrocatalytic activity towards the electrochemical redox activity of DA, due to higher current response and electron transfer. The sensor was further employed to detect DA injection and the recovery is acceptable within the allowed error range.

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Promoting the desired reactions in metal-oxygen/sulfur batteries using redox mediators and environmentally-friendly electrolytes

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Promising post Li-ion technologies include Li-O$_2$ and Li-S batteries, with very high theoretical specific energy, but also alternatives such as Na-O$_2$ and Al-S batteries, which can achieve a very low cost. All these batteries have in common a complicated reaction mechanism, in which the discharge reaction involves the formation of insoluble and insulating solid discharge products (typically, Li_2O_2, Li_2S, NaO_2 and Al_2S_3), which can passivate the positive electrode thus resulting in a low practical capacity. Tuning the electrolyte properties is a promising approach to optimize the solubility of intermediate products and mitigate passivation issues. In the case of Li- and Na-O$_2$ batteries, using redox mediators has demonstrated even more dramatic improvements in capacity. This talk presents some of our recent work on the incorporation of redox mediators in Li- and Na-O$_2$ batteries [1-5] and environmentally-friendly electrolytes in Li- and Al-S batteries. The use of polyoxometalates (metal-oxygen clusters with multiple oxidation states) appears as a particularly promising avenue, due to the very high chemical stability of this new type of redox mediator against degradation reactions [5]. Figure 1 illustrates the effectiveness of the polyoxometalate $\alpha\text{-}SiW_{12}O_{40}^{4-}$ in mitigating the passivation of a flat (glassy carbon) electrode in a Li-O$_2$ battery electrolyte. $\alpha\text{-}SiW_{12}O_{40}^{4-}$ is reduced to $\alpha\text{-}SiW_{12}O_{40}^{5-}$ at the electrode surface, which then diffuses away to the the solution and reacts with O_2 forming solid Li_2O_2 and regenerating the initial $\alpha\text{-}SiW_{12}O_{40}^{4-}$. Since, in the presence of $\alpha\text{-}SiW_{12}O_{40}^{4-}$, Li_2O_2 is formed in solution, passivation of the electrode by deposition of Li_2O_2 is prevented in this reaction pathway.

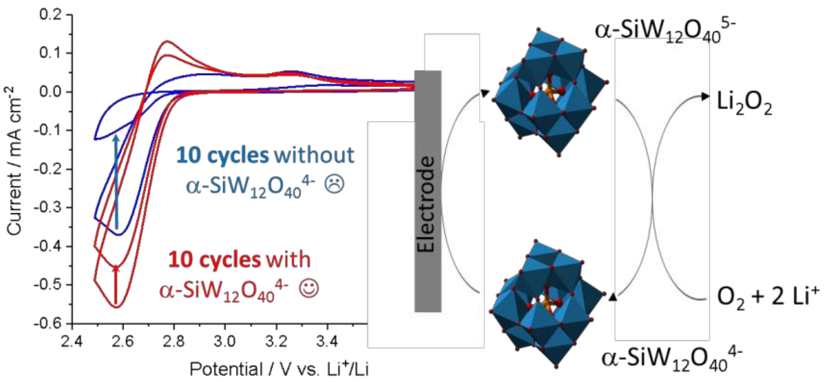

Figure 1. Cyclic voltammogram of a glassy carbon electrode in O_2-saturated 1 M LiTFSI in DMSO, with (**red**) and without (**blue**) 10 mM $TBA_4SiW_{12}O_{40}$. Scan rate: 20mV s^{-1}.

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Electrochemical Selectivity in the Industrial Production of Sodium Chlorate

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The undivided electrochemical cells, typically used in the industrial production of sodium chlorate, necessitate the use of selective electrodes, avoiding the losses due to unwanted electrochemical reactions.[1] The use of dimensionally stable anodes has been an ideal solution for anodes in the past decades, ensuring high Faraday efficiency for chlorine (and hypochlorite) evolution. At the cathode hydrogen is produced, but as the electrochemical cells are undivided, there is a risk of reducing the anode products. A high hydrogen evolution reaction (HER) selectivity is induced by adding chromium(VI) species to the electrolyte. This not only induces high HER selectivity (due to a thin protective layer formation), but also increases the selectivity and rate of chlorate formation from hypochlorite in the solution.[2] The highly toxic nature of all chromium(VI) species and the respective regulations in Europe however urge the identification of more sustainable alternatives for the current technology.

Here we present two alternative scenarios: (i) the direct replacement of chromium(VI) by a compound which remains in solution during chlorate production, and is just removed when crystallizing the product (ii) ex situ forming electrodes which are selective for hydrogen evolution even in the presence of hypochlorite and/or chlorate. The effects of different alternative solution additives, e.g. permanganate [3] and metavanadate [4] ions and cerium(III) salts on the HER selectivity in presence of different easily reducible species are evaluated. Most importantly, using various electrochemical techniques we demonstrate, that the addition of these compounds increases the hydrogen evolution selectivity in hypochlorite or chlorate solutions, suppressing the unwanted electrochemical reactions without significantly affecting the HER kinetics. In all these cases, the deposition of amorphous coatings (oxide/hydroxide) on the cathode during electrolysis is evidenced. Notably, a similar selectivity can be achieved by ex situ coating electrodes with similar oxides.

The fact that the HER kinetics on a covered electrode is similar to that of the underlying electrode material suggests these layers to be passive elements in the electrochemical reactions. In line with the advancements in other research fields,[5] these protective coatings are believed to act as diffusion barriers, hence influencing the electrode selectivity. A more detailed understanding of the function of these oxides is also discussed.

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Electrochemical degradation of dyes in aqueous solution

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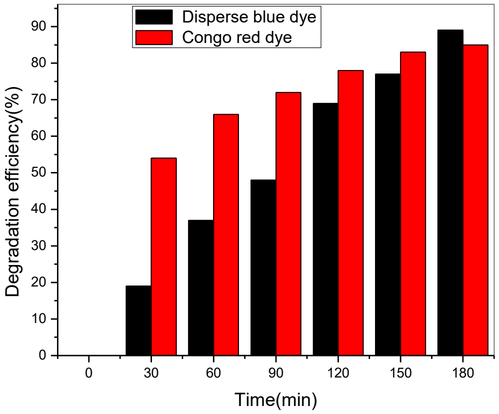
In recent times, the use of electrochemical methods has become increasingly useful as efficient and promising technologies for the degradation of organic contaminants in water. One advantage of DC electrochemical degradation is the possibility of designing the system to use photovoltaic (PV) cells to convert sunlight to electricity for field applications. The present study describes DC electrochemical degradation of disperse blue and Congo red dye in aqueous solution using graphite electrodes. We identified various key parameters that mostly influence dye removal to include initial concentrations of dye contaminant, reaction time, current density, pH and temperatures was studied. Results obtained showed faster degradation rates under conditions of low initial dye concentrations, low pH, high temperature (up to 50 °C) and most importantly, with more time.



DC electrochemical degradation efficiencies for disperse blue dye and Congo red dye

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On the use of well-defined model systems in electrocatalysis: the case of NH_3 oxidation

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The intrinsic catalytic and electrocatalytic activity of materials is critically dependent on their composition and surface orientations. It is well known that the addition of a second element (bimetallic catalysts) to a metal has a profound effect on the activity and stability of the resulting materials through ensemble, ligand, and strain effects. Likewise, it has been known for a long time that an element's electrocatalytic activity is critically dependent upon surface orientation and atomic surface arrangement. For example, the following electrocatalytic reactions occur more easily at metals that exhibit perfect two-dimensional (100) terraces: (i) reduction of CO on copper; and (ii) ammonia oxidation on platinum. Other examples abound in the literature. Accordingly, it is of the utmost importance to control both the composition and surface orientation of electrodes to determine as precisely as possible the intrinsic electrocatalytic activity of materials.

Pulsed laser deposition (PLD) was used to prepare epitaxial thin films with well-defined composition and surface orientation. PLD is a particularly attractive deposition method for the formation of epitaxial layers, since it has an unmatched ability to vary the kinetic energies of the species impinging on the substrate, along with the nature and the pressure of the gas in the deposition chamber. Most importantly, almost all elements can be deposited by PLD. Moreover, PLD is considered a non-equilibrium deposition technique and several metastable alloys have been prepared so far, allowing the investigation of bimetallic compounds that are kinetically stable but would be difficult to obtain by following a heat-treatment step, as the elements are not miscible, or only partially so.

In this presentation, we will focus on Pt alloys thin films with (100) orientation and investigate the effect of the alloying element (Ir, Ru, Rh and Pd) on the electrocatalytic activity for the oxidation of ammonia (NH_3). We first undertook a detailed investigation of the growth and the surface arrangement of Pt thin films deposited on (001)-oriented MgO substrates as a function of the deposition conditions. It will be shown that the width of the (100) terraces vary with the deposition temperature and shows a maximum value corresponding to 9 atoms at 325° C. Then, we will look at the effect of the alloying element on both the growth mode and the electrocatalytic activity. We will show that all Pt alloys thin films investigated here exhibit only one diffraction peak (the (001) peak) and a 4-fold in-plane symmetry, indicating epitaxial growth is achieved independently of the deposition temperature. The pole figure indicates that all films exhibit a Pt(001)[010]//[010](001)MgO cube-on-cube epitaxial relationship, consistent with the AFM images. The effect of the alloying element (Ir, Ru, Rh and Pd) on the electrocatalytic activity for the oxidation of NH_3 will be discussed.

Electro-Analytical Protocols for determining Polyphenols in Winery Cellar Effluent

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Keywords: effluent, winery waste water, vinification, polyphenols, metal ions, polymer, contaminators, tyrosinase

Abstract

The winemaking industry produces large volumes of wastewater that pose an environmental threat if not treated correctly. The increasing numbers of wineries and the demand for wine around the world are adding to the growing problem. This increase has further aggravated the pressure which the industry exerts on natural resources such as water, soil and vegetation. The growing conflicts over water resources are set to worsen in the context of climate change [1].

This increase has occurred at a time when regional and national legislation are becoming increasingly stringent control should be taken to offset environmental damage. Such control can only be achieved through the implementation of effective environmental systems. Wastewater is regarded as the most significant environmental risk at wineries and because water is a limited natural resource in South Africa, water monitoring and saving should be encouraged [2].

Electrochemistry is a clean, versatile and powerful tool for the detection of organic pollutants in water. Thus electrochemical sensors are a good tool for testing pollutants in winery water waste. We will present the development of a biosensor developed at a Boron-doped Diamond (BDD) platform for the determination of polyphenols in real winery wastewater samples. The BDD surface was electrochemically coated with polythiophene (Pth) film, onto which tyrosinase (Tyr) was deposited. Electropolymerization of Pth was done via cyclic voltammetry (CV) at 50 $mV.s^{-1}$ versus Ag/AgCl. The morphology of the composite films where studied by scanning electron microscopy (SEM). Detection of polyphenols was done using CV and square wave voltammetry (SQW). Uv-/vis spectroscopy was used to verify the conservation of polyphenols during the electrochemical and enzyme oxidation steps.

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Study of the Diffusion of Cu(I)/Cu(II) through Simulated Particle Pores in an Electrochemical Model System

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In heap leaching, the oxidative dissolution of value minerals encapsulated deep within large particles cannot be fully understood on the basis of the bulk solution conditions relative to variable solution conditions near the mineral surface. In the present study, the diffusion of the oxidising species through inner particle pores is simulated in a model apparatus that separates an inert platinum electrode under controlled reduction potential from the bulk solution through narrow pores of varying length. The Cu-NH_3 system was selected as a model system and Cu(II)/ Cu(I) as the redox couple of interest. Platinum probes inserted in the pores allowed the measurement of varying redox potentials along the pore length.

Results showed that in a 10 mm pore, there exists a narrow (0.5 mm) zone near the reduction surface that is depleted of the oxidant and in which its supply is strongly diffusion limited, even if it is in abundance in the bulk solution. The consistent presence of this narrow diffusion region across all experimental results indicated that the transportation of the reduced species away from the reaction surface had the most significant influence on the potential variations within the pore. This was further supported by the minimal effect of varying concentrations of both Cu(II) and dissolved oxygen on the solution potential within this region.

Multifunctional electro active green method synthesized metal nanoparticles

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Green nanotechnology is a new field aiming to replace the classical chemical and physical methods of obtaining nanoparticles which employ toxic and expensive chemicals with high energy input and negative effects on the environment. Ever since the introduction of the concept by which an individual atom and molecules were manipulated and developed, a discovery of the novel properties of nanomaterials was made. These are currently being exploited over a wide range of applications such as drug delivery systems for diagnosis and treatment, in the technology field where they are used as semiconductors as well as in environmental applications and industrial as catalyst. Consequently, due to the increase in demand for the development of nanomaterials across a widespread of applications, this may result in unintended exposure to human beings and the environment. Hence, a necessary step to ensure a sustainable future is imperative and can be achieved by the use of biological systems such as microorganisms, fruit and plant extracts. These alternatives not only suffice as environmentally friendly routes but are also economically sustainable. Green synthetic route has several merits such as their simplicity, low cost, non-toxic by products and good stability of nanoparticles. Reported herein are the microwave irradiation (MI) and/or the conventional heating biosynthesis methods of silver nanoparticles (AgNPs), gold nanoparticles (AuNPs), indium nanoparticles (InNPs) and zinc oxide (ZnONPs) using organic material such as caffeine, *Aspalathus linearis*, *Musa paradisiaca,* and *Vitis vinifera*. In each case, the structural and optical properties of the as-synthesized nanoparticles have been confirmed by Fourier transform Infrared (FTIR), Energy Dispersive X-ray (EDX) and Ultraviolet visible Spectroscopy (UV-vis) while their crystal structures and particles sizes were determined using High Resolution Transmission Electron Microscopy (HRTEM), X-ray diffraction (XRD) and Small angle X-ray (SAX). Electrochemical studies revealed the nanoparticles' potential application in sensor development due to their high electro-conductive nature and their use as platforms in the detection of Tuberculosis treatment drugs and antiretroviral drugs. Additionally, the multifunctional aspects of these nanoparticles was also observed in the growth of *Sorghum bicolor* seedlings and their antifungal effects towards *Candida albicans*.

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Semiconducting junctions based on amorphous silicon: a possible platform for high-resolution light-addressable amperometric devices.

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Addressing an electrochemical reaction with spatial resolution is at the vanguard of recent progress in electrochemistry. This is usually done by the fabrication of electrochemical arrays or by the use of scanning electrochemical microscopes, with significant achievements reported on both strategies [1]. However, an intrinsic characteristic (and to degree a limitation) of these strategies is that while electrochemical arrays require considerable space for the pad connections, scanning probe methods are sequential in nature and can only address one discrete area at a certain time. Photoelectrochemistry provides a solution to these limitations, as proposed in our recent published work on light-activated electrochemistry (LAE) [2,3]. Mainly, it has been shown that serial or parallel beams of light can selectively activate precise regions of a single-lead Si(100) electrode, such that electrochemistry can be performed with a spatial resolution of 30 µm. [4].

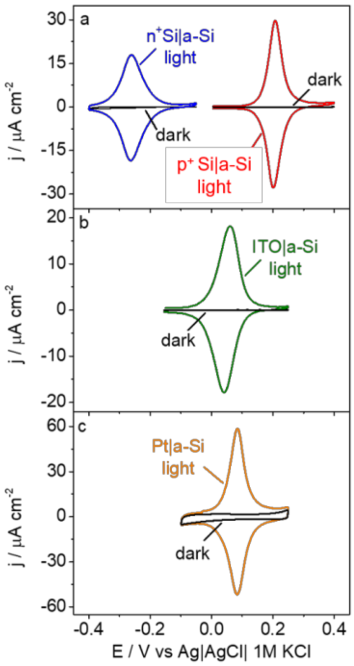

Fig.1 – Cyclic voltammetry of a model ferrocene redox probe attached on four different configurations of amorphous silicon-based heterojunctions.

The 30 µm dimension of the "virtual electrode" is controlled by the size of the light beam and by the diffusion length of minority charge carries into the non-illuminated area. In order to minimize the magnitude of the "virtual electrode", we propose the formation of semiconducting heterojunctions based on amorphous silicon. The amorphous material contains trapping states into the band gap, which heavily diminish the carries diffusion length. [5] Here, we report that a spatial resolution of only 3 µm can be achieved with amorphous silicon-based materials, which is close to the size of the light-beam probe. The phenomenon has allowed us to explore the electrochemical patterning of metallic features on a semiconducting surface.

Furthermore, the semiconducting heterojunctions reported here were formed by depositing a thin layer of photoactive amorphous silicon on four types of electronic bulk conductors: n-type and p-type Si(100), indium tin oxide [6] and platinum. The consequence of this approach for LAE is that the process of electron-transfer is not exclusively driven by the amorphous silicon|electrolyte interface, but it is concomitantly dependent on the charge transfer properties of the bulk conductor|amorphous silicon interface. Here, it is also shown and discussed how the nature of the formed semiconducting heterojunction can affect thermodynamics of light-driven redox processes. This is done by correlating electrochemical results with band diagrams that represent each heterojunction. Mainly, it was learned that (i) the thermodynamics of a ferrocene redox molecule can be tuned by varying the bulk conductor on which amorphous silicon is deposited; (ii) the electrochemical window on which photoactive processes are able to be conducted on heterojunctions are greatly expanded in comparison with Si(100) electrodes.

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A Novel Procedure for the Preparation of Copper Nanowires and Nanomeshes

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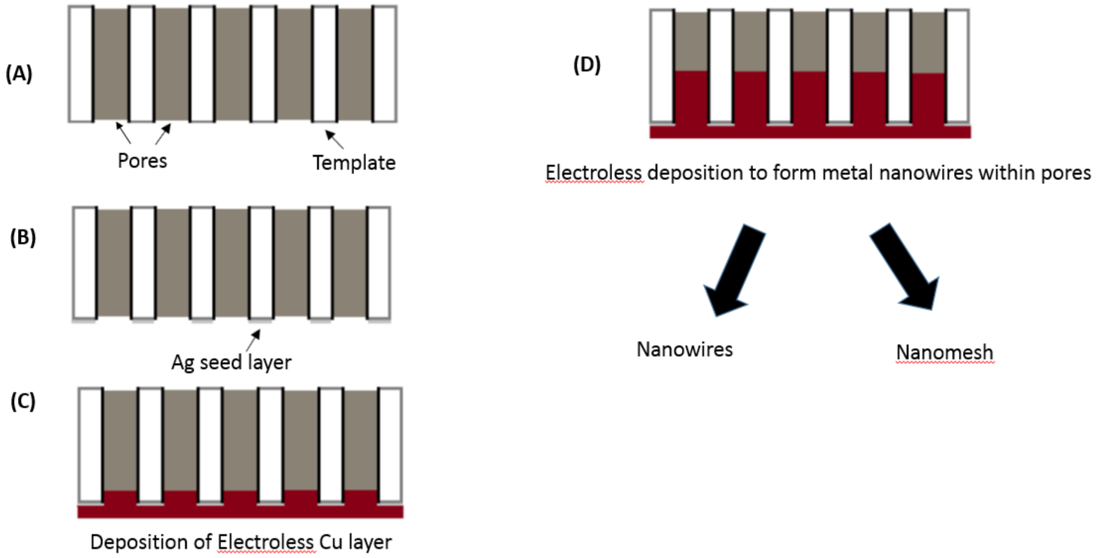
Nanostructured metals with a high surface area and a large porosity have great potential for many electrochemical applications. They show promise as battery current collectors[1], and as electrodes in sensors and electrolysers[2]. Metal nanowires can form 2D and 3D networks without the need for support materials and thus could eliminate issues with substrate corrosion. Current methods of preparation of nanostructures from metal nanowires include filtration, drop casting and template freezing [1,3].

In this work, we describe a new simple method for the preparation of copper nanowires and nanomeshes, see Figure 1. The procedure uses polycarbonate membranes in a template assisted method (A). The key step is the deposition of a copper layer which seals the pores of the template and allows further growth of the metal nanowires using a non-galvanic 'bottom-up' plating method. In the first step of the process a thin layer of sputtered silver (≤15 nm) is applied to one side of the template (B). This layer can be used to catalyse the electroless deposition of copper and grow a ≈300–500 nm layer on the surface of the template (C). If required the layer can be thickened by electrolytic deposition. Through flipping over the template in the plating cell, the electroless plating process can continue and nanowires grown to the thickness of the membrane (D). The top layer can also be thickened by electrolytic copper deposition. Depending on the procedure used, a variety of nanostructures can be prepared. To demonstrate the process copper nanowires and nanomeshes were prepared and characterized.

Figure 1. Novel procedure for the preparation of nanowires and nanomeshes



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Engineering Bio-inspired Tunnelling Junctions

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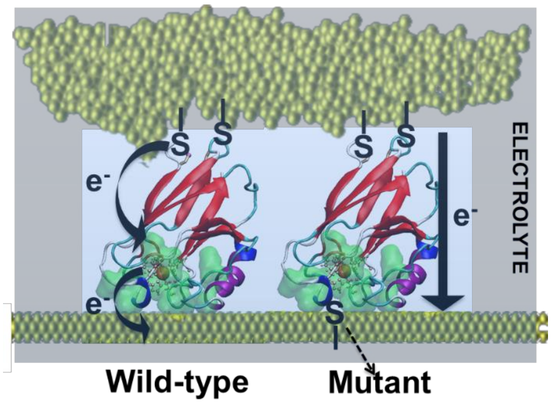
Bioelectronics is rapidly moving towards designing nanoscale electronic platforms that allow *in vivo* determinations. Such devices require interfacing a complex biomolecular moiety as the active sensing unit to an electronic platform for signal transduction. Inevitably, a true systematic design goes through a bottom-up understanding of the structurally related electrical signatures of such hybrid biomolecular circuits, which will ultimately lead us to tailor its electrical properties and exploit them as high performance bioelectronic devices with a wide variety of applications in organic electronics, sensing, biomanufacturing, *etc.*

In this contribution, we will present our latest efforts to try to understand and engineer charge transport in biomimetic single-protein junctions. The first part of the contribution will consist on a quick survey on how we build electrical connections with individual molecules between two macroscopic metal electrodes under near physiological conditions. Here we will particularly focused on new methodologies to trap redox proteins in a tunneling junction in a "gentler" manner [1,2]. Then the presentation will move on to the main core where we will try to show the feasibility to study charge transport in a single-protein junction using a simple redox protein model such as a bacterial blue Cu-Azurin. We will start showing the main observed electrical signatures of these systems that make them particularly efficient in translocating charge as compared to any other synthetic macromolecular homologous. We will then move to our latest results where we start bioengineering the outer protein surface through point-site mutagenesis to try to understand the transport mechanisms through the protein backbone. It is suggested that such modifications allow us tuning the extension of the electrical coupling between the protein and the metal electrodes [3]. These latest results are slowly leading us towards paving the way to rationally design the protein/electrode communication in a nanoscale hybrid bioelectronic device. The contribution will conclude by showing how our novel approach that might help in the future to understand complex biomolecular functions such as enzymatic catalysis. In particular, the concept of *electrostatic catalysis* of a well-known coupling reaction is demonstrated in a single-molecule junction [5].



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Electrochemical analysis of three-dimensional cultured cells using bipolar array devices

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In tissue engineering and organs-on-a-chip, three-dimensional (3D) cultured cells are widely used. These applications require a method that can easily measure cell activities of 3D cultured cells without any cell damages. For the purpose, electrochemical approaches are proposed [1, 2]. For examples, respiratory activities of them can be measured via detection dissolved oxygen near them.

For detection of respiration activity, several kinds of electrochemical systems/devices have been proposed. For example, scanning electrochemical microscopy (SECM) is widely used. In the detection, a probe electrode is moved above samples. The method is very useful, but it takes long time to get whole image of the samples due to moving the electrode. As a method without moving an electrode, several electrode arrays have been proposed [3-7]. The detection system is useful for real-time imaging, because it rapidly obtains 2D electrochemical images consisting redox currents at target positions. However, many leading electrodes and connector pads are required, which might limit the number of the sensors and the device size.

To solve the problem, we developed an electrochemical device containing bipolar electrodes (BPEs). Since anodic and cathodic reactions can be induced at both ends of the BPE with only a pair of driving electrodes, many sensing elements can be incorporated into a small chip without complex wiring. The system is applied for not only chemical sensing, but also biofabrication [7]. In the present detection, oxygen reduction currents at the sensor near 3D cultured cells are converted to electrochemiluminescence (ECL). Thus, ECL intensity depends their respiratory activity. Since chemicals for ECL might be toxic for mammalian cells, the anodic and cathodic reactions were separated by using a closed bipolar system.

By using the detection system, the respiratory activity of a single cell aggregate as a cancer model was successfully measured. In addition, 32 detection points were measured using only a pair of driving electrodes. Thus, the bipolar electrode arrays with the simple structures are useful for cell analysis.

Acknowledgements

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Improved ORR electrocatalysis inside nanochannels in nanozymes: nanoparticles that mimic enzyme architecture

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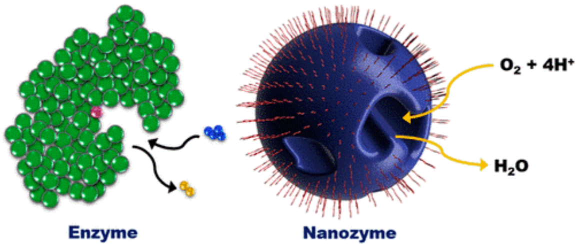
Nanoparticle electrocatalysts and enzymes present common features such as their size and the reactions they catalyze. One main difference between them is that while the active sites of nanoparticles are in direct contact with the electrolyte, enzymes have their catalytic sites spatially separated from the solution environment, providing high reaction kinetics and selectivity.

It is expected that such an approach applied to nanoparticles design can influence both the electronic properties of the catalytic site[1] and the transport of reactants and products[2,3] with benefits to the electrocatalytic performance. Thus, in this work the enzyme architecture is used as inspiration to make *nanozymes*[4]: nanoparticles containing isolated channels and with the outside surface electrochemically passivated to enable the electrochemical reaction to happen exclusively inside those channels. With that, it was able to study the effect of having an electrocatalytic reaction happening in a different solution environment of the bulk electrolyte, like in an enzyme. Among the different possibilities, PtNi nanoparticles for the oxygen reduction reaction (ORR) was chosen as a concept model for this study.



The nanozymes presented improved ORR activity with respect to both spherical nanoparticles and mesoporous nanoparticles that have interconnected pores instead of isolated channels. A dependence of the channels size was also observed: nanozymes with smaller channels are more active than the nanozymes with larger channels at lower overpotentials. With increasing overpotential, the nanozymes with larger channels become more active than the ones with smaller channels. These results shine light into the origins of the improved ORR activity inside those confined environments.

Overall, it has been shown that recessing the active sites in nanoparticles has a great potential for improved electrocatalysis and a new concept to study electrocatalytic reactions that can be further extended beyond the ORR was introduced.

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Neutron reflectometry as a probe of the electrical double layer in ionic liquids

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Ionic liquids (ILs) are promising materials for electrochemical devices. To maximize the performance of such devices, it is important to understand and to control the molecular-level structure of ILs at the electrochemical interfaces. Several unique features have been found at the IL interfaces. The most prominent one would be the spontaneous formation of ionic multilayers at the IL interfaces, revealed using interface-selective techniques such as x-ray reflectometry (XR) [1-4] and molecular dynamics simulation [5,6]. From the electrochemical point of view, the behavior of ILs in the electrical double layer (EDL) is also unique partly because of the multilayer formation, showing camel-shape and bell-shape potential dependence of the capacitance experimentally [7-9]. In this presentation, I will present the results of our recent study using neutron reflectometry (NR) to clarify the EDL structure in an IL [10]. I will also discuss some characteristic features of NR in comparison with XR as interface probing techniques with molecular resolution.

Acknowledgements
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Ab initio modeling of electric double layers on single crystal electrodes

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Single crystal electrochemistry plays significant role in providing microscopic understanding of electrified interfaces. Atomically flat single crystal electrode surfaces can be made with high precision and cleanness. Equipped with highly sensitive spectroscopic and microscopic techniques, one could investigate these highly complex electrochemical interfaces. The interpretation of spectra however is not always straightforward, which often can be complemented with computation. We have developed ab initio methods simulating electrochemical interfaces using density functional theory based molecular dynamics (DFTMD). Electrochemical environments can be simulated with well-defined (computed) voltage conditions, so that the computed structures and electrochemical properties of interfaces can be directly compared with experiment. In this talk, I will present some of our recent work on simulation of electric double layers on Au and Pt single crystal electrode surfaces, and their comparison with available experiment.

Bio-Hybrid Solar Cells: Putting Photosystem I to Work

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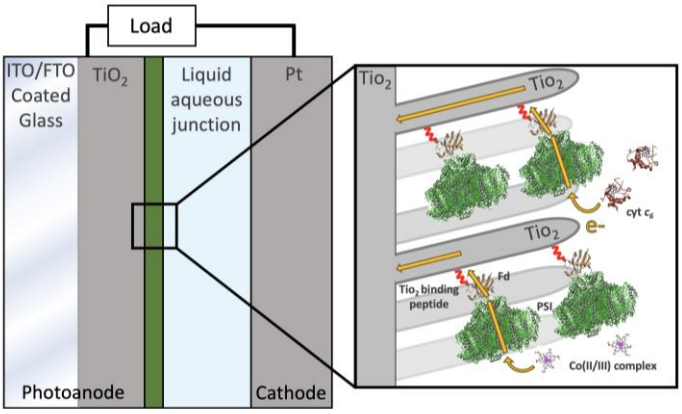
Future energy resources on Earth must be renewable, carbon-free, and sustainable. Most energy analysts recognize photovoltaics (PV) as a major contributor to help meet this need. However, many PV materials are difficult to fabricate and are often resource-limited, such as indium or other rare metals[1]. However, naturally occurring photosynthetic organisms utilize earth-abundant metals to harness and convert solar energy into a work-available form. These photosynthetic organisms harness solar energy via direct conversion to electronic energy using protein-pigment complexes, known as photosynthetic reaction centers (RC), with a quantum efficiency approaching unity. The field of applied photosynthesis aims to integrate RCs into novel, biohybrid solar cells[2-4]. Our lab has worked to integrate Photosystem I (PSI) from the thermophilic cyanobacterium *T. elongatus* into TiO_2 based solar cells[5]. The device is built around the direct attachment of PSI to the TiO_2 via a TiO_2 binding peptide attached to the PSI electron acceptor protein, ferredoxin (Fd)[6,7]. Currently we are using computational tools to bioengineer the affinity of Fd to the surface of PSI[8] to enable a tight and properly-oriented attachment of Fd-PSI to TiO_2 nanoparticles. This design places PSI on the TiO_2 surface with the lumenal surface exposed permitting reduction of photo-oxidized PSI by a water-soluble donor. However, one of the major limitations of these biohybrid devices is the slow reduction rate of *T. elongatus* PSI which leads to a loss of photocurrent. Therefore, we are also working to enhance the rate of electron donation to PSI using native, non-native, and synthetic donors. The first approach involves bioengineering of the native *T. elongatus* PSI electron donor protein, cyt. c_6. The second method comprises characterization of non-native algal/cyanobacterial cyt. c_6 interactions with PSI to identify features that promote the ~1000-fold increase in e^- transfer rate seen over evolutionary time. The third approach takes a different approach, namely the development and characterization of synthetic organometallic complexes utilizing the abundant transition metal, cobalt in a manner that is compatible with biological PSI. Collectively, this research aims develop methods of enhancing the electrochemical activity of PSI in a sustainable, non-toxic manner to facilitate bioenergy and device applications.



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Electrochemical Impedance Spectroscopy Analysis of FeF_3 Cathode for Lithium-ion Battery in Initial Discharge and Charge

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FeF_3 cathode is one of promising cathodes for lithium battery because of high theoretical capacity of 712 mAh/g involving insertion and conversion reactions.[1] However, the FeF_3 cathode has drawbacks of large polarization and poor cycle durability. Thus, the reason of the polarization and degradation have to be solved for its practical realization. While electrochemical impedance spectroscopy (EIS) is a powerful tool to analyze electrochemical processes on the basis of their characteristic time constants[2,3], FeF_3 cathode has not been analyzed in detail by EIS. The impedance of the FeF_3 cathode is considered to be apparently different from conventional cathodes whose reaction progress due to insertion reaction, because charge-discharge process of the FeF_3 cathode is composed of insertion reaction and conversion reaction. In the presentation, FeF_3 cathode in initial charge-discharge cycle was analyzed by means of EIS.

Coin-type cells were assembled with the composition of FeF_3 as cathode, Li as anode, and 1 M $LiPF_6$/ ethylene carbonate (EC) -diethyl carbonate (DEC) (DEC) (1:1 vol.) as electrolyte. The assembled cells were subjected to 1-cycle aging with a current equivalent to 0.05 C and a cut-off voltage of 4.5 - 1.0 V, and then impedance measurement was performed. EIS was carried out after every 50 mAh / g discharge from fully-charged state with 24 hours rest. The EIS conditions were frequency range: 100 kHz - 1 mHz, voltage amplitude: $V_{0\text{-}p}$ = 10 mV, and the number of measurement points: 10 points / decade.

To evaluate behavior of FeF_3 cathode impedance, EIS was carried out with every discharging of 50 mAh/g after 1-cycle aging. First three and rest ten Nyquist plots represent the impedance responses in the region of insertion and conversion reactions, respectively. Nyquist plots revealed that the impedances in low frequency region are obviously different before and after the boundary between insertion and conversion reactions. This difference was derived from differences of charge transfer reaction and diffusion in solid. In the presentation, the attribution of the FeF_3 cathode impedance is discussed from the EIS data obtained by using a FeF_3 symmetric cell with variation of measurement temperature and state of charge. In addition, the reaction mechanism of FeF_3 cathode during charge and discharge is speculated from the EIS data.

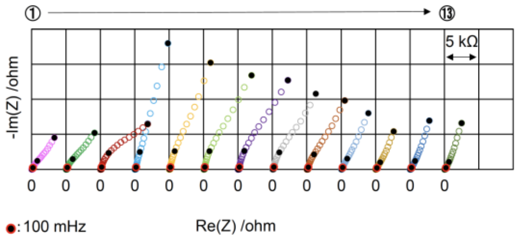

Fig. 1. Nyquist plots of Li/FeF_3 battery at different depth of discharge (every 50 mAh/g).

Acknowledgement
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Electrocatalytic reduction of CO_2 over nanostructured catalysts

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Electrocatalytic reduction of CO_2 (CO_2RR), powered by renewable or surplus nuclear electricity, can convert CO_2 into high value-added fuels and chemicals such as CO, formic acid, hydrocarbons and alcohols under mild reaction conditions.[1] CO_2RR has been attracting promising applications for carbon recycling utilization and clean CO_2-free electricity storage. Key scientific challenges in the research and development of CO_2RR include: (1) low Faradaic efficiency due to competitive hydrogen evolution reaction (HER); (2) limited current density due to low solubility of CO_2 in aqueous solution (~33 mM); (3) insufficient energy efficiency due to high overpotential and sluggish kinetics. Aiming at these key scientific challenges, we regulate the active site of nanostructured catalysts, construct gas diffusion electrode and assemble solid oxide electrolysis cell (SOEC) to improve the Faradaic efficiency, current density and energy efficiency of CO_2RR, respectively.[1-4]

Different metal/oxide interfacial nanostructures have been constructed for enhancing CO_2RR. The CO Faradaic efficiency reaches 89.1% over Au-CeO_x/C at −0.89 V vs. reversible hydrogen electrode (RHE), which is significantly higher than 59.0% and 9.8% over Au/C and CeO_x/C at the same potential. In situ scanning tunnelling microscopy and synchrotron-radiation photoemission spectroscopy show that the Au/CeO_x interface is dominant in enhancing CO_2 adsorption and activation, which can be further promoted by the presence of hydroxyl groups. Density functional theory (DFT) calculations indicate that the Au-CeO_x interface is the active site for CO_2 activation and the reduction to CO, where the synergy between Au and CeO_x promotes the stability of key carboxyl intermediate (*COOH) and thus facilitates CO_2RR (Fig. 1a). Furthermore, $Sr_{2.0}Fe_{1.35}Co_{0.15}Mo_{0.45}Co_{0.05}O_{6-\delta}$ (SFMC) is reduced in H_2 atmosphere to construct FeCo/SFMC interface via the exsolution of FeCo alloy nanoparticles from the bulk to the surface of SFMC, and then we prepare gas diffusion electrode to assemble SOEC with solid oxide electrolyte membrane. The FeCo/SFMC cathode shows a current density of 1.21 A cm^{-2} at 1.6 V with an energy efficiency of ~80% and a high stability of 235 h, which is much higher than those over the SFMC cathode (Fig. 1b). We also construct Au/yttria-stabilized zirconia (YSZ) interface to improve the performance of oxygen evolution reaction at the anode of SOEC. The current density of SOEC with Au/YSZ anode for CO_2RR can reach 1.39 A cm^{-2} at 1.4 V and 800 °C, which is much higher than that with infiltrated lanthanum strontium manganite/YSZ anode. Electrochemical characterizations, DFT calculations and *in situ* X-ray photoelectron spectroscopy results reveal that Au particles can significantly boost the process of interfacial oxygen spillover from the YSZ to the Au surface and the OER process.

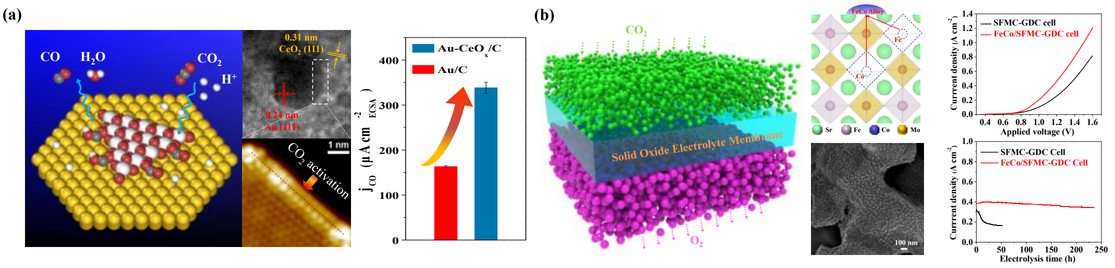

Fig. 1 Au/CeO_x (a) and FeCo/SFMC (b) interface nanostructures for efficient CO_2RR.

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Integrated microfluidic device for the separation, decomposition and detection of low molecular weight S-nitrosothiols

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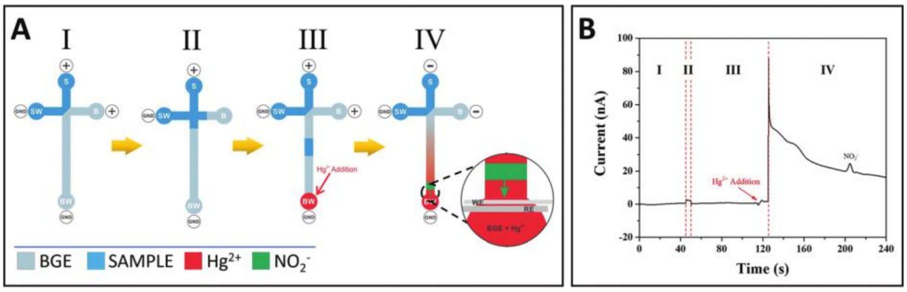
S-nitrosothiols (RSNOs) are considered as biological circulating stocks of nitric oxide (NO) that have many roles *in-vivo*. The variation of RSNOs proportion occurs in several diseases, which makes them potent biomarkers. The identification and quantitation of each RSNO is therefore important for biomedical studies. For now, miniaturized devices have been used to detect RSNOs, based on their total quantitation without a preceding separation step. This study reports on an original and integrated microdevice allowing for the successive separation of low molecular weight RSNOs, their decomposition under metal catalysis, and the quantitation by amperometric detection of the produced nitrite, leading to their quantitation in a single run. For this purpose, a commercial SU-8/Pyrex microfluidic system was coupled to a portable and wireless potentiostat. Different operating and running parameters were optimized to achieve the best analytical performance allowing for LODs of 20 μM (figure below). The simultaneous separation of S-nitrosoglutathione and S-nitrosocysteine was successfully obtained within 75 s. [1]



(A)
Scheme of the main steps for RSNOs quantitation. Loading step (I): Voltages of 800 and 1000 V are applied during 45 s to the sample (S) and buffer (B) reservoirs, respectively, grounding both waste reservoirs (SW and BW). Injection step (II): samples are injected into separation channel by floating the voltage applied to B reservoir during 3 s. Migration step (III): The potentials were then re-established to step I condition allowing the migration of RSNO sample towards separation channel. 15 s before the end of this step, Hg^{2+} was added to BW reservoir. Inversion and detection step (IV): In this step the potential polarity is inverted which leads to the migration of Hg^{2+} into the separation channel faster than RSNO leading to RSNO decomposition. This is followed by nascent nitrite (in green) opposite migration towards the electrodes and detection by applying a potential of 1.2 V *vs Pt*. (B) Typical electropherogram obtained for GSNO (1 mmol/L) analysis characterising all the steps of the process.

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Rapid Assessment of Solid-Electrolyte Interphases on Lithium Anodes by Atomic Force Microscopy

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Li metal anode still suffer from instable SEI and dendrite growth, which are mutually influenced by each other. An ideal SEI, which is stable, compact and smooth, having electrical conductivity almost only to Li ion and with coupled rigidity and elasticity, can suppress Li dendritic growth. Very recently, the authors' group established an electrochemical polishing-based method to construct ultrasmooth and ultrathin SEIs (USUT SEIs) on Li metal [1, 2] and Li-free Cu collectors [3], which are distinctive of not only large-scale smoothness but also spatially alternating arrangement of organic-rich and inorganic-rich layered structure. It may be concluded that morphological features as well as mechanical properties are primary assessments on the quality of SEI, which may be correlated to the performance of the corresponding Li anode.

AFM is advantageous in both high-resolution imaging and precise force probing, and can thus serve as a powerful mean to characterize the smoothness, thickness as well as stiffness of the SEI. Such investigations on Li surfaces have been achieved, but challenging, because of difficulties in working with thin SEI on generally rough and soft Li metal surfaces [1]. In this work, by employing the electrochemical polishing-based method, we fabricated three types of SEIs, which are large-scale flat yet with typical mechanical properties ranging from ultra-hard, to ultra-soft, and to hard-soft interleaving, to facilitate AFM indentation measurements. The AFM force ~ indentation curves are measured, and statistical analysis on the stiffness and thickness are performed. On the other hand, the cycling performance of the three types of SEI are measured in Li||Li symmetric cells and correlated with the feature of the force ~ indentation curves of corresponding SEIs. We thus established AFM-based methodology for evaluating the mechanical property of SEI and predicting the performance of the corresponding Li metal anode. Our work may be used for rapid screening of methods or the preparation conditions of the methods for constructing ideal SEIs on Li metal anodes.

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On the use of N_2-doped and pristine CQDs to improve the storage performance of bio-sourced quinone-based electrodes

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The foremost challenge in energy crisis management is to meet the ever-rising demand for the continuous supply of energy to the technology-driven twenty-first century. The depletion of fossil fuels and environmental pollution impose an immediate need for green energy. Moreover, the intermittency nature of the most reliable green energy sources, the Sun, requires high performance energy storage technologies [1]. Recently researchers have focused on the development of high-performance supercapacitor materials, such as carbon-based materials, conducting polymers, and metal oxides [3-5]. It was found that the composites of carbon-based materials with other materials such as metal oxides, conducting polymer have excellent electrochemical performance [6-9]. However, most of the currently used energy storage devices make use of electrode materials and electrolytes with limited environmental sustainability: a change of paradigm is needed to identify non-toxic, abundant, environmentally benign materials for energy storage [10]. Among bio-sourced materials, eumelanin is a redox active quinone-based biomacromolecule found in flora and fauna; it has fascinating properties, such as strong broadband UV-visible absorption and metal binding affinity [11].The synergy between the redox activity of the building blocks and the capability of several of their functionalities to reversibly bind cations constitutes the foundation for the use of eumelanin in energy storage systems [12]. In this work, we report on the electrochemical energy storage performance of composites of N_2-doped and pristine CQDs with melanin. The composites were prepared at different weight ratios (melanin monomer: CQD; 1:0, 1:0.4, 1:1, 1:2) through a solution-based process followed in situ polymerization. From electrochemical characterization of the composite electrode (melanin: pristine CQDs; 1:1), through cyclic voltammogram, galvanic charge/discharge and electrochemical impedance spectroscopy in nearly neutral aqueous electrolyte solutions, it has been possible to deduce an increase of the areal capacitance from 0.64 to 533 $\mu F/cm^2$ and a decrease of the charge transfer resistance from 2000 Ohms to 38 Ohms.

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Impact of Transport in Gas-Diffusion-Electrode Performance

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Transport phenomena in porous electrodes is increasingly seen as a key factor in their overall reaction rate, selectivity, and performance. This is true in polymer-electrolyte fuel cells, vapor-fed electrolyzers, and carbon-dioxide-reduction devices. In all of these applications, the local conditions of reactant and product concentration, ion concentration and type (including activity), which typically exists within polymer electrolytes, and electron accessibility, in concordance with local temperature, pressure, etc. result in a complex response. Mathematical modeling at multiple scales is ideally suited to tackle this complex problem and unravel the various dominating phenomena during operation.

In this talk, we will explore these interactions and how modeling can be used to elucidate the controlling phenomena and suggest ways in which to optimize performance. Specific topics discussed include modeling the gas-transport related losses that occur with low-Pt loadings in polymer-electrolyte fuel cells with a focus on the multiscale interactions from the Pt site inside high-surface-area carbon primary particles to transport throughout the electrode layer. We will also discuss optimization of the ionomer coverage for fuel-cell operation over the various operating range considering the impact of the local effects. In the second part of the talk, we will discuss how transport impacts local reactivity and selectivity in gas-diffusion electrodes for carbon-dioxide reduction. Here, the focus is on multiple ion interactions within the ionomer and how that impacts product selectivity on Ag and Cu containing electrodes. Time permitting, our recent work on multiscale modeling including microkinetics and surface reactions and structures for low-temperature electrolysis and oxygen evolution on IrO_2 will be introduced.

Acknowledgements

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Shear Thickening Electrolyte Functions as Both Battery and Protection Materials

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Safety issues have received significant attention for lithium ion batteries. Currently, most works focus on external packaging to address this problem. However the adding of external protection packages causes the disadvantage of heavy weight. Using solid electrolyte, solid polymer electrolyte or ionic liquids to replace the commonly used flammable liquid organic electrolytes is another solution. However, such electrolytes normally suffer from low ionic conductivity, leading to inferior performance, particularly at high current drains. In addition, they cannot provide protection against physical impacts.

As demonstrated by our previous work, we have developed a new strategy to improve battery safety as well as maintain their performance by introducing shear thickening properties into electrolytes. These electrolytes not only show higher ionic conductivities but also exhibit the shear thickening effect under pressure or impact. Shear thickening electrolytes have been considered as one of the most promising methods of ensuring safety in lithium ion batteries.

Shear thickening fluids (STFs) are an example of a non-Newtonian fluid, often termed as a dilatant fluid. At low shear rates, this fluid has low viscosity, acts as a lubricant and flows easily. However, upon impact, the fluid adopts a rigid-like state due to a rapid increase in viscosity and thus becomes less penetrable. Their unique material properties make them ideal for many applications, including liquid body armour and shock absorbers. Adding STFs into ballistic fabrics to create “liquid body armour” to improve kinetic impact resistance has been proven. STF also reduces the trauma resulting from kinetic impacts due to its increased energy dissipation capacity.

Here, for the first time, we have tried to turn “liquid body armour” into a battery system which is not only able to supply power, but also to provide protection against bullet impacts. The components that make liquid body armour, ballistic fabrics and STF, are designed to perform the function as electrodes, separator and electrolyte. Such multifunctional energy storage systems can share space and weight with existing body armour. Batteries with different combinations of Kevlar-based electrodes, Kevlar separator and shear thickening electrolytes have been assembled, their electrochemical and against a range of kinetic impacts including ballistic performances have been investigated.

Continuous Interstitial Glucose Monitoring Sensors for *In Vivo* Evaluation in a Dog Model

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Reliable, user-friendly *in vivo* glucose sensors should have a significant impact on diabetic health care. Indeed, a continuous interstitial glucose monitoring sensor provides maximal information about widely varying blood glucose levels throughout the day, and thus is able to facilitate the making of optimal treatment decisions for diabetic patients. However, upon implantation of a sensor into the body, a cascade of inflammatory response (known as the foreign body response, FBR) is initiated, ultimately making *in vivo* glucose measurement erratic. Therefore, the appropriate fusion of biocompatible coating materials and glucose sensing devices has been one of the most critical issues. With discovery of nitric oxide (NO) as a potent anti-thrombotic and anti-inflammatory agent, a variety of NO storage/release nanomaterials have been reported to improve the biocompatibility of indwelled medical devices, including metal/metal oxide clusters, silica nanoparticles, dendrimers, and polymeric nanofibers. Herein an implantable glucose microsensor modified with NO-releasing silica/polymer *hybrid* nanofibers is demonstrated. By controlling NO release properties (e.g., total NO storage amount, half-lifetime of NO release, and maximum flux), the sensor performance *in vivo* (using a dog model equipped with a wireless signal transmitter/receiver device) will is evaluated, in terms of sensor lifetime, accuracy, and stability.

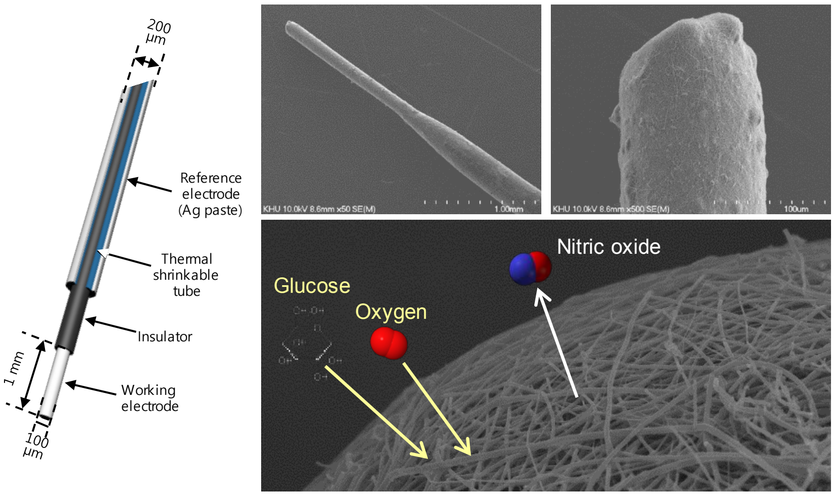

Figure 1. Schematic illustration of an indwellable glucose microsensor and SEM images of the sensor modified with NO-releasing silica/polymer *hybrid* nanofibers.

Novel *Operando* NMR and IR Methods for Studying Battery Chemistries

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Operando molecular spectroscopic methods are increasingly in high demands for advancing battery development because they can unravel battery chemistries in real time in working devices. Notwithstanding both NMR[1] and IR[2] have long been successfully applied *in situ*/*operando* to investigating battery chemistries, there still exists plenty of room for further developments. In the presentation, we will describe two recent such developments: *operando* stripline NMR[3] and dual-IR window/electrode attenuated-total reflection (ATR) – IR absorption[4] spectroscopic methods for battery research.

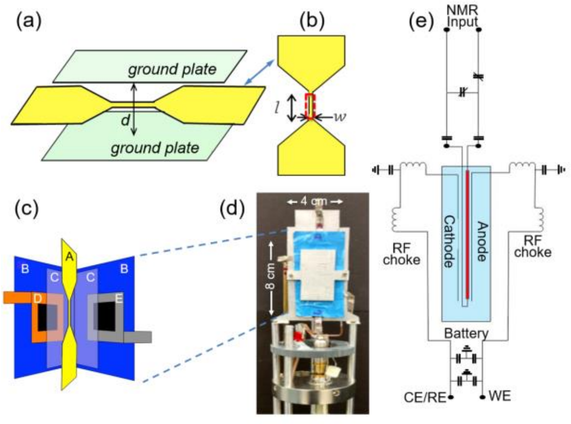

Figure 1

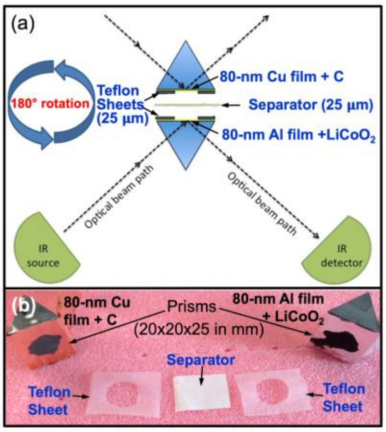

Figure 2

Fig. 1 shows the schematic of the *operando* stripline NMR probe: a) Side view of the stripline detector. b) Front view of the central stripline which was made from a 35 μm thick copper sheet. c) Li-ion pouch battery cell schematic. The stripline detector (A) is covered in Kapton to isolate it electrically from the electrolyte and further isolated from the anode (D) and cathode (E) by a Celgard separator (C). The components are enclosed in a laminated Al pouch cell material (B). d) A pouch cell battery mounted on the homebuilt EC-NMR probe. e) Circuit diagram of the stripline EC-NMR probe. The heavy red line between the anode and cathode is the stripline, which is connected to the NMR resonant circuit.

Fig. 2 presents (a) schematic diagram and (b) individual physical components of the rotating dual-IR window/electrode *operando* ATR-IR setup. The two prisms were clamped together tightly by which an air-tight, IR accessible functional Li-ion battery (LIB) was formed. During the battery charging or discharging process, the setup was mechanically controlled by a computerized step motor that flipped it 180° step-wise periodically, moving one prism to a fixed position for synchronized sequential IR measurements without interrupting the battery operation.

Both were applied to studying LIBs with graphite anode and $LiCoO_2$ cathode. On the one hand, it was demonstrated that the *operando* stripline NMR addressed simultaneously the three key technical challenges encountered in the current *in situ* NMR studies of batteries: (1) the perennial intrinsic incompatibility between improving traditional coil-based NMR detection and conducting materials necessary for a working battery or other EC systems, (2) low sample filling factor, and (3) inferior detection sensitivity. On the other hand, the *operando* IR results showed that the solid-electrolyte interphase (SEI) layer was formed on both graphite anode and $LiCoO_2$ cathode; (2) the anode and cathode SEI layers had different molecular compositions which had different stability during the LIP operation; and (3) over-discharging generated =C–OH groups on the graphite surface; and (4) higher charging current produced CO_2 at the $LiCoO_2$ cathode.

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Carbonisation Temperature Dependence of Electrochemical Activity of Nitrogen-Doped Carbon Fibres from Electrospinning as Air Cathode for Aqueous-Alkaline Metal-Air Batteries

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The limiting factor in state-of-the-art aqueous-alkaline metal-air batteries are usually the air electrodes.[1] To circumvent the challenges of commercialised pressed carbon powder based air electrodes electrospun carbon-nanofibres (CNFs) have been identified as viable alternative electrode frameworks, as they are mechanically stable, but also light weight with a high surface area.[2] Carbon fibres derived from electro-spun poly-acrylonitrile are a suitable candidate for an electrode framework, due to its nitrogen content, as nitrogen-doped carbons are known to auto-catalyse the oxygen redox chemistry in alkaline metal-air cells.[3]

In our study, we have focussed mainly on obtaining a fundamental understanding of the correlation of the electrochemical performance of PAN-derived carbon fibres with their composition and structure. The main focus was set on the changes in the material caused by the carbonisation temperature, which has been meticulously scanned from 300 °C to 1400 °C. The properties of the material have been analysed by ICP-OES, XPS, SEM and Raman spectroscopy. The electrochemical properties were investigated using linear sweep voltammetry in 6 M aqueous KOH.

Overall the high potential for PAN-derived carbon fibre based electrodes was successfully demonstrated. Based on the three descriptors: Open-circuit potential, cathodic current at a given overpotential and overpotential at a given cathodic current, the electrochemical performance is assessed. The highest cathodic currents are obtained for samples carbonised at 850 °C, which shows a maximum in the amount of graphitic nitrogen.

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Electrochemical Detection of Metal Oxide Nanoparticles in Forced Convection Conditions

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The electrochemistry of suspended nanoparticles received attention as one of the methods of their characterization and detection [1]. Apart from the studies in quiescent conditions at ultramicroelectrodes, we demonstrated that it is possible to detect suspended nanoparticles at millimetre size electrodes in forced convection conditions. Such electrochemical detection of nanoparticles and other nanoobjects at rotating disc electrode (RDE) is possible due to their electrocatalytic [2-4] or redox [4,5] properties. In the case of flow system also electrocatalytic properties of nanoobjects were explored [6]. In some cases electrocatalytic reaction was preceded by chemical reaction(s) of analyte [7,8].

There are very few electrochemical studies of suspended metal oxide nanoparticles [9,10]. In one of these papers, voltammogram of suspended magnetite nanoparticles at RDE was presented [10]. Here we will present results of electrochemical studies of suspension of metal oxide (Fe_2O_3, Fe_3O_4, ZnO) nanoparticles at RDE and in the flow. We will demonstrate it is possible to obtain the electrochemical signal resulting from the redox processes of metal (Fe_2O_3, Fe_3O_4) and another signal (at lower potential) due to the electrocatalytic reduction of H_2O_2 or O_2 on iron oxide nanoparticles. These signals are proportional to the concentration of suspended nanoparticle. In the case of ZnO nanoparticles, a voltammetric signal related to electroreduction to metallic Zn deposited on the electrode surface is seen. These results will be compared to our earlier studies [2-8].

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Semiconductor thin films for electron- and hole-selective interfaces in photovoltaics

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Compact thin films of oxide semiconductors (TiO_2, SnO_2) find application as the electron-selective contacts in dye-sensitized solar cell (DSSC) [1] and in the perovskite solar cell (PSC) [2]. Irrespective of the device type, a thin (3-50 nm) electron-selective layer, also called blocking layer, is a used at the negative electrode. It transport electrons from the photoexcited dye or perovskite to the collecting terminal (usually F-doped SnO_2, FTO) and prevents recombination of these electrons with a hole-transport medium and/or the photoabsorber. In DSSCs, the blocking layer is important in solid-state devices and in the liquid-junction solar cells using organic dyes. In general, the blocking layer should be pinhole-free [3,4], allowing fast electron injection and transport, and its conduction band minimum (CBM) must be properly aligned with the CBM of perovskite [5] or LUMO of the dye in DSSCs [1]. Amorphous ALD-made SnO_2 or TiO_2 films block holes for thicknesses down to several nm, but amorphous and crystalline ALD SnO_2 films differ in their conduction band positions. The energy of CBM is usually measured by optical spectra (giving the band gap) and photoelectron spectra (XPS, UPS) providing VBM. The electrochemical alternative is the measurement of the flatband potential, which yields CBM, too. However, there is a considerable controversy between the electrochemical and vacuum (XPS, UPS) techniques concerning the position of CBM in TiO_2 (anatase, rutile, including the crystals with distinguished facets). A refined electrochemical analysis of single crystal TiO_2 electrodes (anatase, rutile, brookite) together with vacuum and near-ambient pressure XPS studies as well as theoretical (DFT) modelling point at the effect of interface influencing the CBM positions. Even 1-2 monolayers of water cause significant shifts, which could explain these conflicts. TiO_2 rutile thin films and or rutile/anatase double-layers turned out to be useful for PSC, too, outperforming even the anatase layers. Optically transparent rutile thin films can be most simply prepared by thermal oxidation of Ti at FTO. Similar tasks about band alignment are addressed at the positive (hole-selective) terminal of PSC. A promising hole-conductor to replace *spiro*-OMeTAD is CuSCN, particularly if it is interfaced to reduced graphene oxide (rGO) [6]. The natural p-doping of CuSCN is demonstrated by both Hall-effect and by Mott-Schottky plots in aqueous electrolyte solution. The corresponding flatband potentials (in V vs. Ag/AgCl) varied with the substrate type as follows: 0.12 (CuSCN@FTO), 0.08 (CuSCN@Au), -0.02 (CuSCN@glass-like-carbon) and 0.00 V (CuSCN@rGO). The acceptor concentrations determined from electrochemical impedance spectroscopy are by orders of magnitude larger than those from electrical conductivity and Hall effect. Raman spectra confirm that thiocyanate is the dominating structural motif over the isomeric isothiocyanate. In-situ Raman spectroelectrochemistry discloses substrate-specific intensity changes upon electrochemical charging. The blocking function of CuSCN is tested by a newly designed redox-probe, $Ru(NH_3)_6^{3+/2+}$. It has not only the appropriate redox potential for investigation of the CuSCN films, but also avoids complications of the standard 'ferrocyanide test' which is normally used for this purpose. **Acknowledgement**: This work was supported by the Czech National Science Foundation (contract No. 18-08959S).

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Investigation of Electrolyte Additives on the Cathode/Electrolyte Interphase (CEI) Formed on $LiNiMnCoO_2$ (NMC)

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Having high energy density, low self-discharge and long cycle life, lithium ion batteries (LIBs) are being used for consumer electronics, electric vehicles (EV), and other industrial energy storage devices. Two main factors determining the Li-ion batteries performance are specific capacity and operating voltage. Lithium nickel manganese cobalt oxides ($LiNi_xMn_yCo_zO_2$) are among the most promising cathode materials for LIBs due to their high specific capacity and good structural stability. However, their relatively high cut-off voltage upon charge exacerbates the electrolyte oxidation leading to extreme surface film formation, transition metal dissolution and ultimately diminishing the cycling stability. Therefore, the introduction of additives in the electrolyte formulation, to reduce or even suppress the parasitic reactions at high voltage is a very appealing approach.

In this work we employed three different additives, namely, fluoroethylene carbonate (FEC), propane sultone (PS) and vinylene carbonate (VC), in NMC half- and full-cells to investigate their impact on the cathode electrolyte interphase (CEI) formation and, ultimately, the cell performance at the high cut-off voltage (4.5 V). In both configurations, all three additives revealed positive effect on the electrochemical cycling. In NMC|Li metal cells, VC and PS containing cells showed the highest capacity retention. According to the XPS results, the enhanced electrochemical performance results from a compromise between thickness and composition of the CEI. Regarding to NMC|Graphite cells, PS surprisingly didn't show considerable beneficial effect, which can be attributed to its consumption contributed to thicker CEI at cathode side. Among all additives, VC showed the best performance, demonstrating its positive impact on both cathode/ and anode/electrolyte interphase formation.

New Decentralized Platforms for On-body Analysis of Sweat and Interstitial Fluid Using Potentiometric Sensors

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Wearable analytical devices are extremely attractive for clinical diagnostics and sport performance monitoring owing to the uniqueness of on-body observations accomplished by the integration of different kinds of sensors into conventional materials and objects. Specifically, when potentiometric sensors started to be utilized as the readout of these gadgets, this supposed a true revolution in the field and nowadays, wearable potentiometric ion sensors (WPISs) are being widely proposed in the literature mainly for sweat analysis during sport workout.[1] However, none of the currently developed WPISs have achieved their expected outcomes, being the validation of on-body measurements the main bottleneck to achieve this purpose. On the other hand, while sweat analysis is really spread due to the easy accessibility for this sample to be collected, other biological fluids are not analyzed by WPISs despite their clinical interest.[2] In this talk, two new decentralized platforms to asses ion detection in sweat and interstitial fluid are introduced. The first platform comprises WPISs for pH, Na^+, K^+ and Cl^- detection in sweat while the individual is performing a sport activity whereas the second one is based on a microneedle-patch that has been modified for the transdermal detection of K^+ in interstitial fluid.

The WPISs for sweat analysis presented herein are constituted by potentiometric electrodes of screen-printed type modified with ion-selective membranes, according to the ion target, and a reference membrane. Then, the electrodes are embedded into a sampling cell specially designed to avoid sweat evaporation and contamination while providing a reliable passive sweat flow through the channel in which the electrodes are placed. The most important part of the developed work with the WPISs is based on the validation of on-body measurements by means of sweat collection at different times of the work out practising with an adapted version of the so-called 'Regional Absorbent Patch'. The samples are then analysed using: (i) a twin wearable device but operating ex situ owing to the coupling of a peristaltic pump, (ii) micro pH electrode and (iii) ion chromatography. To the best of our knowledge, this is the first time that such complete validation is accomplished for on-body measurements using WPISs. The good correlations found between the data observed during on-body measurements with the developed WPISs and those analysed with the gold standard techniques pointing out the potential of the device towards its use in daily scenarios. In this sense, real-time profiles under different physical activities and comparing the performance of different subjects will be shown.

The microneedle-patch is based on commercial microneedles modified with a potassium-selective membrane and the reference membrane.[3] An exhaustive characterization of the analytical performances of the patch together with the physical dimensions and cytotoxicity demonstrate the suitability of the device towards transdermal potassium detection in humans without pain during skin insertion and portability. Importantly, the citotoxity tests show that the microneedles can be inserted into the skin no more than 72 h due to a leaching of the ionophore form the membrane. The patch has been successfully applied to detect K^+ changes in artificial interstitial fluid using chicken skin in ex-vivo experiments. Further work will involve the appropriate validation of ex vivo observations towards the final in vivo application.

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Understanding Gas Evolution on Si-containing Electrodes Processed from Aqueous Slurries

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For the near term, Silicon/Graphite (Si/G) composite anodes have been considered as a promising candidate for replacing conventional graphite anodes. By controlling the electrodes' Si content to a maximum of 15% by mass, a theoretical electrode capacity can reach up to 917 mAh/g, which is roughly 2.5 times higher than in graphite. For Si-containing electrode preparation, aqueous slurries employing lithium substituted polyacrylic acid (LiPAA) as binder are commonly used. Due to strong interaction of LiPAA and hydroxyl groups on the surface of Si particles, better homogeneity of the electrodes can be achieved [1]. However, a previous study shows that Si-containing electrodes which are processed from aqueous slurries yield H_2 gas as by-product. This is because Si, which is a strong reducing agent, can react with water during slurry preparation following this reaction: $Si + H_2O \rightarrow SiO_2 + 2H_2O$ [2]. In our study, the effect of aqueous slurry processing on the gas evolution during SEI formation of the Si/G blended electrodes is investigated, using operando Gas Chromatography Mass Spectroscopy (GCMS) and Fourier-Transform Infrared Spectroscopy (FTIR) analyses. By coupling GCMS and FTIR analyses, both continuous gas production from electrolyte decomposition and surface oxidation of Si-containing anodes during cycling are monitored. The Si/G electrodes are prepared with LiPAA binders both in water- based (pH 6.5) and in NMP-based slurries. Rate capability testing using constant current constant voltage (CCCV) mode shows that the electrodes prepared from aqueous slurry exhibit faster degradation compared to those prepared in NMP. In addition, ex-situ Electrochemical Impedance Spectroscopy (EIS) techniques are carried out to analyze the resistance growth after cycling.

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Novel Printable Electrochemical Sensor on Flexible Substrate for Flow Analysis Applications

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Electrochemical sensors are widely used due to their simplicity and inherent miniaturization. Moreover, the analysis is very fast, highly sensitive and low cost. However, one of the challenges related to these devices is extend its application for real samples at the point-of-care and in the field. Thus, it is demanded a new generation of sensors simpler, smaller, easily integrable (bendable substrate), but robust. In this sense, printing technologies offer a suitable solution for the development of flexible electrodes as well as electronics. Thus, these technologies open the gate for the development of a whole new range of flexible devices for many applications in biosensing, Point-of-Care (PoC) analysis and wearable systems.

In this work, the fabrication process of carbon-based electrochemical sensors on flexible plastic substrates has been optimized. Thus, different flexible substrates; including several materials, thickness and color; have been evaluated for printing the new sensors. These sensors have been printed using different carbon and silver ink formulations with several mesh screens (stainless steel, polyester…). The selection of the ink formulations and mesh affects to the final surface morphology as well as the shelf-life and performance of electrodes. In the same way, a critical step in the fabrication of flexible sensors has been the selection of the drying conditions. This step enables the curing of the inks by removing the organic solvents, but without affecting to the flexible substrates. In most of the cases, the plastic substrates show a low glass transition temperature. Therefore, the drying time and temperature as well as the methodologies (box oven, conveyor dryer…) have been essential for avoiding some physical change in the substrate and electrode surface. As a flexible substrate is used, the final electrode structures should also show stretchable features.

A microscopy and electrochemical characterization has been carried out with the new flexible carbon-based electrodes. The final sensor consists of a multilayer structure integrating the working (WE), reference (RE) and counter (CE) electrode as well as a dielectric layer on the same bendable substrate (***Figure 1A***). Thus, the surface morphology of the electrodes was observed by using scanning (SEM) and transmission (TEM) electron microscopy in order to check the effect of the substrate, printing conditions and ink compositions. The performance of new electrodes has been also evaluated by using different electrochemical techniques such cyclic voltammetry (CV), amperometry and electrochemical impedance spectroscopy (EIS), in static, and specially, dynamic conditions.

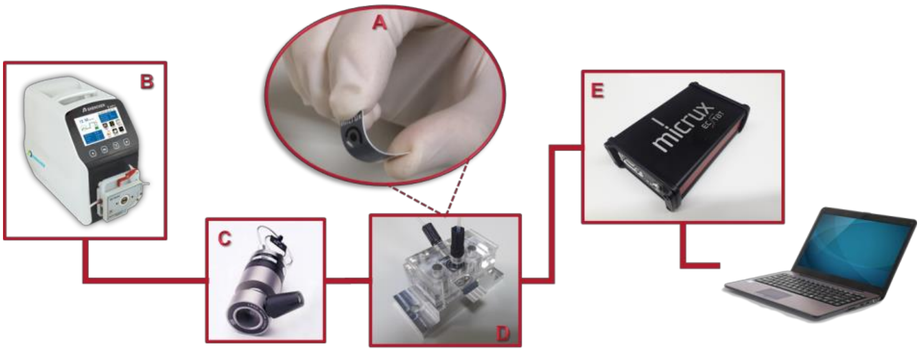

Figure 1. *Experimental set-up including flexible sensor (**A**), peristaltic pump (**B**), injection valve (**C**) modular wall-jet flow-cell (**D**) and portable electrochemical station with built-in impedance analyzer(**E**).*

The new flexible sensors were integrated into a basic flow system by using a modular platform (***Figure 1D***). This platform enables the interfacing between the sensor and the other components of the FIA system; peristaltic pump, injection valve and electrochemical station (***Figure 1***). A portable *All-in-One* electrochemical station with built-in EIS analyzer was used for performing the electrochemical measurements. The performance of the new flexible electrochemical sensors has been evaluated with different benchmark redox compounds in the FIA system.

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Anodizing and post-anodizing treatments for enhancing corrosion resistance of Al Alloys

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Aluminum alloys are employed in many engineering and architectural applications such as aerospace, automotive and building industries for their low specific weight, high specific strength, good conductivity and low price. However they have a poor corrosion resistance in presence of water-containing chloride ions, thus Al alloys are subjected to surface treatments must to improve their performances. Among the anodizing is a widely used surface process to produce anodic oxide coatings that can protect aluminum alloys, developing a porous oxide layer separated from the metal surface by a thin barrier type layer. Several anodizing baths can be used for anodizing processes such as sulfuric acid, oxalic acid and, in the case of AA2024 for aeronautic industry, chromic acid. However, the high toxicity associated with Cr (VI) has imposed restrictions on their use in industrial applications and recently, a new anodizing procedure, involving the addition of tartaric acid in dilute sulfuric acid electrolyte and called tartaric-sulfuric acid anodizing (TSA), was introduced [1].

The corrosion behaviour of the anodic oxide can be further enhanced by post-anodizing treatments such as sealing, that can be carried out in different electrolytes at elevated temperature involving the partial hydration of the aluminum oxide and closing (partially or completely) the porosity [2]. The temperature, composition and fluid-dynamic conditions of the sealing solution affect significantly the processes and the coating properties.

In this work we want to study the effect of a second post anodizing treatment on aluminium alloys aimed to modify the hydrophilicity of the oxide, and, hence, improving their corrosion resistance. The anodizing was carried out potentiostatically in sulphuric acid solution and TSA for 6065-T4 and AA2024-T3, respectively. The sealing of the grown porous layers was carried out in deionized high temperature water without and with the addition of aluminum salts to assess their role in influencing the hydration process, as well as using water vapour. The surface of anodized and sealed Al alloys was then modified using long chain fatty acids for making the coatings hydrophobic or superhydrophobic. Their adsorption was induced by a simple and adaptable solution immersion process [3-4]. The effective linkage of the molecules and the substrates was confirmed by FTIR-ATR analyses, while the wettability of bare and treated samples was measured by contact angle measurements with a FTA1000 (First Ten Angstroms Inc.) instrument.

The corrosion resistance of the alloys soon after these surface treatments was investigated in aggressive (3.5 wt. % NaCl solution) and not aggressive (0.25 M Na_2HPO_4) environments using open circuit measurements, recording polarization curves and using electrochemical impedance spectroscopy (EIS).

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Instantaneous electrochemical impedance spectroscopy as a powerful tool to characterize the breakdown of corrosion properties of model organic coatings

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Organic coatings are a key component in corrosion protection for metals. Breakdown of these coatings can occur due to exposure to water during prolonged periods of time. The water uptake of organic coatings has been studied and modelled extensively in literature. The coating capacitance is typically measured as a function of time and, through the extraction of the dielectric constant of the coating, the water content in the coating is estimated through the Brasher-Kingsbury formula. Yet recently the validity of this approach is challenged in literature [1].

In this work, we want to contribute to that discussion. We will study the breakdown of the corrosion properties of organic coatings considering all physical phenomena that might occur during the exposure to an aqueous solution. To that purpose, we study the behaviour of model coatings with different chemistries. They are based on acrylic and/or methacrylic backbones. Several monomers are used to form the polymer matrix of the model coatings and phosphonic acid or carboxylic acid are used as adhesion promoters.

As is commonly done, we will use Electrochemical Impedance Spectroscopy as experimental technique. By relying on the specific features of Odd Random Phase Electrochemical Impedance Spectroscopy (ORP-EIS) [2], we can provide new insights in the time dependent behaviour of the coatings. We measure the impedance behavior immediately after immersion of the coating in solution and register its evolution as a function of time. As the coating properties are changing rapidly, non-stationary behaviour is observed within the measurements. This non-stationary behaviour is quantified using the time-resolved instantaneous impedance calculation from ORP-EIS measurements [3]. The instantaneous coating capacitance is determined and its evolution is studied as a function of the coating chemistry.

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Carbon-dioxide reduction on N-doped carbon electrodes: structure-activity-stability relationships.

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Nitrogen-doped carbons (N-C) are emerging catalysts in the field of electrochemical CO_2 reduction, because of their high activity, tunable structure, yet significantly lower cost compared to precious metal catalysts. Several studies investigated the role of different types of N atoms on the CO_2 reduction activity and selectivity recently[1]. Many questions, however, remain open as changing one synthesis parameter to tune the N-content and/or N-type will affect other properties such as porosity, conductivity, etc.

By systematic studies we aim to elucidate the effect of the *N/C precursor* as well as the *porosity* on the CO_2 reduction performance of these metal-free catalysts. On one hand, we start from different precursors, but develop very similar pore structures during synthesis; hence the effect of the chemical structure of the catalyst can be explored. On the other hand, we employ the same starting material, but obtain catalysts with systematically varied porosity, unveiling the role of differently-sized pores. These two synthetic approaches give a comprehensive picture about how to optimize the properties of an N-C catalyst to simultaneously tune the product distribution and the activity.

In my presentation I am also going to point out the importance of *isotopic labeling* studies. Such experiments are important in confirming the reduction products being originated from CO_2, and also furnish mechanistic insights into the reduction process. In our recent study, by using non-equilibrated solutions of the selectively labeled the initial carbon sources (i.e., $^{13}CO_2$ and $H^{13}CO_3^-$), bicarbonate anion was identified as the predominant source of the carbon monoxide reduction product.[2,3]

Better understanding of the above-listed parameters is very important in designing new electrodes, such as the metal-nitrogen doped carbons, and new electrochemical cell configurations to scale-up this technology.

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Chemical-mechanical modeling of SEI on silicon particles

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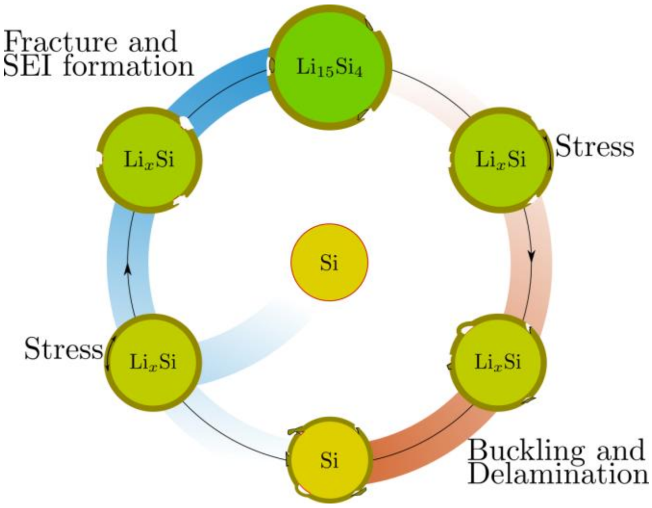
Lithium-ion batteries combine good long-term stability and performance. These properties have made Lithium-ion batteries the benchmark energy storage for hand-held electronics and electric vehicles. Nevertheless, there is an industrial urge to further push the technology towards higher capacities and longer battery life. Increasing the lifetime of Lithium-ion batteries is currently a fundamental challenge for battery research. One important mechanism contributing to the capacity loss is the growth of a solid-electrolyte interphase (SEI) during storage and cycling.

Silicon anodes are a promising approach for further increasing the capacity of Lithium-ion batteries, as they show the tenfold theoretical specific capacity of the currently used graphite anodes. However, the SEI growth is even more severe for silicon anodes: large volume expansions of ~300% exert high mechanical stresses and fracture the SEI. The resulting cracks subsequently expose the pristine electrode leading to SEI reformation and thereby continuous capacity decrease.



In order to further understand SEI growth, our group developed a model describing SEI growth on graphite during storage [1-4]. Thereby, the diffusion of neutral Li interstitials from the electrode to the electrolyte was found to cause the long-term growth of the SEI [1,2].

Additionally, a thermodynamical framework was developed to describe the coupling of chemical, electrical and thermal effects [5]. We extend this model for mechanical effects and investigate how the interplay of chemistry and mechanics impacts stability and growth of the SEI during battery operation.

Understanding these relationships identifies critical operating conditions and aid in the design of new electrodes. Thereby, batteries with higher capacity and long-term stability can be developed.

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Tailoring the electrochemical activity of primary Mg aqueous batteries: anode and electrolyte perspective.

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Many research teams and industrial companies in Asia, USA and Europe are looking for low cost and environmental friendly energy storage solutions. In this context, aqueous primary Mg-based batteries might offer a promising alternative to conventional energy storage devices, attributed to the highly negative electrode potential and high volumetric capacity of metallic Mg. Obviously, developing water-compatible electrode material and electrolytes would greatly simplify processing, reduce manufacturing overheads and expedite recycling efforts. Nevertheless, several factors limit Mg-battery power and shorten the operating lifetime: formation of the blocking deposits and parasitic self-corrosion of Mg electrode.

In this work the enhancement of the battery performance was achieved through optimization of Mg anode via alloying with Ca. Additionally, the battery performance was enhanced via control of self-corrosion by electrolyte additives.

The addition of Ca as alloying element resulted in grain refinement, which was beneficial for the self-corrosion resistance. The optimized Mg anode with small addition of Ca increased the cell voltage and improved discharge properties of the aqueous battery [1].

Further enhancement of Mg-aqueous battery was achieved by addition of complexing agents into aqueous electrolyte [2]. The effect of the electrolyte additives was investigated by different electrochemical techniques (electrochemical impedance spectroscopy EIS, galvanostatic discharge of half and full cell). These additives formed complexes with Mg ions, thus preventing the formation of the precipitates on the surface of the Mg electrode and therefore, increase the cell voltage and specific energy of Mg-Ca based battery. Moreover complexing agents reduced the Mg spalling during discharge which was advantageous for the improvement of utilization efficiency of the Mg-air battery.

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FeCrNi stainless-steel electrodeposition of coatings and micro-nano components from a “green” Cr(III)-based mixed solvent electrolyte

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Stainless steel (SS) alloys are widely used in many applications for their corrosion and wear resistances as well as their mechanical properties. Specifically, AISI 304 (18Cr-10Ni) and 316L SS are important in biological and medical areas. Instead, electrodeposition is a cost-effective and versatile fabrication technique. Indeed, amorphous SS-like FeCrNi electrodeposits have been achieved showing excellent corrosion resistance, bio-compatibility and tuneable soft-magnetism[1]. Therefore, creation of SS-like micro-nanocomponents by electroplating inside micro-nanotemplates has been investigated in this study. First, FeCrNi nanotubes (NTs) and nanowires (NWs) have been achieved by electrodepositing inside 350 nm porous alumina using a Cr(III)-based mixed solvent electrolyte (30vol.% ethylene glycol (EG)). Comparison of FeCrNi films obtained from aqueous and mixed solvent solutions depict that the elemental composition (Fe-Cr-Ni-O-C-N-H), obtained by XPS and ERDA analysis, is similar in both cases. However, estimated current efficiency from XRF is the double for EG-based electrolyte. Indeed, SEM cross-section confirms that electroplating inside AAO templates from the 30vol.% EG solution gives a much higher pores filling ratio with respect to the aqueous electrolyte deposition. In case of FeCrNi mixed solvent, high applied current density results in nanotubes, whereas low current density in compact nanowires. EDX-SEM analysis on different points of a dispersed NW depicts a rather homogenous composition along the wire length (average at%: 62.6Fe-5.5Cr-31.9Ni). However, different NWs from the same sample present heterogeneous Fe-Cr-Ni average content. In the second part, FeCrNi micro-components have been created by electroplating inside two-photon lithography moulds. Different designs have been employed (i.e. pillars and helixes) in order to correlate composition and microstructure with respect to various materials' properties (i.e. mechanical, magnetic, cytotoxicity) at the micro-scale.

In conclusion, FeCrNi mixed solvent electroplating shows enhancement in the current efficiency, therefore a decrease of hydrogen evolution reaction with consequent improvement of the material filling ratio inside micro-nano templates. The growth of Fe-Cr-Ni inside AAO pores is dictated by the current density, producing either NTs or NWs. The versatility of FeCrNi electroplating, when using miniaturised templates, makes this fabrication process very interesting for creating stainless steel-like micro-nano components for state-of-the-art bio-medical/micro-robotics applications, e.g. for magnetically-assisted drug delivery devices.

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Minimizing Fouling of Microelectrode For in vivo Measurement

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Resisting biomolecule adsorption onto the surface of brain-implanted microelectrodes is a key issue for in vivo monitoring of neurochemicals. Furthermore, biofouling often triggers foreign-body responses, leading to the formation of a foreign-body capsule surrounding the implanted electrode and thus isolating it from the tissue. This hinders or completely prevents analyte from reaching the electrode and hence inactivates the implanted microsensor, leading to decreased sensitivity and prolonged response time for in vivo measurements. Coating antibiofouling films has proven to be one of the most effective strategies. The antibiofouling film should be bio- compatible and easily coated onto the surface of the micro- electrode.

Towards the goal of minimizing the protein adsorption on the brain-implanted microelectrodes, we found that pre-treatment of carbon fiber microelectrode (CFEs) with bovine serum albumin (BSA) can minimize further adsorption of proteins when the electrodes are implanted into the rat brain. We demonstrate that electrode precalibration in aCSF containing BSA is valid and effective for in vivo measurements. In this case, the electrode/electrolyte interface formed in the medium employed here for electrode precalibration (i.e., in aCSF containing BSA) may be considered to be similar to that formed in real brain environment in short-term in vivo analysis, from the electrochemical point of view. However, this also causes significant sensitivity drop of CFEs to neurochemicals, including DA.

To in vivo tracking of neurochemical dynamics without decrease of electrode performance, we report an ultrathin cell-membrane-mimic film of ethylenedioxythiophene tailored with zwitterionic phosphorylcholine (EDOT- PC) electropolymerized onto the surface of a carbon fiber microelectrode (CFE), which not only resists protein adsorption but also maintains the sensitivity and time response for in vivo monitoring of dopamine (DA). As a consequence, the as- prepared PEDOT-PC/CFEs could be used as a new reliable platform for tracking DA in vivo and would help understand the physiological and pathological functions of DA

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Theoretical Insight into Electrochemical Properties of Carbon Nanotubes as Doped with Nitrogen and Iron

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Carbon nanotubes (CNT) consisting of a carbon-carbon bond structure have been applied to various energy fields as catalyst supports, including membrane fuel cell[1], electrical conductivity[2], electrochemical energy storage for batteries, and super capacitors[3]. The major reason of use of the CNT material is that they can overcome their inherent electric characteristics (low electric density and sluggish electron flow rate of C atom) using doping methods, electrodeposition, and so on. In our study, CNTs were doped with two nitrogen sources (pyridinic N, N_P, and graphitic N, N_G) and iron to improve oxygen reduction reaction (ORR). Experimental work has shown that CNT doped with N and Fe (CNT/N/Fe) increases ORR efficiency. However, in practical applications, there are limitations due to the uncertain active sites for oxygen and its intermediates, the controversial views on the roles of N_P and N_G, and the ambiguous interaction between N and Fe.

To overcome the limitation, density functional theory (DFT) calculations are performed by selecting a single-wall CNT (10, 0) as a prototype of (10, 0) CNT/N and (10, 0) CNT/N/Fe[4]. During the geometry optimization, the co-existence of N_P and N_G (CNT-III) was greatly extended to CNT diameter 8.78Å compared to single N_P (CNT-I) or single N_G (CNT-II). Besides, CNT-III has higher electrical conductivity and a metallic property since it has no band-gap energy. One of the interesting results is that the N_P-Fe coordination sites provide more active sites for ORR than N_G-Fe coordination sites. Because of the high overlap of Fe *d*-states and N *p*-states at Fermi level, they are energetically stable to give electrons to the oxygen. We have also found that high content of N source and Fe affected to determine catalyst ability of the doped CNT. The CNT with 1.48 % Fe and 2.49 % NP (labeled "Fe-CNT-PA") shows stronger hybridization between N/Fe and C than another CNT with 0.90% Fe and 1.81 % NP (labeled "Fe-CNT-Py"). The Fe-CNT-PA which showed an excellent catalyst for ORR was also applied to CO_2 reduction reaction (CO_2RR) to predict the reaction mechanism and products. In the CO_2RR process, we have observed that CO_2 prefer to produce CO over HCOOH in the process of electron-proton transfer. In conclusion, the high contents of N_P and Fe and N_P-Fe coordination sites provide good active sites for ORR or CO_2.

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Electrochemical primer extension based on polyoxometalate electroactive labels for multiplexed detection of single nucleotide polymorphisms

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Polyoxometalates (POMs) are anionic metal oxygen clusters with remarkable properties including tuneable redox properties, magnetism and biocompatibility, and are formed from early transition metals (such as W, Mo or V), oxygen, often also bearing a heteroatom (Si, P, Ge, etc). Recently we demonstrated the successful bioconjugation of polyoxotungstates $[SiW_{11}O_{39}\{Sn(CH_2)_2CO)\}]^{4-}$ ($SiW_{11}Sn$-Keggin) and $[P_2W_{17}O_{61}\{Sn(CH_2)_2CO)\}]^{6-}$ ($P_2W_{17}Sn$-Dawson) with DNA primers (Debela *et al.*, 2014, 2015), and deoxynucleotide triphosphates (Debela *et al.*, 2017) and we reported on the incorporation of these POM-primers and POM-dNTPs in PCR. In both cases, the electroactive properties of POM allowed rapid and sensitive electrochemical detection of a DNA target. Here we describe the extraordinary possibilities of POMs in electrochemical genotyping, by their application in the detection of single nucleotide polymorphisms (SNPs) through an electrochemical primer extension reaction. A SNP is a DNA sequence variation occurring when a single nucleotide in the genome differs between members of a species or paired chromosomes and occur in at least 1% of the total population.

Polyoxymetalates (POMs) ($[SiW_{11}O_{39}\{Sn(CH_2)_2CO)\}]^{4-}$ and $[P_2W_{17}O_{61}\{Sn(CH_2)_2CO)\}]^{6-}$) were used to modify dideoxynucleotides (ddNTPs) through amide bond formation. Electrodes of an array were functionalised with short single stranded thiolated DNA probes, specifically designed to extend with the POM-ddNTP at the SNP site to be interrogated. The functionalised electrode array was applied to the simultaneous detection of 4 SNPs within a single stranded 103-mer model target, which was generated using asymmetric PCR, demonstrating the potential of POM-ddNTPs for targeted, multiplexed SNP detection. The four DNA bases were successfully labelled with both ($[SiW_{11}O_{39}\{Sn(CH_2)_2CO)\}]^{4-}$ and $[P_2W_{17}O_{61}\{Sn(CH_2)_2CO)\}]^{6-}$), and $[SiW_{11}O_{39}\{Sn(CH_2)_2CO)\}]^{4-}$ demonstrated to be the more suitable due to its single oxidation peak, which provided an unequivocal signal. The POM-ddNTP enzymatically incorporated to the via elongation of the DNA probe anchored to the surface was imaged using AFM with functionalised gold coated mica. The developed assay has been demonstrated to be highly reproducible, simple to carry out and with very low non-specific background signals.

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Biophotovoltaic Algal Fuel Cells for Sustainable Biorefineries

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The world uses more than 550 EJ (EJ=10^{18} J) of primary energy per year, most of it derived from fossil hydrocarbons and carbon that are not renewable. These raw materials are also very advantageous (due to the low oxidation state of C, and therefore possibility to take part in exothermic synthetic reactions) for the production of all types of products through chemical processing. Fossil hydrocarbons are much more difficult to replace as raw materials for the chemical industry than as primary energy. However, the industrial economy of the future should be biorefinery-based in an integrated manner (with both energy and raw materials produced) since biomass is the only renewable primary source with sufficient technical potential to satisfy humanity's needs.

Algae biorefineries (AB) do not compete for land and water with agriculture or other human activities and are therefore considered the most sustainable solution for the future productive model. Although at sufficient scale the AB can become economically sustainable by exploiting the high added value fraction of algal biomass, there is still room for innovation in extracting directly electrical energy from algae if it can be done with high efficiency. Some species of algae and cyanobacteria have been shown to be electrogenic and with optimisation could provide enough energy (through biophotovoltaic fuel cells) for the AB operation. Optimisation should achieve three or four orders of magnitude higher power density from such cells compared to the current state of the art. One school of thought sustains that type IV conductive pili grown by algae can achieve such improvement through direct electron transfer to the electrodes. However, to date, only *Shewanella* species (a marine proteobacterium) have shown pili formation and relatively efficient direct electron transfer to anodes.

In this work we investigate the possibility of direct electron transfer for cyanobacteria and algae that are fast growing and that can grow under heterotrophic conditions as well as perform photosynthesis. For this, we first explored different immobilization methods by means of electrode surface modification and nanostructuring. Secondly we interrogated the electrodes to detect any direct or indirect (through mediators) electron transfer, and finally we have tried ot induce pili formation and determine if they played a role in electron transfer. We show our results with *Scenedesmus* and *Synechocystis* sp. using low cost electrodes (carbon fibre anodes and stainless steel cathodes) and our efforts to characterise the growth conditions that permit the formation of electrogenic biofilms on electrodes. We discuss how more efficient electron transfer from such species could allow the operation of waste-based ABs whereby, urban or industrial waste water and flue gases can be converted to valuable products and direct electricity. In one embodiment mixed urban/industrial waste allowed productivity of more than 10^5 cells/day/mL with particularly rich protein, lipid and carotene fractions.

This work has been carried out with financial support from King Abdulaziz University collaborative project "Sustainable Biorefineries for the Future of Chemical Industry".

Do azolium cations catalyzes CO_2 conversion?

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Azolium cations are conjugate acids of N-heterocyclic carbenes. These cations are considered air and water stable with well-proved performance in different area of catalysis[1]. Here it is shown that the presence of low amount of azolium cations (1 to 5 molar percentage) can catalyze electrochemical CO_2 conversion to CO with almost 100% faradaic efficiency. It is observed that the structure of cations has a subtle effect on catalytic role with 1,2-Dimethyl-3-butylimidazolium (BMMIM) cation having the best apparent performance among tested cations. With 0.1 M BMMIM present in acetonitrile, current density for CO_2 conversion is enhanced by 13 times as compared to that with 0.1 M tetrabutylammonium hexafluorophosphate (TBAP) as supporting electrolyte [Figure 1] . The better performance for BMMIM as compared to other benchmark imidazolium cations is attributed to a different mechanism for catalysis when the carbene carbon center is changed from the 2th position (N_1-C_2-N_3) to a more nucleophilic 4/5th position (N_3-C_4-C_5).

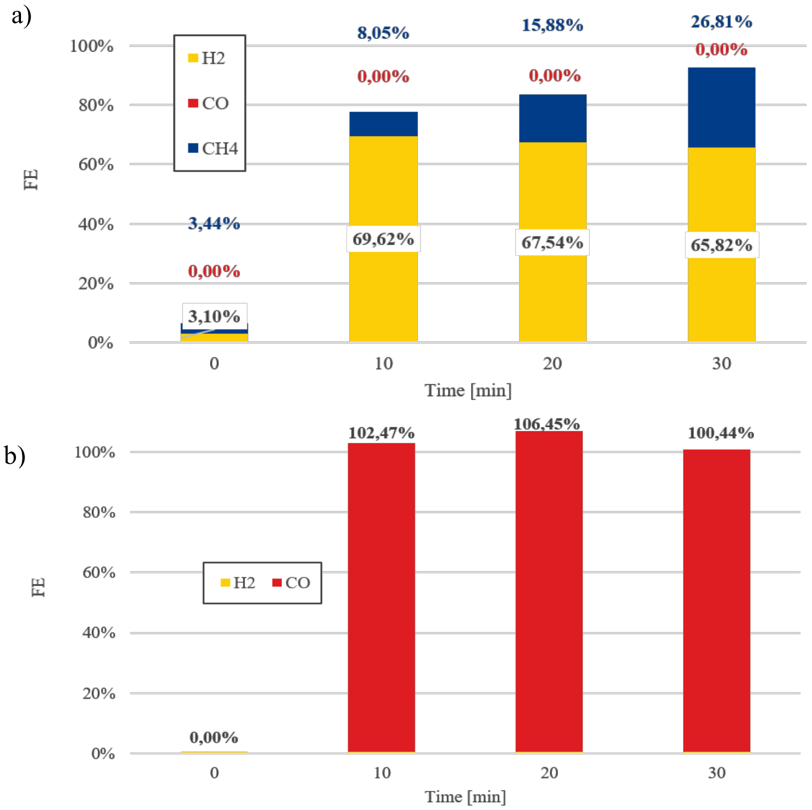

Figure 1. Faradaic efficiencies for CO_2 reduction in acetonitrile a) with 0.1 M tetrabutylammonium hexafluorophosphate (TBAP) and b) with 0.1 M 1,2-Dimethyl-3-butylimidazolium (BMMIM) as supporting electrolyte. As seen, with BMMIM cation HER is almost completely suppressed and 100 % faradaic efficiency for CO is achieved.

Application of an antimony film sensor for sensitive rare earth metal analysis in tap water samples

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This study showcases the development of an antimony sensor for the adsorptive stripping voltammetric determination of rare earth elements in environmental samples. The electrochemical procedure is based on the oxidation of the rare earth elements complexed with alizarin complexone at a glassy carbon electrode that was *in situ* modified with an antimony film, during an anodic scan from –0.2 V to 1.1 V (vs. Ag/AgCl) and a deposition potential of –0.1 V (vs. Ag/AgCl). The sensor operation was optimised by optimising the factors influencing the adsorptive stripping capability of the sensor, which included the complexing agent concentration, plating concentration of antimony and deposition time. Specific rare elements (e.g. La, Ce and Pr) were targeted in the analytical procedure. Voltammetric analysis was realised using a 0.08 M sodium acetate (pH = 5.8) solution as supporting electrolyte, with 2×10^{-6} M alizarin complexone and 1.0 mg L^{-1} antimony solution. The sensor was found to operate under optimised conditions, with a deposition time of 360 s and a linear response was observed between 1 and 25 µg L^{-1}. The reproducibility of the voltammetric measurements was found to be within 5.0% RSD for 12 replicate measurements of cerium(III) concentration of 5 µg L^{-1} using the same electrode surface. The detection limits obtained using stripping analysis was 0.06, 0.42 and 0.71 µg L^{-1} for Ce(III), La(III) and Pr(III), respectively. The operation of sensor using voltammetric stripping analysis showed a limit of detection of 0.06, 0.42 and 0.71 µg L^{-1} for Ce(III), La(III) and Pr(III), respectively. The antimony film sensor was further successfully applied to the determination of cerium, lanthanum and praseodymium in municipal tap water samples.

Keywords: Adsorptive stripping voltammetry; alizarin complexone; antimony film electrode; rare earth elements; tap water

Application of a bismuth-silver bimetallic nanosensor for improved ascorbic acid analysis in pharmaceutical samples

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Ascorbic acid (AA), vitamin C, or 2-(1,2-dihydroxyethyl)-4.5-dihydroxyfuran-3-on is an essential nutrient required by the body for the development and maintenance of scar tissue, blood vessels, and cartilage. Vitamin C is also necessary for creating ATP, dopamine, peptide hormones, and tyrosine. As a powerful antioxidant, vitamin C helps lessen oxidative stress to the human body and is thought to lower cancer risk. It's also enhances iron bioavailability, strengthens and protects the immune system and is thought to help reduce cholesterol levels. Vitamin C deficiency leads to the development of well-known syndrome called scurvy. It is also used for the treatment of many disorders, including cancer, atherosclerosis, Alzheimer's disease, infertility as well as HIV infections. Different voltammetric methods have been proposed and utilised for the determination of AA, using various types of electrodes, but the confidence and applicability of some of these electrodes decrease with repeated use, due to adsorption of the products generated in the AA oxidation. In this study a bismuth-silver bimetallic nanoparticles glassy carbon electrode (Bi-AgNPs/GCE) was employed for the determination of ascorbic acid (AA) in fruit and pharmaceutical samples. This involved the application of a Bi-AgNPs/GCE nanosensor that showed excellent electrochemical catalytic activities toward AA oxidation compared with a bare GCE sensor. Ascorbic acid gave a sensitive oxidation peak at 0.23 V (vs. Ag/AgCl) using differential pulse voltammetry. Under optimised experimental conditions, the limit of detection for AA was found to be 0.16 µM (for S/N = 3), the analytical range for AA was between 0.4 and 1.2 µM ($R^2 = 0.994$) and the RSD was 5.84 % ($n = 10$). The proposed method showed good stability, reproducibility, and repeatability as well as good recovery in fruit and pharmaceutical samples.

Keywords: Bismuth-silver nanoparticles; ascorbic acid; differential pulse voltammetry; fruit samples; pharmaceutical samples

Fabrication of an Immobilized Sensor for the Detection of Creatinine in Urine

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Creatinine (Crn) is produced by creatine and phosphocreatine in the metabolism of muscles. It is a critical indicator for kidney′s function. The normal concentration of Crn in human blood ranges from 53~115 μM while the range of Crn in urine is around 3~23 mM. There are a variety of analytical methods for Crn such as enzymatic method, spectrophotometry method, and LC (liquid chromatography) method. Among these, spectrophotometry method is the colorimetric measurement based on Jaffe′ method. In this work, we proposed the electrochemical detection of Crn with the approach modified from Jaffe′ method. Instead of picric acid in Jaffe′ method to form an orange pigment from the reaction, 3,5-dinitrobenzoic acid (DNB) was used. In this way, rapid detection as well as miniaturization can be accomplished. The reaction of Crn with DNB was confirmed by both UV-Vis spectrophotometry and FTIR analysis. Additionally, different concentrations of Crn were detected and calibrated by the potential changes from the DNB immobilized electrode (Figures 1(a), (b)). The urine specimens were also measured by the as-prepared electrode to evaluate the accuracy on the detection of creatinine concentration (Fig. 2).

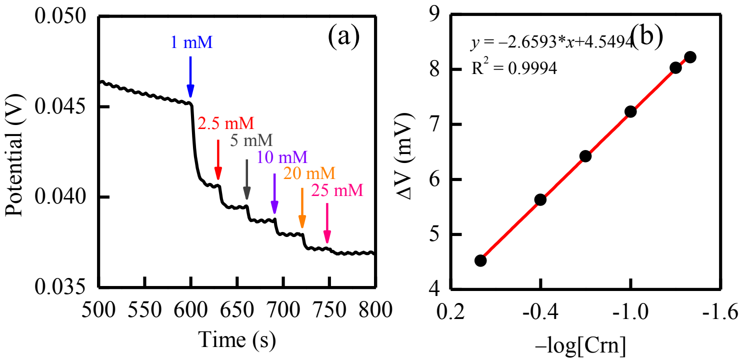

Fig. 1 Detection results from the as-prepared electrode. (a) potential change for different Crn concentrations; (b) calibration curve.

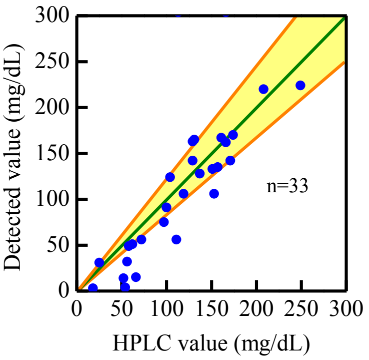

Fig. 2 Crn concentration of urine specimens detected by the as-prepared electrode and by HPLC.

Keywords: creatinine, urine

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C/Au nanostructured electrodes for electroanalytical environmental analysis in water

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Nanostructured materials, such as carbon nanotubes (CNT) and metallic nanomaterials (NMS), have been widely used, in the last years, to modify electrode surfaces because they increased the sensitivity of electrochemical response of organic electroactive compounds and metals in aqueous media as natural waters

In this work, the electrochemical determination of phenolic compounds and metallic ions in aqueous media (environmental matrices), was performed using a glassy carbon electrodes (GCEs) modified with both, multiple-walled carbon nanotubes functionalized with amine groups (MWCNT-NH_2) and oxidized nanotubes (MWCNT-COOH). Moreover, gold nanorods, nanospheres and nanoprisms were synthesized (AuNR, AuNS, AuNPr respectively) and used together MWNTC in the modification.

It is possible to improve the selectivity and sensitivity of signals obtained using nanostructured electrodes with C/Au nanomaterials due to superconducting and electrocatalytic properties of these nanomaterials. The synthesized nanoparticles were analyzed by different techniques, such spectrophotometry UV-VIS, DLS, Zeta potential and SEM.

GCEs were modified with aqueous dispersions that simultaneously contained MWCNT and gold NMS by drop coating method.

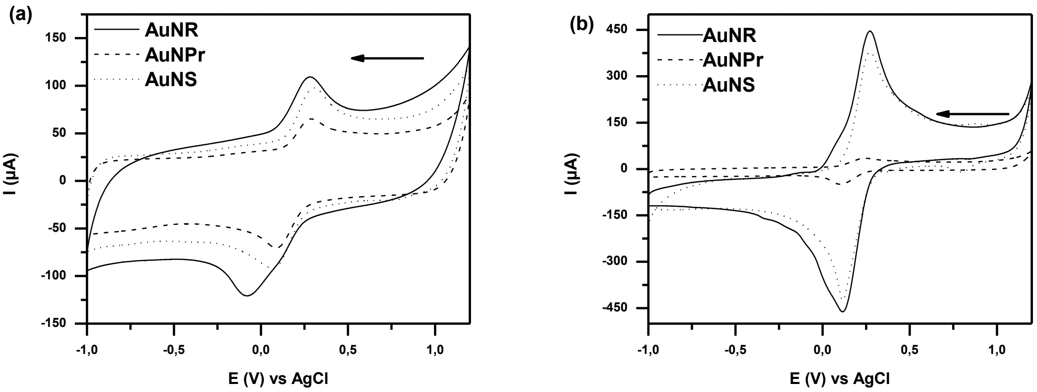

Figure 1. Cyclic voltammogram obtained using modified GCE with (a) MWCNT-COOH modified with gold nanoparticles and (b) MWCNT-NH_2 modified with gold nanoparticles. Conditions: [Fe $(CN)_6$]$^{3-}$/ [Fe$(CN)_6$]$^{2-}$ 0.01 M in 0.1 M KCl. Scanning speed: 50 mVs^{-1}

The presence of AuNS increased the current response for the Fe^{2+}/Fe^{3+} couple in concordance with the results obtained by SEM that shows an increase in the area surface.

An analytical methodology was developed for the detection of polyphenols and metals in waters with highs recoveries.

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Electro-oxidation pathway and determination of cefadroxil at carbon nanotube / gold nanoparticle modified glassy carbon electrodes

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The mechanism of action of pharmaceuticals often involves charge transfer processes which can be investigated in vitro using electrochemical techniques, since most of their products are also generated *in vivo* after enzymatic intermediation. Specific tailoring of electrode surfaces, allowing the detection of reactive intermediates (usually radicals) during electrochemical oxidation, can be correlated with the compounds' biological activity. Cephalosporins are a group of β-lactam antibiotics related to penicillins, with structural differences in the thiazine/thiazolidine ring close to the β-lactam moiety [1]. Their bactericidal action is related to the inhibition of the active site of penicillin-binding proteins, which catalyze the synthesis of peptidoglycan, a component that confers rigidity to the cell wall of prokaryotes.
The electrochemical behaviour of cefadroxil, a first-generation semisynthetic cephalosporin was initially investigated at bare glassy carbon electrodes (GCE). The first oxidation process, at the phenol moiety, follows an ECE mechanism, generating catechol and resorcinol derivatives as sub-products, which are then reduced and oxidized in subsequent cycles. The sulphur heteroatom in the cyclic structure close to the β-lactam moiety is oxidized at higher potentials in two steps generating sulphoxide and then sulphone. The products of these oxidation processes are the most likely to influence the interaction between the β-lactam site and penicillin binding proteins and, therefore, the biological efficiency of the antibiotic.

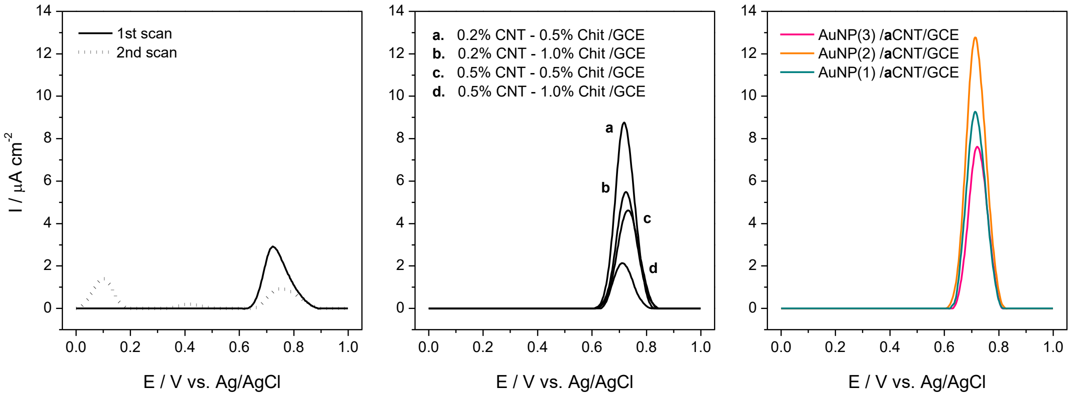

Fig. 1. DP voltammograms at (A) bare GCE, (B) MWCNT/GCE and (C) AuNP/MWCNT/GCE in 0.1M phosphate buffer solution pH 7.0 with 100 μM cefadroxil, Pulse amplitude = 50 mV, step potential = 2.5 mV, $v = 5$ mV s^{-1}.

The electrochemical characterization of cefadroxil was performed at GCE modified with different loadings of multiwalled carbon nanotubes (MWCNT) dispersed in chitosan and gold nanoparticles (AuNP) and differences in the potentials and currents associated with the oxidation process compared with bare GCE will be discussed. Optimization of the modified electrode architecture for sensing, Fig. 1, was carried out using differential pulse voltammetry in phosphate buffer solution. Higher sensitivity by a factor of 5 and a lower limit of detection of 0.2 μM were obtained compared to the bare GCE, attributed to adsorption effects from the subproducts derived from the first oxidation process being hindered. Finally, determination of cefadroxil in commercial samples was successfully carried out.

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Corrosion performance of anodized Mg alloys by Micro-Arc Oxidation (MAO)

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Abstract:

Micro-arc coatings were developed on Magnesium and its alloys AZ91 and AM60, using alkaline KOH. Micro-Arc oxidation was performed with varied conditions i.e. current and voltage. Unipolar and bipolar current were applied. Specimens were characterized by X-Ray diffraction (XRD), X-Ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM). The Corrosion performance was investigated by Potentiodynamic polarization scan and Electrochemical Impedance Spectroscopy (EIS). The results show clear improvement of corrosion resistance for the coated samples.

Key Words: Micro-Arc Oxidation (MAO), AZ90, AM60, EIS

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The effect of graphene addition on mechanical and corrosion properties of carbon steel Ni-P/Graphene coating

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Abstract:

The studies and applications of electroless plating are highly expanding due to its unique characteristics like uniformity and continuity of coating since its dawn in 1946 by Brenner & Riddell. Graphene as a good self-lubricant has been introduced to the nickel phosphorous matrix as Ni-P-C composite by electroless deposition on carbon steel plates and investigated thoroughly through the paper. The conventional Ni-P with and without a surfactant and Ni-P-C with different graphene loads, 8mg/l, 4mg/l and 0.8mg/l, coated samples were examined, as deposited and annealed, to investigate their surface topography by scanning electron microscopy (SEM), morphology and microstructure by X Ray Diffraction (XRD) and Energy-dispersive X-ray spectroscopy (EDX) and micro-hardness by a Vickers hardness tester. Corrosion performance was studied by potentiodynamic polarization and Electrochemical Impedance Spectroscopy (EIS) in 3.5 wt.% NaCl. The mechanical properties and corrosion protection were improved significantly by graphene inclusion.

Key Words: Ni-P Electoless deposition, Graphene, Corrosion resistance.

ACKNOWLEDGMENT

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Corrosion performance of anodized 2XXX Aluminum alloy by Plasma Electrolytes Oxidations (PEO)

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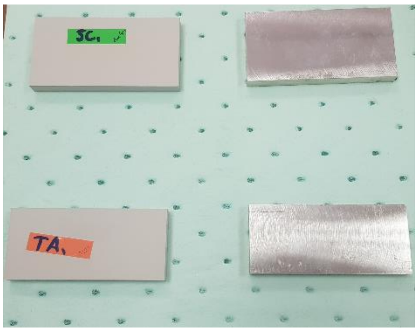
Abstract:



Plasma Electrolytic Oxidations (PEO) were applied on Aluminum and its alloys using alkaline based electrolyte. Plasma Electrolytic Oxidations was performed with unipolar and bipolar current conditions. Structure and morphology were analyzed by X-Ray diffraction (XRD), X-Ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM). The Corrosion performance was investigated by Linear polarization resistance, Tafel plots, and Electrochemical Impedance Spectroscopy (EIS). The results show significant enhancement of corrosion resistance for the treated samples.

Key Words: Plasma Electrolytic Oxidations (PEO) , 2XXX Aluminum alloy, AZ90, AM60, EIS

ACKNOWLEDGMENT

The authors are grateful to King Abdulaziz City for Science and Technology (KACST) for supporting this work.

Facile Synthesis of New PdSnP/C Ternary Nanocatalysts as Highly Active and Stable for Ethanol Oxidation in Alkaline Media

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Outstanding efforts are being carried out to develop new alloy catalysts for direct ethanol (DE) alkaline anion exchange membrane fuel cells (AEMFCs) anodes with free or low platinum loadings and showing a larger efficiency toward the oxidation of ethanol with relatively fast kinetics and large durability. Essentially, it is critical to develop catalysts that avoid the poisoning effect of adsorbed intermediate species during ethanol oxidation reaction (EOR).

A significant enhancement of the EOR catalytic activity of palladium (Pd) has been reported by using Pd non-metallic-based catalysts. Pd deposited onto nickel-zinc-phosphorus (Ni-Zn-P)/carbon (C) alloy, Pd-P/multiwalled carbon nanotubes, dealloyed Pd-Ni-P film and carbon-supported Pd-P, Pd-Ni-P, PdS_x porous nanospheres are some representative examples of this strategy, but the work reported so far on this subject is scarce [1-5]. The incorporation of metallic and non-metallic components in the main catalytic metal Pd may influence the geometric and electronic properties of Pd surfaces and/or block the adsorption of poisoning species [3,4].

In this work, novel C-supported PdSnP catalysts were synthesized under different conditions using both sodium hypophosphite and borohydride as reducing agents. The physico-chemical characterization was carried out by using EDX, XRD, HRTEM and XPS. EOR was evaluated by cyclic voltammetry and chronoamperometry in alkaline medium. The effect of sodium citrate and C pre-treatment on the physico-chemical and electrochemical properties of the catalysts were also studied. The high activity and stability of PdSnP-citrate, due to the nanoparticles size/dispersion on the C support, specific composition and alloying degree, were tuned by citrate used as complexing and stabilizing agent. The kinetic study showed that the rate-determining step in EOR was the removal of the adsorbed ethoxi species by the adsorbed hydroxyl radicals. Current studies are now focused on the evaluation of the catalytic activity in an air-breathing micro-alkaline direct ethanol fuel cell.

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Acknowledgments

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A diamondoid-based additive to mitigate the growth of dendrites in sodium-oxygen batteries

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Recent years have seen a massive increase in the demand for improved lithium ion batteries – especially in view of electromobility and sustainable materials used. Concerns over limited supply of lithium led to the exploration of alternative battery technologies, e.g. based on sodium. The sodium ion technology is currently being pursued as one of the highly promising alternatives [1]. Moreover, using pure metal anodes enables much higher theoretical capacities of 3860 mAh/g and 1160 mAh/g for lithium and sodium, respectively [2]. However, the commercial use of metal anodes is difficult to realize due to dendrite growth [3], thus challenging the processing and fabrication of “next generation” batteries utilizing the metal anode.

In this work, we investigate cycled symmetric Na/Na cells as well as Na/O_2 cells with sodium electrodes utilizing a diamondoid as additive in the liquid electrolyte: Encouraged by the work of Cheng et al. [4] we explore the use of the compound *bis*-N,N´-propyl-4,9-dicarboxamidediamantane – aiming to validate its effectiveness as an additive to suppress the dendrite growth.

By means of electrochemical characterization (battery cycling, impedance spectroscopy), we are able to show the positive effect of the diamondoids by revealing a better cyclability and a slower growth of dendrites at the anode surface. Supported by scanning electron microscopy and rnergy-dispersive X-ray spectroscopy analysis the effect of the additive on the dendrite growth is investigated ex-situ and a working mechanism for the diamondoid-guided co-deposition process is proposed.

The results obtained emphasize that diamondoids are a promising additive with regard to minimize the extent of the dendrite growth. However, cell failure cannot be prevented fully and the improvement of the cyclability of the Na/O_2 cells is less pronounced than for the symmetric Na/Na cells, thus evidently revealing the significant influence of the SEI formation and the passivation of the anode. Consequently, we outline the necessity to use additives in the electrolyte only in combination with a solid electrolyte that separates anode and cathode in a so called hybrid cell setup. In the end, using the hybrid cell setup will enable to fully utilize the positive effect of the additives in electrolytes also for other next-generation battery types.

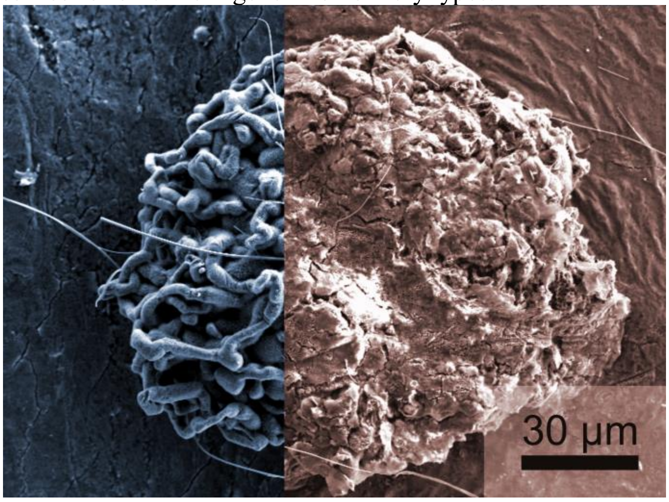

Figure 1: Ex-situ scanning electron microscopy images from a cycled Na/O_2 cell: left – dendritic structure grown on the Na metal anode without the additive in the electrolyte, and right – dendritic structure of similar size obtained with the additive in the electrolyte. It appears that the additive was incorporated into the dendritic structure, thus changing its morphology significantly.

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Fe3O4 Nanoparticles with Dual Electromagnetic Functions for Highly Efficient Catalytic Advanced Oxidation Processes

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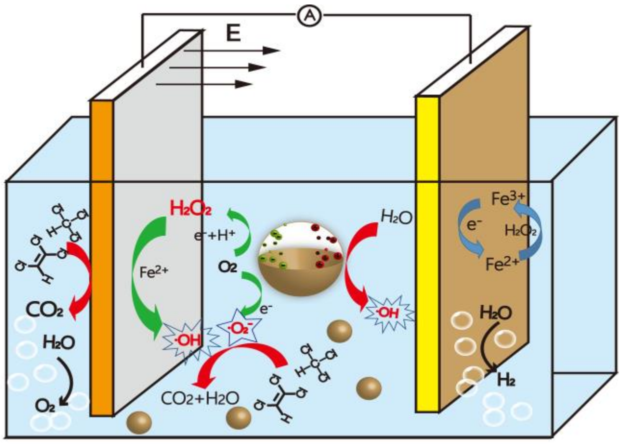
Abstract: Chlorophenols (CPs) belong to a group of ubiquitous contaminants in the environment, which have been listed as environmental priority pollutants by both China and U.S. EPA due to their strong toxicity and even carcinogenic property to human beings. The development of effective remediation strategy for recalcitrant pollutants including CPs is one of the central topics and key issues in the environment field. Here we propose the concept of nano-galvanic cell, with the goal providing a promising alternative strategy, new insight and a guide for highly efficient degradation of water pollutants from contaminated sites. Magnetic Fe_3O_4 and its derivative (Pd/Fe_3O_4) were chosen and prepared as model nanoparticles because of the excellent recovery property of Fe_3O_4 and the high catalytic ability of Pd. These particles exhibit dual functions as galvanic cell and magnet in the electrochemical system (or in electromagnetic field). The spherical Fe_3O_4 nanoparticles are polarized to form numerous nano-galvanic cells under the electric field force, with high accumulation of positive charge Fe-based species on one side and concentration of negative charge (electrons) on the other, respectively, which simultaneously facilitates electron transfer for triggering reduction (e.g., O_2 reduction to produce H_2O_2 and $\bullet O_2^-$) and oxidation (e.g., 4-CP and its intermediates activation) reactions. We show that the nano-galvanic cell system exhibits a strong oxidation capacity for the degradation of 4-CP, which was completely removed in 1 h and further efficiently mineralized as revealed by total organic carbon (TOC) removal efficiency of beyond 90% at 8 h. Meanwhile, the charged Fe_3O_4 nanoparticles induced by current can give rise to magnetic field, which further accelerates the corrosion of Fe-based species and in turn, contributes to producing nanoparticle galvanic cells *via* facilitating surface Fe^{2+}/Fe^{3+} moving to the high magnetic field direction. The strength of this approach lies in a methodology that overcomes the common problems of heterogeneous electrochemical process, such as limited electrode area, mass transfer limitation and poor current efficiency, and realizes synergistic electromagnetic interaction for effective removal of organic pollutants.



Schematic representation of nano-galvanic cell system for effective degradation of 4-CP

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Carbon Based-Nanomaterials for Analytical Applications

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Several azulene-tetrazoles have been investigated as ligands for heavy metal ions recognition. The compounds were studied by electrochemical methods (cyclic voltammetry, differential pulse voltammetry and rotating disk electrode voltammetry). The conditions for complexing films preparation on glassy carbon electrodes were established in correlation with their structure [1-3]. The films were characterized by ferrocene probe testing, impedance spectroscopy, SEM and AFM [4]. The complexing properties of the ligands and their modified electrodes have been investigated towards heavy metals analysis in water solutions by anodic stripping technique [5-6].

Acknowledgments
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Deep eutectic solvent/carbon materials interfacial studies for potential energy storage applications – Effect of carbon modification

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Renewable Energy, coupled with energy efficiency improvements are key elements for the Global Energy Transition Roadmap in bringing a sustainable, safe and smart energy future [1]. Accordingly, supercapacitors are drawing deep attention as high-performance energy storage devices for high energy demand applications. Energy storage is a very challenging topic that may enclose complex mechanisms occurring during the energy harvesting, conversion and storage steps.

Carbon materials can play an important role for storage of energy. Carbon materials can be present in different forms and in conjunction with different solvents and electrolytes [2].

In this work, we present recent results that may contribute to a new generation of electrodes based on carbon materials with the potential application on supercapacitors. Specific capacitance was measured for graphene, graphite and structurally changed graphite/glassy carbon composite electrodes in contact with choline chloride: ethylene glycol (1:2) deep eutectic solvent. Stability was followed by measuring charge/discharge curves at different current densities. CV analysis was also performed.

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Compatibility of High-Concentrated Solvate Ionic Liquids and Low-Viscosity Dilute Solvent for High-Performance Li-S Batteries

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Lithium-Sulfur (Li-S) batteries are attracted attention as next-generation battery for large reversible theoretical capacity of 1,672 mAhg^{-1}. One serious problem of Li-S battery is dissolution of lithium polysulfide (Li_2S_x) as reaction intermediate into the electrolyte solution during charge/discharge reaction. In order to solve this problem, "solvate ionic liquid (SIL)" is proposed as new electrolyte, because dissolution of Li_2S_x can be suppressed[1]. SIL consists glyme solvent of ether molecule and Li salt. Glyme molecules and Li cations can form quite stable coordinated cations, such as $[Li(Glyme)]^+$. [Li(glyme)]TFSA hardly interact with Li_2S_x, and can suppress the dissolution of Li_2S_x into electrolyte solution. However, high Li concentration electrolyte exhibits large viscosity, and has risks of rate performance for high rate charge/discharge operations. Thus, in order to eliminate this disadvantage, we proposed to low-viscosity dilution solvent into electrolyte. In this study, we investigated physicochemical effects and battery characteristics in order to understanding compatibility of two effective approaches as following, 1. excess Li concentration of electrolyte, 2. low-viscosity dilute solvent.

In this study, SILs, $[Li_a(G4)_1]TFSA_a$ (a=1, 1.25) (G4:CH_3-O-$(C_2H_4O)_4$-CH_3, TFSA:$N(SO_2CF_3)_2$) was prepared in Ar-filled glovebox. In addition, we added given predetermined amount of 1,1,2,2,-tetrafluoroethyl-2,2,3,3-tetrafluoropropylether (HFE) dilute solvent into SIL, and measured composition dependences of density for prepared sample.

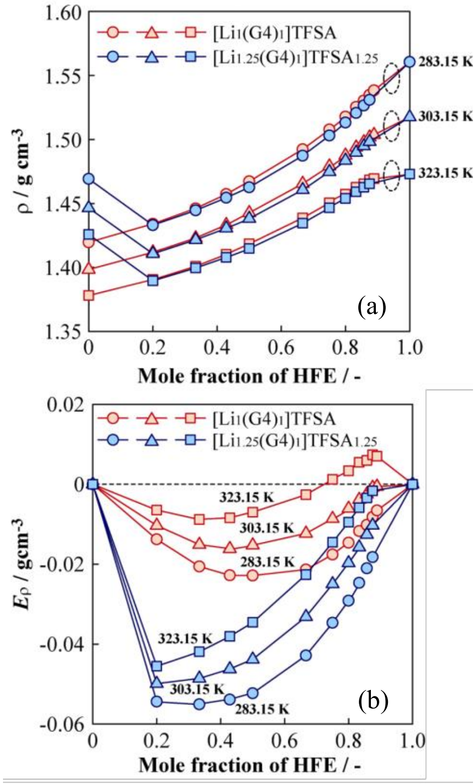

Fig.1 Composition dependence of density (a), Composition dependence of excess density (b) for SIL-HFE mixture.

Fig.1(a) shows the HFE composition dependence of density (ρ) (a=1, 1.25) diluted with HFE. ρ of a=1.25 showed higher density than that of a=1 one. However, by small amount dilution of HFE, ρ of a=1.25 system showed almost the same value with a=1 system. This result suggest HFE may have effect which making similar liquid structure of a=1.25 and a=1 by HFE addition. Furthermore, we calculated excess density (E_ρ) with given equation ($E_\rho = \rho - (x\rho_{\mathrm{SIL}} + (1 - x)\rho_{\mathrm{HFE}})$), where x, ρ_{SIL} and ρ_{HFE} are mole fraction of SIL, ρ of neat SIL and HFE, respectively. Fig.1(b) shows the HFE composition dependence of E_ρ of HFE diluted SIL (a=1,1.25). At the temperature range of 303.15 K or below, E_ρ always showed negative value, and SIL/HFE mixture was expanded (repulsion). SIL/HFE mixture have significant interaction (phase segregation), was inferred. This result correlates with the result that coordination structure the of Li cation and glyme doesn't change greatly when HFE is diluted into a=1 by spectroscopic method[2]. In this presentation, we will report on detailed physical properties and effect for Li-S battery characteristics by results of ionic conductivity, thermal characteristics, Li-S battery performance, self-diffusion coefficient, etc. In addition, we will also report the battery characteristics of this electrolyte systems for other electrode systems.

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Proposal of Sulfolane Electrolyte with High Lithium-salt Concentration for Realization of Next-generation Batteries

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Background

Recently, next-generation batteries with high energy density are required for environmental problem. Energy density of battery increases with operating voltage and capacity. However, when batteries operate over 4.0V, the electrolyte solutions were oxidized and decomposed. Significant improvements for stability (thermal, electrochemical) of electrolyte solution were reported by high Li-salt concentration (ether series [1] / acetonitrile [2]) because of strong interaction between Li salt and solvent molecule. Here, we proposed two approaches are proposed as design of electrolyte solution for high voltage operation.

1. Using sulfolane as a solvent
2. High salt concentration for stabilizing

In this study, we investigated composition dependence of thermal (TG, DSC) and physicochemical (density, viscosity, ionic conductivity) properties in electrolyte solutions. In general, viscosity increases with Li salt concentration, which leads to a bad influence (e.g., rate properties) on batteries. Therefore, hydrofluoroether (HFE) was applied to the sulfolane electrolyte for low-viscous electrolyte systems.

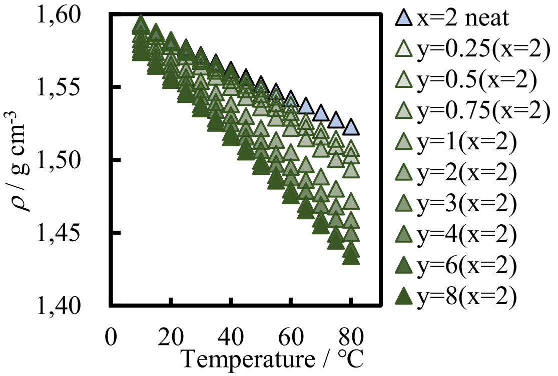

Fig.1 Temperature dependence of density.

Experiments

The samples were prepared by mixing $LiN(SO_2CF_3)_2$ (LiTFSA) to sulfolane (SL) in an argon-filled inert glove box. Solid samples at room temperature are heated by thermoplate. Thermal properties of prepared samples were investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC). Moreover, we investigated density and viscosity of liquid samples by Stabinger-type viscosity / density measurement system.

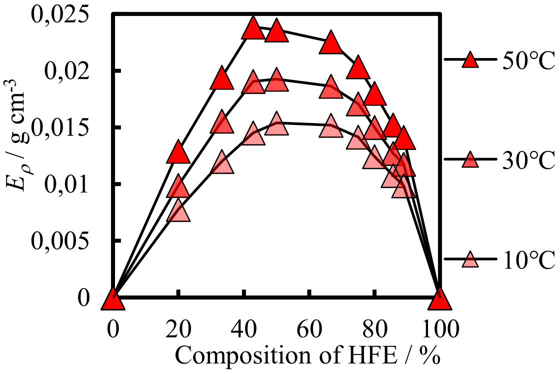

Fig.2 Mole fraction dependence of E_ρ for electrolyte-HFE mixture at each temperature.

Result & Discussion

Fig.1 shows the temperature dependences of density of SL:LiTFSA=2:1 sample (neat) and added HFE samples (*y*=0.25 to 8). The meaning of *y*=0.25(*x*=2) is HFE:Electrolyte (SL:LiTFSA=2:1)=0.25:1. The density was decreased with LiTFSA concentration.

At this time, we assumed electrolyte (SL+LiTFSA) as one molecule, excess densities (E_ρ) were expressed as following,

$$E_\rho = \rho - (z\rho_{SL} + (1-z)\rho_{HFE})$$

Where z, ρ_{SL} and ρ_{HFE} are mole fraction of sulfolane electrolyte (SL), ρ of neat SL and HFE, respectively. Fig.2 shows mole fraction dependences of E_ρ for SL electrolyte-HFE mixtures at each temperature. E_ρ always shows a positive value in the all temperature range. Therefore, obtained density increased by mixing SL electrolyte and HFE. This result indicates SL electrolyte and HFE should have aggregating interactions.

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Temperature dependence of lithium-sulfur battery performance

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Lithium-sulfur (Li-S) battery is expected for next generation rechargeable battery owing to have high capacity (1,645 mAh g^{-1}) compared with conventional Li-ion batteries. However, Li-S battery has serious problem that lithium polysulfide (Li_2S_x), which is an intermediate product, dissolves into electrolyte. To suppress the dissolution of Li_2S_x, we use solvate ionic liquid (SIL) electrolytes. SIL is mixture of 1:1 complex from low-molecular weight ether (glyme) and Li salt (LiTFSA), which have high thermal / electrochemical stabilities owing to strong interaction of between ether oxygen and Li cation. SIL electrolytes have low solubility of Li_2S_x owing to their low Lewis acidity / basicity and suppress dissolution of Li_2S_x into electrolyte.

However, electrolytes based on 1:1 glyme:Li$^+$ complexes can be locally destroyed to form free glyme during charge/discharge cycles$^{1)}$. Free glyme can cause Li_2S_x dissolution, which is major factor in Li-S battery degradation. To decrease local generation of free glyme, we developed glyme:Li$^+$ electrolytes with higher ratio of Li salts, to control Li_2S_x dissolution into the electrolyte and the effect of suppressing the cycle degradation of lithium sulfur battery is confirmed.

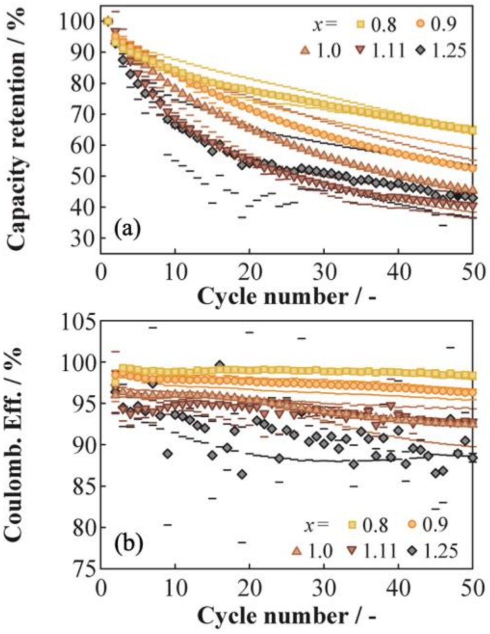

Fig. 1 cycle number dependences of discharge capacity retention per positive electrodes (a) and coulombic efficiencies (b) at 45°C ([S|

Fig. 1 (a) shows cycle number dependences of discharge capacity retention of Li-S batteries using five electrolytes ($[Li(G3)_x]TFSA$ (x=0.8 - 1.25)). The voltage range is 1.5 - 3.3 V, the current is *ca.* $C/12$ and the temperature was set at 45°C to eliminate viscosity effects and accelerate the cycling life tests. The retained discharge capacities after 50 cycles were 64.7% at high LiTFSA concentration electrolyte ($[Li(G3)_{0.8}]TFSA$). A similar improvement in coulombic efficiency was observed with increasing LiTFSA concentration (Fig. 1 (b)). The cell with $[Li(G3)_{0.8}]TFSA$ retained a coulombic efficiency above 98% after more than 50 cycles, and the effect of the deterioration control was confirmed. Under high temperature conditions, dissolution of Li_2S_x is promoted and the deterioration rate is considered to be faster than room temperature.

It is essential to clarify the influence of temperature for practical application of Li-S battery. Furthermore, it is thought that the battery life can be easily estimated by the accelerated degradation test at high temperature. And, reduction of test time for charge / discharge cycle life was expected. Therefore, we have to investigate the relationships of between direct solubility of Li_2S_x into electrolyte and the Li-S battery performance. In this presentation, we will report on the solubility of Li_2S_x using a fluorometer equipped with a thermostat and the temperature dependency of Li-S battery performance.

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Electrochemical Methane Production Using Coenzyme F430 as an Electrocatalyst

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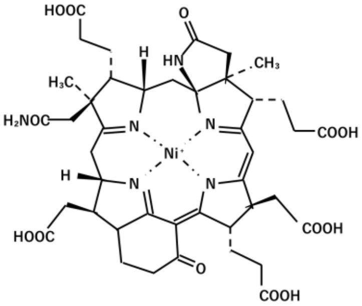

Fugure1. Coenzyme F430

Coenzyme F430 is the hydrocorphinoid nickel complex which is contained in the enzyme, methyl coenzyme M reductase (MCR). MCR is responsible for the final step of the methanogenic reaction in the methanogenic archaea.[1] F430 is known to be involved in the reduction of methyl coenzyme M to methane as active center of MCR.[2] F430 resides at the end of the hydrophobic channel in the MCR.[3] Due to the hydrophobic channel, MCR has strict reaction selectivity and can utilize only methyl coenzyme M (CH_3-S-CoM) as a substrate.

F430(red) + substrate → F430(ox) + methane + product

The reduced form of F430 has Ni(+1), whereas oxidized form has Ni(2+).

F430(ox) is known to be reduced by using a reducing agent such as titanium citrate (III).[4] In this study, we utilized purified F430 as an electrocatalyst to produce methane from a variety of substrate which contains methyl group.

F430(ox) + e^- → F430(red) (at electrode)

The electrochemical methane production allows continuous methane production without any reducing agent.

CH_3-S-CoM did not show any electrochemical response on carbon, gold, and Pt electrode. Thus, we investigated the electrochemical reduction of CH_3-S-CoM using F430 as an electrocatalyst in pH 10 CAPS buffer solution. However, the CV did not change when we added F430 into the CH_3-S-CoM solution. Even the redox response of F430 on the electrode surface was not observed. We introduced redox mediator to facilitate the electron transfer between F430 and electrode. An increase of reduction current, starting at −1 V vs. Ag|AgCl was observed by adding methyl viologen into the F430 and CH_3-S-CoM solution. Because no catalytic current was generated in the absence of F430, we can conclude that F430 can catalyze the reduction of CH_3-S-CoM with an aid of methyl viologen as a redox mediator. Constant potential electrolysis at −1.3V vs AgAgCl was conducted using carbon cloth electrode in sealed electrolysis cell. The gas bubble was generated on the electrode surface after starting the electrolysis. The catalytic current was continuously generated for more than 10 hours. We finally analyzed the gas in the headspace generated from the electrode surface; gas chromatography analysis revealed that the gas contains not only methane, but also ethylene. No hydrogen gas was detected.

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Li-Fluoride protective coating on $LiMn_{1.5}Ni_{0.5}O_4$ cathode for high-energy storage applications

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We intend to present, for the first time, atomic layer deposition of a protective LiF coating on $LiMn_{1.5}Ni_{0.5}O_4$ cathode powder material for high-energy storage applications.. The Li-containing thin-film serves as a protective layer against Mn dissolution during battery operation and contributes to high capacity and prolonged stability.

The Mn dissolution is enhanced at the typical operating temperatures of EVs, according to the following mechanism:

$$(1) \qquad 2Mn^{+3}_{(solid)} \rightarrow Mn^{+4}_{(solid)} + Mn^{+2}_{(solution)}$$

This reaction reduces the durability of the cathode and damages the overall cell performance, due to the formation of side products that accumulate at the anode-electrolyte interface and hinder safe Li^+ transfer. One possible solution to this problem is the coating of the cathode material with a protective layer. The coating layer must be stable under the operating conditions of the battery, while allowing migration of Li^+ and at the same time the coating must preven Mn dissolution from the electrode. Metal fluorides, and specifically LiF, are good candidate for this task, as will be illustrated during this work.

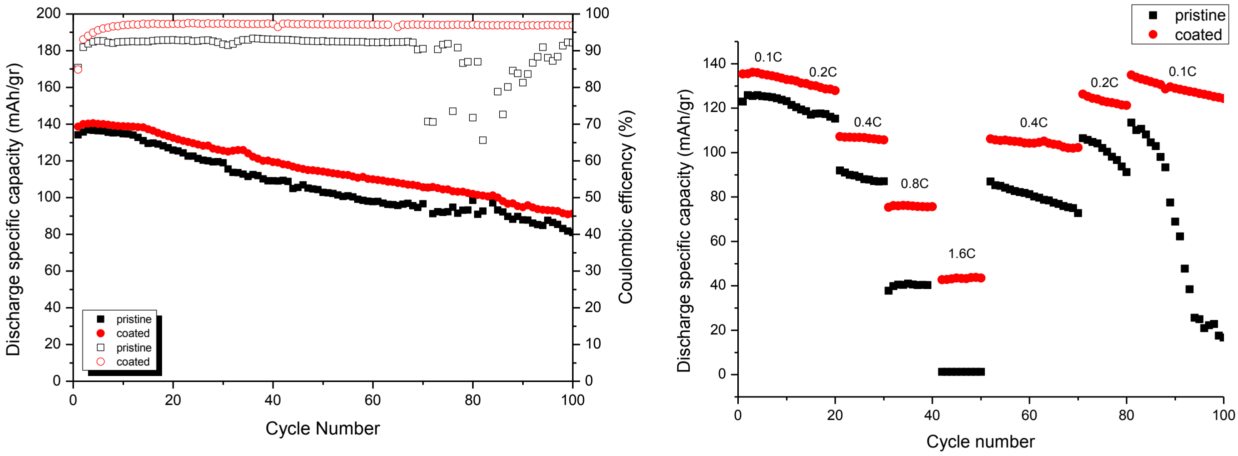

Figure 1. (a) Capacity vs. cycle of pristine and coated electrodes in 1[M] LiPF6 EC:DMC half-cells vs. Li/Li+. (b) C-Rate performance for pristine/coated electrodes in the same configuration.

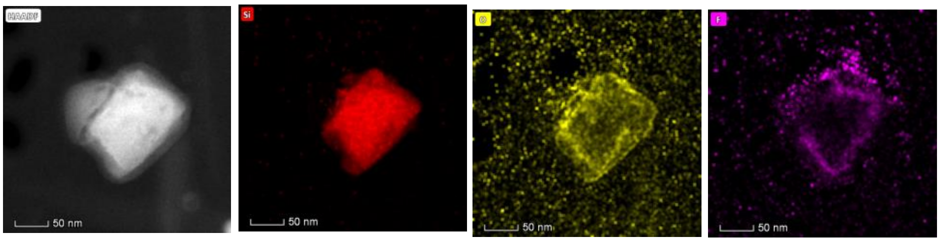

Figure 2. HAADF TEM scan of Si particle (red), showing SiO_2 layer in yellow and F coating in purple.

Diazonium Electrografting for Stripping Analysis and Fabrication of Biomembrane-like Film

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The aromatic diazonium salts can be electrochemically grafted onto various materials, such as carbon materials, metals, and semiconductors. The diazonium-modified electrodes can withstand long-term storage in air, sonication, and repeated redox cycling over a wide electrochemical window. This modification method is a very versatile and simple way to graft various functional groups for diverse applications. The high stability of the diazonium-modified electrode and the versatility of the diazonium modification method make diazonium-modified electrode attractive for various applications.

We reports here that diazonium electrografting can be used to modified electrode with carboxyl group and alkyl group as well as the resulting modified electrode for the applications of stripping analysis and the fabrication of biomembrane-like films and its biosensing applications [1-2]. The benzoic acid-modified glassy carbon electrode enables sensitive stripping analysis of Cd^{2+} and Pb^{2+}. The biomembrane-like films facilitate direct electrochemistry of myoglobin, enabling sensitive detection of hydrogen peroxide based on electrocatalytic reduction.

Acknowledgements This work is kindly supported by the Ministry of Science and technology of the People's Republic of China (No.2006BAE03B08), the National Natural Science Foundation of China (No. 20875086 and 21175126), the Academy of Sciences for the Developing World (TWAS), Chinese Academy of Sciences (CAS), HEC Pakistan, and The Islamia University of Bahawalpur Pakistan.

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Fabrication of Solar Cells With Electrically Enhanced Transition Metal Dichalcogenides As Charge Transporting Layers

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Transitional metal dichalcogenides (TMDs) are compounds with the general formula MX_2, were M is transitional metal and X is chalcogen. These materials are arranged as layers stacked together by weak van der waals forces. They have found application in photovoltaic cells due to their high carrier mobility, chemical stability and flexibility. Exfoliation of the bulky TMDs maintains these properties and further imparts properties such as switching the bandgap from indirect to direct which increases the carrier mobility of the material [1]. Exfoliated MoS_2 was characterised by XRD, Raman spectroscopy and SEM. XRD studies showed prominent peaks (002) and other weak reflections at (100), (103), (006) and (105). Comparing the exfoliated with the bulk, the weakening of reflection at (002) shows that the material is highly exfoliated (fig. 1) [2]. Raman spectroscopy (fig.2) showed the E^1_{2g} (393 cm^{-1}) and A_{1g} (409 cm^{-1}) peaks for exfoliated MoS_2 are closer together compared to their bulk counterparts (378 cm^{-1} and 408 cm^{-1}, respectively) [3], this confirmed exfoliation. Exfoliation was further confirmed by SEM. The exfoliated TMDs were used to make a p-n heterojunction in a solar cell with the following architecture: FTO/Nickel phthalocyanine/MoS_2/Ag. The incorporation of the TMDs resulted in a flexible solar cell with enhanced stability and enhanced charge carrier mobility compared to conventional solar cells.

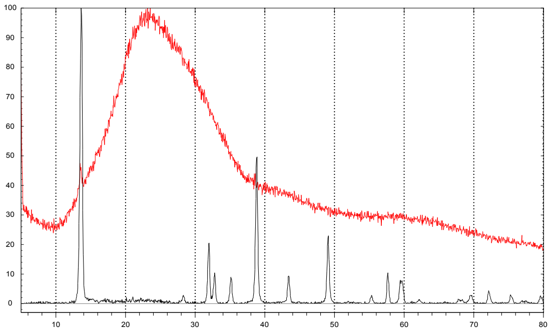

Fig. 1: XRD patterns of (black) bulk MoS_2 and (Red) exfoliated MoS_2 sample

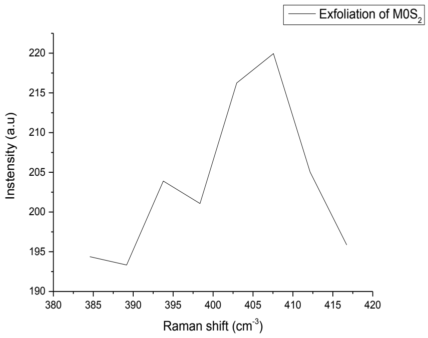

Fig. 2: Raman fingerprint for exfoliated MoS_2 sample

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Synthesis and Properties of CdTe nanowires fabricated electrochemically via template method

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Nanowires are of great interest due to their dimensionality which plays an important role in determining the properties of materials. One of the most versatile such nanostructures are semiconductor nanowires because they allow a control of key parameters such as chemical composition, diameter, length, dopping, electronic properties. [1] From the semiconductor compounds in group II-VI, CdTe has a high optical absorption coefficient in the visible range of the electromagnetic spectrum, thus is a very good candidate for manufacturing various sensing devices. [2,3,4]

The first step of our research consisted in fabricating and characterizing CdTe nanowires of different composition and dimensions. The method chosen to produce the nanowires was electrochemically using bottom-up template method. The template was a polycarbonate membrane of 20µm, irradiated with heavy ions having a flux of 10^9 ions/cm^2. We modified the composition throughout the electrodeposition potential and we controlled the dimensions first of all by modifying the diameters of the polycarbonate membrane pores and secondly the length was manipulated adjusting the time of deposition.

In the next step we characterized the CdTe nanowires employing techniques such as scanning electron microscopy, energy-dispersive X-ray spectroscopy, reflection, X-ray diffraction. Thus we were able to analyze the morphology, the composition, the structure and the value of the bang gap.

Afterwards we focused on studying the influence of growing parameters over the electric behavior of the nanowires. Since the final purpose is to manufacture electronic devices, of great importance is contacting the nanowires on an oxide substrate in order to obtain an Ohmic response. Using electron beam lithography, followed by Au/Ti sputtering we assembled the contacts between the nanowires and Au/Ti interdigits.

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Influence of electrodeposition parameters and electrochemical bath composition on the electrical properties of multichannel ZnO nanowire field effect transistors.

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Zinc oxide is an attractive material for many applications due to its properties, low toxicity and high natural abundance. This material presents polymorphism, a wide range of nanostructures as nanowires, nanotubes, spheres, tripods, urchins and so on, being synthesized. One-dimensional (1D) nanostructures such as nanowires are very interesting and studied due to their exceptional electrical and optical properties. Field effect transistors based on ZnO nanowire are of interest for sensor applications including for biodetection. Electrochemical deposition is a technique which may be successfully used to deposit nanowires in certain range of experimental conditions. In this work, lithographically patterned electrodes on Si/SiO_2 substrates were employed as working electrodes in the process of depositing zinc oxide nanowires. Cobalt doping was achieved from the growth step by adding a cobalt salt to the electrochemical bath. Cobalt doped ZnO nanowires were grown in this way. Electrical transport properties were measured for samples fabricated in this way and the results were correlated with those obtained from optical, structural and compositional characterization and with deposition parameters. By combining photolithographic technics with electrodeposition, low cost devices can be fabricated. By controlling the electrodeposition parameters, the device characteristics can be controlled.

Electrochemistry of Particulate Electrodes Based on Magnetite Aggregates for Electrochemical Extraction and Recovery of Metals

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In current research, micro and nanoparticulate electrode materials have taken their place because they offer a large internal surface area with respect to the macroscopic dimensions of such electrodes [1]. The nano-impact method is a powerful tool that enables the characterization of individual particulate nano-objects in solution and study of their reactivity [2]. A three electrodes setup system working as a standard electrochemical cell is typically used. Magnetite (Fe3O4) nanoparticles with the strongest saturation magnetization of all naturally occurring iron oxides, combined with properties such as low toxicity, good biocompatibility, high stability, and low production costs, have attracted a lot of interest [3]. There is also substantial interest in their use as magnetic fluids, in data storage, in catalysis, and as electrode materials.

In this work, magnetite micro and nanoparticles have been synthetized by chemical precipitation method in presence of surfactants or functional organic polymer. The use of surfactants to stabilize these synthesized nanoparticles is crucial, as Fe3O4 nanoparticles have high surface energies and tend to aggregate. They also have high chemical activity. Magnetite particles are used as particulate electrode in different fluid and characterized into a three electrodes cell in order to evaluate their electrochemical behavior. A deeper understanding of the particulate electrode has been performed in situ on supported particles through electrochemical AFM/STM measurements, highlighting the behavior of the single aggregate. Together with the charge transfer characterization as a function of particles size and concentration, functionalization and fluid composition, practical applications of the particulate electrodes will be presented. Specifically, the use of particulate electrodes in the electrochemical metal recovery, showing the ions adsorption properties of magnetite particles as a function of surface functionalization and their electrochemical reduction at the magnetic fluid/current collector interphase will be discussed for specific systems, e.g. copper and lithium.

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Antioxidant and anticancer potentials of *Protorhus longifolia* leaves and its synthesized PCL nanoparticles

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The interest on the use of plant extracts for the treatment of various diseases has intensified due to their promising therapeutic activities. Plant extracts encapsulated into polymeric nanoparticles offer many advantages towards improving the therapeutic activities of active compounds. *Protorhus longifolia* belonging to the Anacardiaceae family possesses some biological active compounds and has been used traditionally to treat different types of ailments. This work aims at fabricating polycaprolactone (PCL) nanoparticles (NPs) using *Protorhus longifolia* leaves extract by emulsification solvent evaporation method. Furthermore, to evaluate their *in vitro* antioxidant and cytotoxicity activities in comparison to the crude extract. The prepared NPs were characterised by Dynamic Light Scattering, Scanning Electron Microscope, X-ray Diffraction and Attenuated Total Reflection Fourier Transform Infrared spectroscopy. Antioxidant activities of crude extracts and nanoparticles (NPs) were determined by 2,2-diphenyl-1-picrylhydrazyl and Ferric reducing ability of plasma assays, cytotoxicity activity of extract and NPs was investigated through MTT assay. The results demonstrated that the NPs exhibited significantly higher antioxidant and anticancer potentials in comparison to crude extract. The information obtained in this study indicates that NPs represent a possible valid system for the enhancement of therapeutic activities.

Carbon Dioxide Sequestration using Electrochemical Technology

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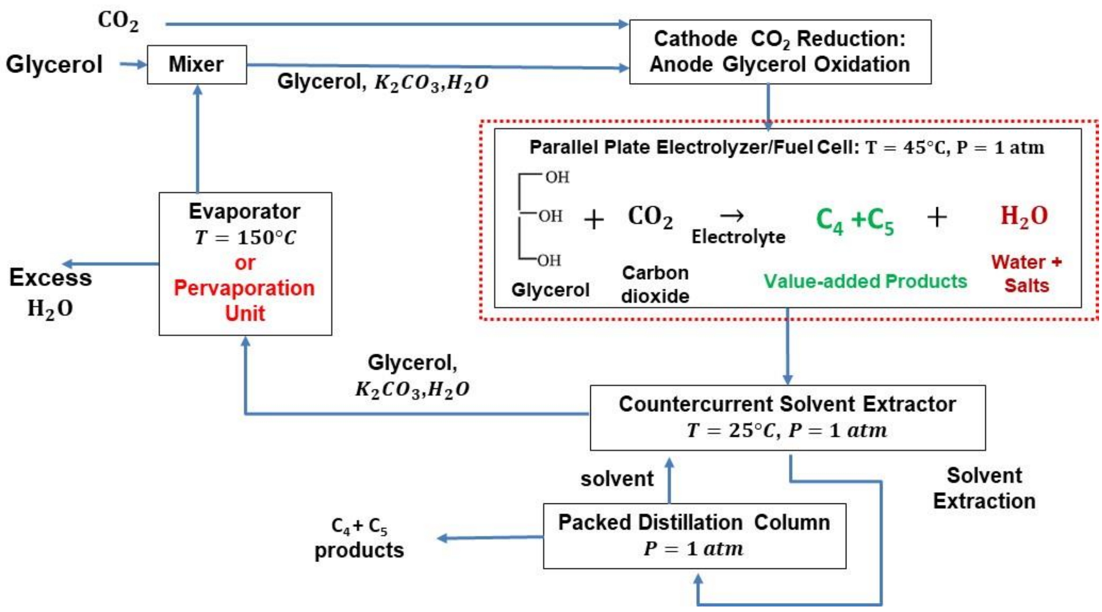
Reduction of carbon dioxide emission to the atmosphere has become a priority for many countries, yet the challenge remains how to accomplish this in an economical and sustainable manner. In-ground storage requires energy for compression and there is concern that the carbon dioxide may escape at some time in the future. Conversion of carbon dioxide and water into useful simple hydrocarbons (synthetic photosynthesis) requires that renewable energy be used. However, direct use of the renewable energy to displace conventional fuels is more efficient and economical than producing synthetic hydrocarbon fuels. Thus there is a need to examine alternative technologies for carbon dioxide sequestration.

The approach taken in this work is to use electrochemical energy to effect coupling of carbon dioxide to existing organic species thereby extending chain length and producing new products which ideally have more value. By starting with an organic molecule much of the energy required for the water and carbon dioxide reaction can be avoided. To demonstrate the approach, the electrochemical conversion of glycerol (C3) to C4 and C5 compounds by the addition of carbon dioxide will be discussed. Glycerol was chosen as a candidate C3 material because it can be a biosourced material, it has hydroxyl groups, it is compatible with aqueous electrolytes and has relatively low market value. The latter low value curiously has arisen from the production of biodiesel as a renewable energy replacement for conventional diesel fuel. Biodiesel is produced by transesterification of oils and fats which produces glycerol on a 1:1 molar basis with biodiesel. This additional source of glycerol has saturated the market and created a new challenge for glycerol marketing.

Thus by using glycerol as a starting material and coupling carbon dioxide to its structure to create C4 and C5 compounds, value can be created to offset process costs and ideally generate revenue.

The electrochemical cell configuration required to demonstrate the reaction and the process for scale up will be described. A schematic of the process is shown below.



Development and comparison of non-imprinted and imprinted polythiophene sensors for the detection of polycyclic aromatic hydrocarbons in aqueous media

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ABSTRACT

Electrochemical reactions occur when a current is supplied externally or produced by a spontaneous chemical reaction. Redox reactions, commonly known as oxidation-reduction reactions are chemical reactions in which electrons are directly transferred between atoms and molecules. Electrochemical oxidation is a vital treatment process for wastewater. In this review, phenanthrene detection was studied through the construction of a non-imprinted polymer (NIP) chemical sensor and molecularly-imprinted polymer (MIP) chemical sensor. Cyclic voltammetry (CV) was used to characterize the NIP and MIP chemical sensors and a glassy carbon electrode (GCE) polymerized with polythiophene was used to study the electrochemical oxidation of phenanthrene using square wave voltammetry (SWV). Analysis of obtained results from SWV showed a very low detection limit of 0.3846 mM with a linear range of 0.08 mM – 0.16 mM for MIP, while the detection limit was found to be 0.9340 mM with a linear range of 0.1 mM – 0.18 mM for NIP. This linear range is proportional to an oxidation peak current and is an indication that MIP enhanced the detection of phenanthrene.

KEYWORDS:

Non-imprinted polymer (NIP) sensor
Molecularly-imprinted polymer sensor (MIP)
Phenanthrene
Cyclic Voltammetry (CV)
Square Wave Voltammetry (SWV)
Glassy Carbon Electrode (GCE)

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Tetrathiafulvalene-Azobenzene Macrocycles: Controlling Electrochemical Properties of Tetrathiafulvalene by Light

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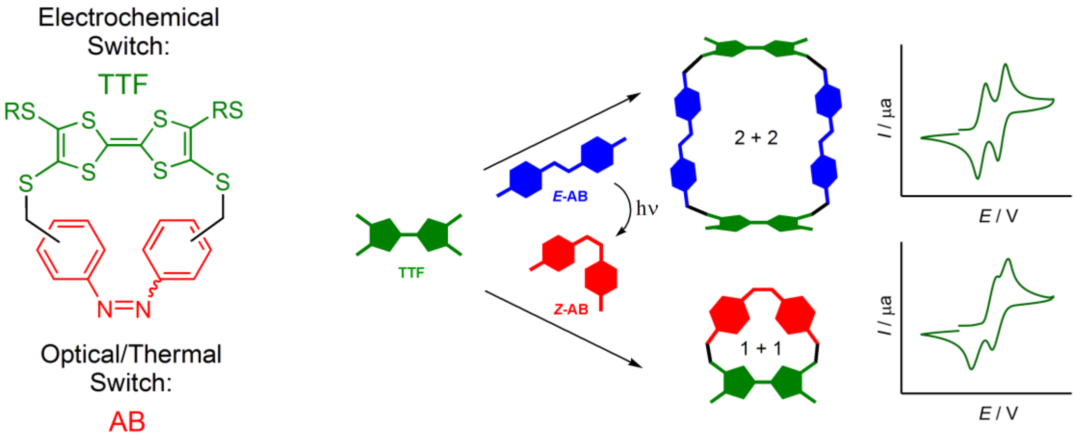
Visual perception is based on the transformation of a photon into an electrical signal via reversible *Z*—*E* isomerization of double bonds in a photochromic molecule. As a possible design for a simple molecular system capable of altering its electronic properties when exposed to light, we have considered molecular architectures containing tightly bound photochromic and redox active units within a rigid macrocycle. We have selected azobenzenes[1] (AB), versatile and easily tunable photoswitches, as optical modulators for our systems, and tetrathiafulvalenes[2] (TTF), redox active heterocyclic compounds displaying two consecutive reversible oxidation potentials, as possible redox-responsive units.



We have investigated macrocyclization between TTF dithiolates and *bis*-bromomethylazobenzenes/*bis*-bromomethylstilbenes under high dilution conditions and have shown that macrocycles of different size can be formed depending on whether the (*Z*)- or (*E*)-isomers of azobenzene or stilbene are used. This represents the first example of a light-controllable cyclization reaction. Using cyclic voltammetry, we have shown that redox behavior of the small, structurally rigid, TTF-AB macrocycle depends on the conformation of the AB moiety. In the macrocycles with *E*-configuration of AB, TTF displayed the features common to typical TTF derivatives, whereas in the macrocycles with *Z*-configuration of AB first oxidation potential was significantly shifted. Results of DFT calculations confirmed that the out-of-plane distortion of the TTF moiety in this macrocycle is responsible for the variation of its oxidation potential upon photoisomerization of the neighboring AB bridge. In future, such switchable macrocycles may serve as prototypes for single molecule memory units with orthogonal write and read modes.

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Electrochemical, optical, structural and microscopic studies of $ZnCrO_4$ nanomaterials prepared via biosynthesis using natural extracts of Hibiscus *Rosa Sinensis*

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The nanomaterials of zinc chromite ($ZnCrO_4$) were synthesized using *Hibiscus Rosa Sinensis* natural extracts as an effective bio-reductive and chelating agent. Zinc chromite ($ZnCrO_4$) is a mixed oxide which crystallizes in the cubic system and has a normal spinel structure [1-3]. The synthesized samples will be characterized by X-ray diffraction (XRD), High resolution scanning electron microscope (HRSEM), High resolution transmission electron microscopy (HRTEM), Energy dispersive X-ray (EDX), diffused reflectance spectroscopy (DRS), photoluminescence spectroscopy (PL) and Fourier transform infrared spectra (FTIR) in order to develop a mechanism of reaction between metal precursor and natural extract. The electro activity of ZnCrO4 nanomaterials was investigated on glassy carbon electrode, drop coated the binary nanomaterials were systematically studied in alkaline medium of potassium hydroxide (KOH) by cyclic voltammetry (CV), square wave voltammetry (SWV) and electrochemical impedance spectroscopy (EIS).

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Preparation and physicochemical properties of nanoformulated N-P-K-S fertilizer

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Abstract

The use of fertilizers has showed an improvement on growth of the crops. However these fertilizers are expensive. Overuse of the current fertilizers has led to environmental pollution and eutrophication. Nanofertilizer technology is seen as the solution to the challenges raised by the current fertilizers because it is cheaper, and it has more increased surface area. In addition, it has been found that there is a lack of sulphur in the North-West soils (Mafikeng) especially for the growth of maize [1]. In this study, N-P-K-S fertilizer was encapsulated using chitosan-tripolyphosphate polymer with the pH value of 5.5. The chitosan nanoparticles were further characterized by ultraviolet-visible spectroscopy, Fourier transform infrared spectroscopy, scanning electron microscopy, X-ray diffraction and zeta-sizer. The results showed that formation of chitosan-tripolyphosphate (CS-TPP) nanoparticles was successful, and they showed a very good size in the range of 200-500 nm with low PDI values. Furthermore, the use of nano N-P-K-S displayed a great improvement in the growth of maize. The results obtained showed that CS-TPP nanoparticles have the potential characteristics which can be of great use in encapsulation of the fertilizer in future.

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Cationic dye removal by grafted gum based polysaccharide as adsorbent: effect of various parameters

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There has been a steady drop in fresh water resources worldwide due to rapid industrialization and population growth [1]. As a result, water systems are being compromised due to conventional techniques causing secondary pollution upon usage [2]. The aim of this study was to prepare grafted gum based polysaccharide and subsequently evaluate their efficiency as adsorbent for the removal of methylene blue (MB) from aqueous solution. Additionally, the structure and morphology for the adsorbent were determined using Fourier Transform Infrared Spectroscopy (FTIR) and scanning electron microscopy (SEM), while thermal gravimetric analysis (TGA) was utilized for thermal properties. Consequently, parameters affecting dye removal including adsorbent dosage, pH medium and reaction time were explored. The process of adsorption was found to be strongly dependent on the pH of the dye solution. Results demonstrated that the adsorbent was able to produce percentage removal of 94% with 2 as the optimum pH of the MB solution. The outstanding adsorption capacity of the adsorbent for dye removal was due to the bonding between the anionic adsorbent and cationic dye. Afterward, the stability and surface charge of -36.4 mV for the adsorbent was confirmed by the zeta potential. Furthermore the functional groups responsible for absorption of MB, such as carboxylic group and sulfonic group were verified by FTIR. The information given in this work shows that the prepared adsorbent can have a positive effect for the treatment of industrial wastewater.

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Development and Evaluation of Electrocoagulation Systems from Non-Conventional and Alloy-Based Electrodes

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Keywords: Electrocoagulation, wastewater treatment, Cd II ions, rhodamine B dye, alloy-based electrodes, economical evaluation,

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Electrocoagulation is an electrochemical method in which waste water is treated using electric current. In South Africa, the development of water and wastewater treatment technologies that are cost effective, sustainable, environmentally friendly and economical are essential. Electrocoagulation technique has proven to be an effective wastewater treatment method in separating toxic industrial pollutants from wastewater. The sacrificial anode material is amongst the important parameters in EC, hence in this work, the performances of newer non-conventional electrodes and alloyed electrodes in electrocoagulation processes were investigated. The use of alloys as anode is expected to increase the availability of ions with high charge to achieve high coagulation of the contaminant colloids in the waste wastewater. Simulated wastewater containing 50 ppm rhodamine B dye and 20 ppm Cd (II) was treated in a two-electrode system. The cell was run for 60 min at 250 rpm and 30 V while 10 mL of the aliquot was taken at 15 min intervals. The anode used in this study are copper (Cu) and stainless steel (SS). The effect of initial conductivity of the simulated wastewater, current density, initial pH, inter-electrode spacing and electrolysis time were investigated. The performance of the different alloys was studied by measuring important water parameters such as turbidity, chemical oxygen demand, pH, total dissolved solids, atomic absorption spectrophotometry and UV/Vis (for decolourisation). Costing analysis were carried out and compared to the conventional electrode materials (Fe/Al). Copper dissolves effectively at low pH ranges than at high pH where it deposits into the sample and settles together with the coagulant while stainless steel is effective at a high pH. The initial runs indicate that the electrodes can be alloyed to assist in an increase in pH range that the EC process can be effectively conducted and in increasing the number of ions that will increase the formation of metal hydroxides (coagulants).

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Electrochemical Study of Calcium Carbonate Deposited on Metals

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Calcium carbonate ($CaCO_3$) is the most abundant biominerals on the earth crust. It is formed in geological sources and in biological organisms such as corals, pearls, mollusk shells, and even in egg shells. It is used in industries as pigments and fillers for the improvement of mechanical properties of paper and polymer materials [1-2]. In addition, $CaCO_3$ also displays useful applications in the water purification field [3]. Furthermore, $CaCO_3$ has been studied for drug delivery carriers [4].

$CaCO_3$, exhibits three crystalline polymorphs such as calcite, aragonite and vaterite. Vaterite is less stable than calcite or aragonite, yet its occurrence in nature is rare relative to calcite which is thermodynamically the most stable one. Vaterite can be produced by quickly precipitating concentrated aqueous solutions containing Ca^{2+} and CO_3^{2-}. Through the process of recrystallization /dissolution, vaterite transforms into calcite within few minutes in aqueous medium at ambient temperature. Hence, as reported by many authors, [5] the stability of vaterite micro-particles can be enhanced by using specific additives and processes in a controlled environment.

In electrochemistry synthesis, the electrode act as template on which crystallization of the solid phase take place and the electrode double layer direct the growth. Electrocrystallization allows to control growth rate, amount, and morphology of the deposit. In this study, we aim to electrodeposit $CaCO_3$ on metal substrate and stud the crystallization of $CaCO_3$ under potentiostatic conditions. The samples will be characterized for phase composition and morphology by X-ray diffraction (XRD), Fourier transform infrared (FT-IR), and Scanning electron microscopy (SEM) equipped with Energy-Dispersive X-ray (EDX) spectroscopy.

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Mixed-phase bismuth ferrite- carbon black nanocomposites by green approach as an efficient electrode material for supercapacitor application

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Abstract

Electrochemical supercapacitors have fascinated abundant consideration because of their capacity to distribute high power and energy densities with owing cycling strength[1-2]. Supercapacitor performance of a nanomaterial either in the form of a thin-film or a pallet, used as an electrode can be evaluated by cyclic voltammetry (CV) and galvanostatic charge-discharge measurements. The fast growth of research in the field of electrochemical energy storage systems has been determined by the increased development of nanostructured materials[3]. The use of nanomaterials in energy storage and conversion represents an opportunity to advance the performance, density and ease of transportation in renewable resources[4]. In focus of this work is to synthesize the bismuth ferrite- carbon black nanocomposites by green approach via Moringa Olefeira natural extract as an electrode material for supercapacitor application. Supercapacitor performance of a nanomaterial either in the form of a thin-film or a pallet, used as an electrode can be evaluated by cyclic voltammetry (CV) and galvanostatic charge-discharge measurements. The electrodes are prepared by coating the resulted slurry (bismuth ferrite- carbon black) on the surface area of the glassy/platinum electrode by the drop casting process. Their electrochemical activity, crystalline structure, morphology, isothermal behavior and optical properties will be studied using various characterization techniques such as X-ray diffraction (XRD) and Energy Dispersive X-ray Spectroscopy (EDS) cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) Fourier transform-infrared (FTIR), High Resolution Transmission Electron Microscopy (HRTEM, Differential scanning calorimetry/thermogravimetric analysis (DSC/TGA) Ultra-violet visible (UV-vis) and Photoluminescence (PL).

Keywords: charge-discharge, bismuth ferrite, Green chemistry, Moringa Oleifera, carbon black, supercapacitors

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The effect of temperature on B and N configurations and properties of boron and nitrogen codoped multiwalled carbon nanotubes for use in photovoltaic cells

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Carbon nanotubes are amongst the most interesting carbon nanomaterials which portray outstanding properties. The properties of these materials can be effectively turned by doping with heteroatoms such as nitrogen and boron. Heteroatom doping of multiwall carbon nanotubes (MWCNTs) was reported to alter their symmetry, leading to enhanced thermal and electrical conductivity as well as increased charge transfer properties [1,2]. In an attempt to synthesize CNTs with tunable properties, we performed ex-situ codoping of MWCNTs with boron and nitrogen atoms (B/N-MWCNTs) with reaction temperature study (700 –900 ºC) using atmospheric pressure chemical vapour deposition technique.

High magnification TEM micrographs showed that the morphology of the as-grown B/N-MWCNTs was affected by the doping temperature. At 700 and 800 ºC, the B/N-MWCNTs exhibited two-compartment, comprising of the graphitic bamboo-like tubular inner part (~11.8 ± 4.45 nm) and the amorphous flower-like outer compartment. An increase in annealing temperature to 900 ºC led to alignment of the amorphous flower-like outer compartment onto the graphitic inner tubular compartment; resulting in formation of thicker carbon nanotubes (~24.1 ± 5.04 nm). Raman analysis corroborated morphological studies by indicating that there is variation in the electronic and structural properties of the BN-MWCNTs with increasing doping temperature. Furthermore, XPS data analysis showed that the improved morphology with increasing temperature can be attributed to the better incorporation of boron and nitrogen atom into the carbon lattice with stable sp2-hybridized bonding states such as h-BN, BCN, graphitic-N. Moreover, The optical analyses (UV-Vis and PL) of B/N-MWCNTs were in good agreement with the XPS data, and showed that the optical properties were governed by the type and amount of bonding states within the carbon lattice. Finally, thermal analysis studies revealed that the B/N-MWCNTs were more thermally stable owing to B incorporation. The study reveals that by adjusting the doping temperature used to make B/N-MWCNTs, the properties, such as the optical properties could be tuned. As a result of this obtained properties, BN-MWCNTs can be applicable in electrochemical storage of energy and photovoltaic devices.

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Electrochemical oxidation of polyols on Pt based electrodes

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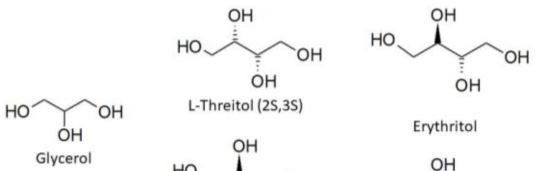
The electrooxidation of poliols (EOP) has been studied during the last decades on Pt_p in acid media[1], and the reaction with all the molecules share several similarities: 1) If the reaction occurs mainly without C-C bond breaking, it is selective to the oxidation of the primary carbon, producing a highly reactive aldehyde that easily react to form the corresponding acid. 2) The C-C bond breaks forming CO, which poison the electrode. 3) CO is not the only reaction intermediate and there exist others species that strongly adsorb on the electrode.

Glycerol (GOH) is an interesting model molecule for the EOP as it is the simplest structure containing a primary and a secondary carbon. Using this molecule, Pt(111) and Pt(100) single crystals electrodes, Garcia et. al.[2] gave the first atomic-level insight about the selectivity of the reaction towards the oxidation of the primary and a secondary carbon. Using computational experiments, the authors concluded that the dehydrogenation steps occur in a different way on both surfaces determining the reaction product.

The polyols with four carbon (C4) are the simplest molecules containing primary and secondary carbons and a pair of diasteromers (figure), allowing to investigate the effect of the spatial orientation of the –OH groups on the electrooxidation reaction. Thus, the C4 can be used as model molecules to understand the electrochemical behavior of important biomass feedstocks with longer carbon chains as sorbitol, ribitol, xylitol and the corresponding acids and aldehydes.

To extent the results of Garcia et. al. we studied the electrochemical oxidation of the C4 on Pt(111) and Pt(100). Besides, in order to investigate the effect of the spatial orientation of the –OH on the EOP we used both isomers, i.e. Erythritol and Threitol.

Electrochemical and FTIR *in situ* experiments show that both polyols oxidize at the same speed (same currents in the entire potential window) and forming the same products, indicating that the –OH spatial orientation do not have any effect on both, the reaction selectivity and surfaces activity. FTIR *in situ* also shows that on Pt(111) at low potentials (0.5 V) the oxidation is completely selective to the secondary carbon (producing the ketone), but on Pt(100) both product are generated from the reaction onset (0.7 V). Computational results shows that the double dehydrogenated intermediates of the C4 are similar to those obtained for GOH[2], i.e., while Pt(111) favors the formation of an intermediate binding the surface using simultaneously their carbons 1 and 2, Pt(100) favors the formation of a double bound using just one of the primary carbons. The enol intermediate formed on Pt(111) is the precursor of the ketone and that formed through the primary carbon on Pt(100) oxidize to form the corresponding aldehyde and acid.



Structural comparison of polyols. The molecular structure of GlOH does not permit the isomers existence. Treitol has two enantiomers (which are diasteromers of Erythritol).

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Co-reduction Behavior of Lutetium Ion on Tungsten Electrode in Molten LiCl-KCl Eutectic with Bismuth Ion

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Pyrochemical processing of spent nuclear fuel will generate the salt waste with various dissolved species which are rare earth metals [1]. Electrochemical behaviors of the dissolved species in the salt waste are to be characterized in order to develop purification method of the salt waste because the salt could be recycled into pyrochemical processeing. Lutetium is also a dissolved species in the salt waste and its behavior in the molten LiCl-KCl eutectic was studied. Electrochemical tests were conducted in a glove box with oxygen and moisture contents being less than 1 ppm. The electrochemical cell was set up inside a steel furnace attached under the glove box. The cell was fabricated to accommodate both working electrodes, counter electrode, reference electrode, and thermocouple. All the electrodes and chlorides were contained in a quartz cell. The electrochemical behaviors were investigated using cyclic voltammetry, square wave voltammetry, and open-circuit chronopotentiometry. The cyclic voltammogram of LiCl-KCl+$BiCl_3$+$LuCl_3$ on tungsten electrode at 773 K showed various redox couples of Lu^{3+}/Lu, Bi^{3+}/Bi, and others. Two redox couples between Lu^{3+}/Lu and Bi^{3+}/Bi were inferred to co-reduction of Lu and Bi ions by intermetallic compound formations which are LuBi and Lu_5Bi_3 phases according to phase diagram of Lu and Bi [2]. The experimental results exhibit that Lu could be extracted from the salt waste by adding the Bi ion and co-reduction.

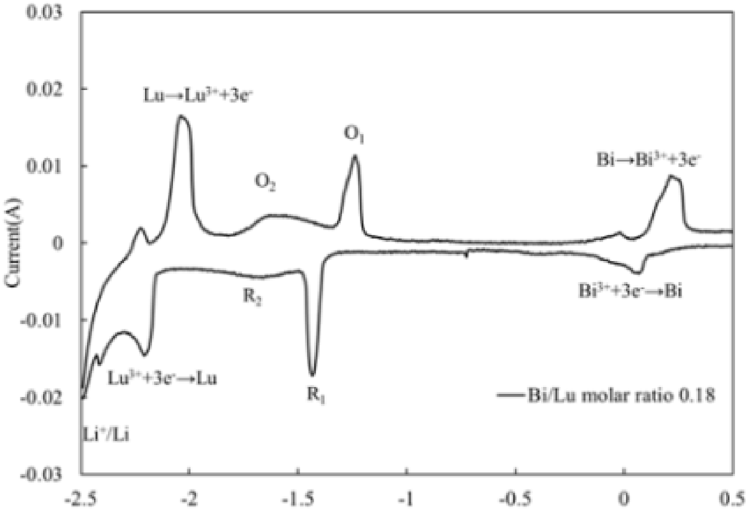

Figure 1. Cyclic voltammogram of LiCl-KCl+BiCl3(0.2wt%)+LuCl3(1wt%) on tungsten electrode (scan rate: 0.1 V/s)

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Feasibility of Electrochemical/Thermochemical Reduction of Titanium Oxide Using Lanthanum as the Reducing Agent

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Titanium (Ti) is industrially produced through the Kroll process. In this process, Ti ore, including Ti oxides, is upgraded and chlorinated to produce $TiCl_4$, which is subsequently reduced by magnesium (Mg) to produce metallic Ti. The Kroll process is excellent in that high purity Ti is stably produced; however, the cost of production is very high because of the batch process and the long processing time.

As an alternate process, a direct metallothermic reduction of TiO_2 to pure Ti has been developed. Because Ti has a strong binding affinity to O, the reducing agents capable for TiO_2 reduction to pure Ti are basically limited to calcium (Ca) and some rare earth elements. Many researchers have tried to develop Ti smelting processes using calcium as a reductant; however, none of their methods were practical.

In this study, a new direct reduction process was proposed, in which lanthanum (La) was used as a reductant. La is one of the rare earth elements and is a by-product of the neodymium (Nd) production process. An oversupply of La is expected because of the lack of its applications[1]. La is used as a reductant in the smelting processes for some rare earth metals[1]; however, to the best of our knowledge, the relevant studies on reduction of TiO_2 using La as a reductant have not been reported so far. Therefore, in this study, a new reduction method of TiO_2 using La as a reductant was developed.

Recently, Okabe et al. reported that the deoxidation limit of O in Ti is 5400 mass ppm O under La/La_2O_3 equilibrium at 1300 K, and the deoxidation limit can be decreased to 80 mass ppm O under $La/LaOCl/LaCl_3$ equilibrium at 1300 K[2]. Then, in this study, the lanthanothermic reduction of TiO_2 in the $LaCl_3$ molten salt was conducted. In the experiment, $LaCl_3$ was generated *in situ* using the following reaction:

$$3\ MgCl_2\ (l) + 2\ La\ (l) = 3\ Mg\ (l) + 2\ LaCl_3\ (l) \qquad (1)$$

Several Ti crucibles, in which La shots, dried $MgCl_2$ flakes and TiO_2 powder were settled, were sealed in a stainless steel crucible. La shots and TiO_2 powder were physically separated with the Ti foil in the Ti crucible. The stainless steel crucible was heated in an electric furnace at 1300 K for 86 ks and then quenched in water. The samples were removed from the Ti crucibles and cleaned by leaching with an acetic acid solution and distilled water. The salt and cleaned samples were analyzed through SEM and XRD.

$LaCl_3$ was detected from the salt, and $LaTiO_3$ and LaOCl were detected from the sample; however, metallic Ti was not detected. It is considered that the formed double oxides, including $LaTiO_3$, separated TiO_2 from the molten salt and retarded the diffusion of O from titanium oxides to the molten salt. It is also considered that the oxide was not reduced because the activity of La on the surface of the oxide was low.

Dring et al.[3] reported the formation of a double oxide, $CaTiO_3$, on the surface of TiO_2 in the FFC process[4] and the OS process[5]. In these processes, a graphite electrode and a TiO_2 electrode are employed as an anode and a cathode, respectively, in molten $CaCl_2$. The reductant metal is precipitated on the surface of the cathode through the electrochemical method. It means that the activity of the reductant metal on the surface of the cathode can be kept high and the formed double oxide can be reduced. When the processes are applied to the La system, the reactions in Eqs. (2)-(5) will occur. Then it will be possible to reduce TiO_2 to metallic Ti directly.

$$\text{Anode:}\quad C\ (s) + x\ O^{2-}\ (\text{in flux}) = CO_x\ (g) + 2x\ e^- \qquad (2)$$

$$\text{Cathode:}\quad La^{3+}\ (\text{in flux}) + 3\ e^- = La\ (\text{on } TiO_2 \text{ cathode}) \qquad (3)$$

$$TiO_2\ (s) + \frac{4+3x-2y}{3}\ La\ (\text{on cathode}) = La_xTiO_y\ (s) + \frac{4-2y}{3}\ La^{3+}\ (\text{in flux}) + (2-y)\ O^{2-}\ (\text{in flux}) \qquad (4)$$

$$La_xTiO_y\ (s) + \frac{-3x+2y}{3}\ La\ (\text{on cathode}) = Ti\ (s) + \frac{2y}{3}\ La^{3+}\ (\text{in flux}) + y\ O^{2-}\ (\text{in flux}) \qquad (5)$$

The feasibility of the electrochemical process is discussed with both experimental and thermodynamic assessments.

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Electrochemical Properties of Nanocomposites Based VOx Prepared by Wet Chemistry

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Proper Mott phase transition present in correlated electron materials can be triggered under applied field electric or by photo and thermal excitations for potential optical switches [1-3]. It has been explored for the first time in VO_2 which has attracted much attention due to the sharp transition metal-insulator with approximately five orders in single crystals at around 68 ° C. This first order transition terminates at a second order critical point where the material behaves with different crossover regimes indicating the change in the material properties. It was shown that the effect of NH_4OH within the solution shifts the pH towards alkaline hydrothermal growth which notify on the formation of larger particles with growth duration time [4-5]. The creation of extra points defects increases with the basicity level due to the increase of free charge carrier density while field-effect mobility decreases [6-7]. Increase cycling stability, specific capacity and high rate capacity are due to the reduced size in nanostructures which promotes the lowering of ion diffusion distance and improved surface area [8]. Layered structures present in VO_2 oxides allow embedment of ions and small molecules between layers which gives high capacity cathode material for batteries. In addition, mixed valence VOx of vanadium oxides with multiple stable oxidation states (III–V) have been discovered for pseudocapacitors with good cycling response and stability [9-12]. Here we present the electrochemical stability of hydrothermal VO_2 (A) and VO_2 (M) for different hydrothermal growth times ranging from 6hrs to 24hrs and the effects of NH_4OH on the structural and electrochemical physical properties of $(NH_4)_2V_3O_8$ nanorods.

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Controlling quantum interference effect in single molecular junction by electrode potential

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Quantum interference effect (QI) in single molecular junctions has been the focus in the recent research, which may be used in future single molecular devices, including switch, transistor[1-3]. Typically, molecules with cross-conjugated structures or *meta*-substitute benzene ring show destructive quantum interference, while constructive quantum interference is observed for molecules with two parallel components without phase shift. Many experiments have devoted their effects to modify the QI performance through designing molecular structure. For example, the changing of redox state of cross-conjugated molecule also varies the single molecular junction with or without QI effect between oxidized or reduced state[2-3]. However, there is less experimental results on the controlling QI through energy alignment between molecule and electrode in single molecular junctions.

Herein, we study the QI effect of *para*- and *meta*-benzene based moelcules in single molecular junction using STM break junctions technique[4-5]. By tuning electrode potential, we experimentally observed the conductance value of *meta*-BT with QI can be largely changed, and can be even bigger than that of *para*-benzene based moelcule at some potentials.

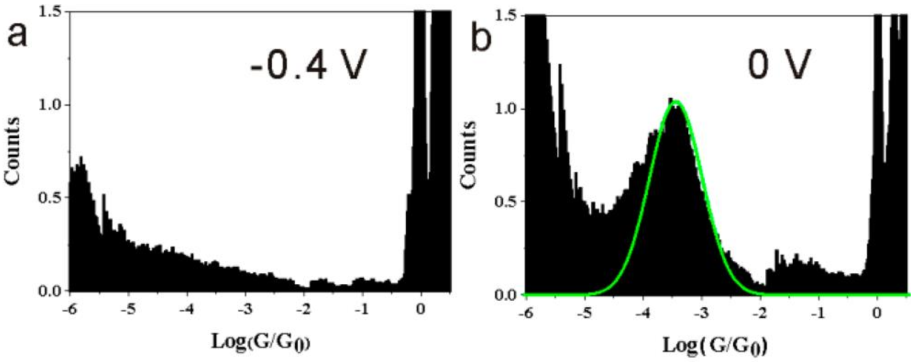

Figure 1. Conductance histogram of *meta*-BT measured at different potential.

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Effect of Metal-Organic Framework (MOF) Decorated on N-doped rGO and N-doped CNT for Supercapacitor Applications

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A rapidly increasing population and energy consumption in the world and the depletion of fossil fuels are justifiable reasons for the much-anticipated need for alternative, clean and sustainable energy. Therefore, intensive studies on advanced materials for energy storage and conversion is of vital consideration. The innovative discoveries on the production of metal-organic frameworks (MOFs) materials have been the center of attention in the realm of material science. MOFs are synthetic porous and crystalline materials that have notably been receiving intense scientific research efforts in their synthesis due to their enhanced chemical properties, and their notable use for gas storage [1]. The intense research and considerable employment of MOFs as precursor for the synthesis of other porous material such as metal-based compounds and porous carbon material, has led to the discovery of the effects that MOFs have upon other materials once it is associated with them [2]. MOFs have gained immense interest from various researchers as electrode materials for supercapacitor applications. MOFs progress in SCs applications is still limited due to their poor electrochemical performance (i.e., redox reversibility, cyclability and stability). Carbon material such as graphene, reduced graphene oxide (rGO) and carbon nanotubes (CNT) have been selected as carbon supports for the development of MOFs composites due to their high chemical and physical stability, including their high conductivity and high surface area [2,3]. Therefore, a great devotion has been invested to improve the electronic properties of MOF nano particles using various synthetic routes. Although intensive study has been done on carbon nanomaterials integrated with MOFs, there is still a limited amount of literature on the application of MOFs integrated on porous carbon materials for SCs applications [4].

In this study, we present the synthesis and characterization of nitrogen doped reduced graphene oxide and nitrogen doped multi-walled carbon nanotubes materials decorated with metal organic frameworks (N-rGO/MOF and N-CNT/MOF, nanohybrids), and their electrochemical performance in supercapacitor applications [1]. The morphological and structural characterization of these nanohybrids and their precursor materials were studied using SEM, EDX, FTIR, XPS, XRD and Raman, whereas the electrochemical characterizations were studied using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS).

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Microwave-Assisted Synthesis Of N-rGO/$Mn_3(PO_4)_2$ and N-CNT/$Mn_3(PO_4)_2$ Nanohybrids and their electrochemical performance in Supercapacitors

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Electrochemical energy storage systems have sparked a global interest in research and development of renewable energy technologies [1]. Nanotechnology has emerged as a ground breaking technology in fabrication of high performing nanostructured materials for applications in supercapacitors (SCs) [2]. This has made nanostructured material to be a key factor in the improvement of energy storage properties of electrode materials in SCs. Carbon-based electrode materials such as carbon nanotubes (CNTs), graphene, graphene oxide (GO) and their hybrid materials have been identified as promising electrode materials for SC applications. Chemical doping of carbon materials with nitrogen is also of much interest in electrode material development due to its ability to improve electrochemical performance of SCs device [3]. Recently, metal phosphates such as manganese and cobalt phosphates ($Mn_3(PO_4)_2$ and $Co_3(PO_4)_2$) have begun to be explored as electrode materials for SCs applications due to their excellent properties such as high theoretical specific capacitance, low cost and abundance in nature. In order to fine-tune the electrode materials suitable for high performance SCs, synthesis techniques such as hydrothermal and microwave are of great importance to synthesize high crystalline metal phosphates containing open-frame work structures with large channels that provide good ion/charge conductivity and charge capacity [4]. Thus, microwave synthesis helps to tune nanoparticles with controllable morphologies characterized by narrow particle size distribution and increased phase purity achieved through varying synthetic time.

This work presents, microwave-assisted synthesis of nitrogen doped reduced graphene oxide with manganese phosphate (N-rGO/$Mn_3(PO_4)_2$) and nitrogen doped carbon nanotubes with manganese phosphate (N-CNT/$Mn_3(PO_4)_2$) nanohybrid materials and their electrochemical performance as electrode materials in supercapacitor application. The microscopic and spectroscopic characterization of N-rGO/$Mn_3(PO_4)_2$ and N-CNT/$Mn_3(PO_4)_2$ nanohybrids and their precursor materials were studied using SEM, TEM, EDX, XPS, Raman and XRD whereas the electrochemical characterization were studied using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS).

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Investigation of highly selective and efficient conversion of CO_2 to fomate by dental amalgam electrode

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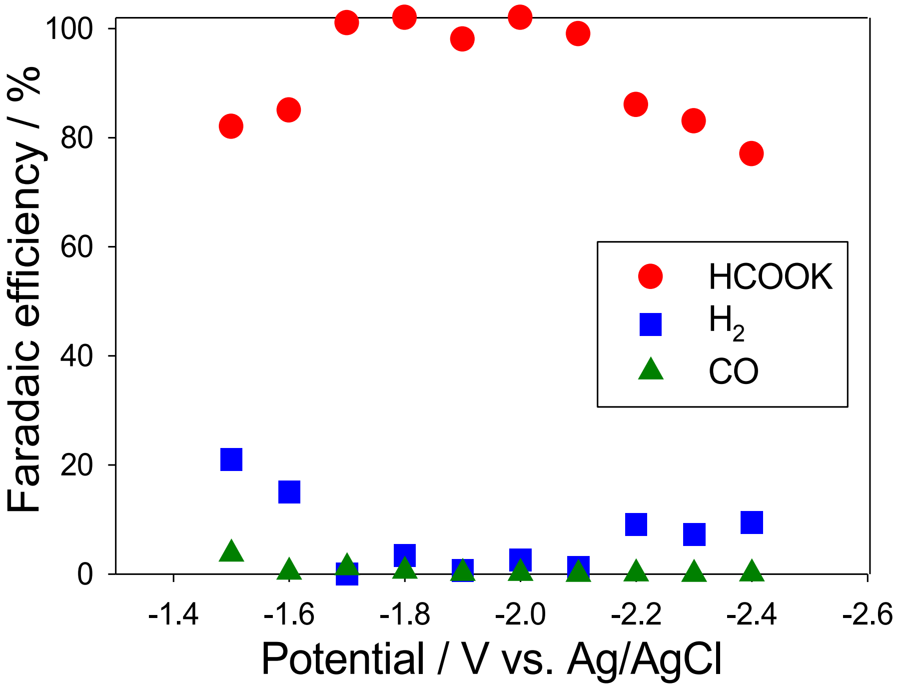
We succeeded in fabricating a dental amalgam composition on a copper foam electrode and could convert CO_2 selectively to formate. The formate was produced at a current efficiency of 80~100% at current densities in the wide range of the potential shown below. The remaining electricity was used only for producing H_2. The CO_2-to-formate conversion system built based on the electrode is shown to be stable in continuous operation at 100 mA/cm^2 for more than a month-long.



Hydrogen Evolution Reaction and CO_2 Reduction Reaction on Customizable Metal Nanostructures on Silicon Electrodes

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The production of solar fuels with a (photo-)electrochemical device is one of the key technologies to achieve a fully renewable economy in future. For this purpose, a light absorbing device must be completed by an electrocatalytic component, which shows long-time stability, high selectivity towards the desired product and minimal kinetic losses.

To this end, we combine a silicon-based light absorber with metal-based catalysts. The method of choice for producing this nanostructured metal/Si interface is lift-off nanoimprint lithography. It allows the cheap fabrication of metal nanostructures with well-defined sizes and shapes on large scales [1]. Furthermore, it is easily possible to vary several parameters of the silicon/oxide/metal interface, such as catalyst material, passivation layer and geometric properties, which, in turn, allows us to perform fundamental studies on the influence of modifications of the interface on different reactions and on the reaction mechanisms.

In this poster, we investigate CO_2 reduction reaction (CRR) and hydrogen evolution reaction (HER) in aqueous electrolyte. We demonstrate that for CRR/HER on copper-plated gold nanostructures, the product distribution (selectivity) depends on the geometric size of the nanostructures. Furthermore, it is shown that for copper-plated gold as well as pure gold nanostructures the HER rate increases with decreasing structure size [2]. By comparing HER on the latter electrodes in acidic and alkaline media, it is shown that this effect is sensitive to the underlying reaction mechanism. A study of nanostructured electrodes with polycrystalline platinum as the catalyst material showed that the increased rate is due to enhanced kinetics of this reaction.

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New insight into lithium intercalation and doping implications at edged graphite in Lithium-Ion Battery

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Li intercalation at interface between electrolyte and graphite is an important step in lithium ion batteries and has a significant impact on battery performance. However, the edge and doping effects of graphite on Li intercalation remain elusive. In this work, based on density functional theory (DFT), two edges of graphite, the zig-zag edge and armchair edge, were comprehensively studied. Compared with the bulk of graphite, the graphite edges show a huge edge effect on Li adsorption and highly promote its adsorption. Furthermore, the adsorption energies of Li at the zig-zag edge are much higher than those at armchair edge, which results from the existence of spin electrons on the edged carbons of zigzag system. The formed unoccupied p_z orbital above the fermi level in zigzag edged system is beneficial to Li adsorption. Besides, boron and nitrogen doping at the edge were identified to change both the adsorption and diffusion behaviors of Li in the two systems, which might give some guidance of graphite modification.

Evaluation of pitting corrosion in different chloride concentratrions

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Abstract

Corrosion is an electrochemical process that involves the migration of anions and cations in an aqueous medium. Electrons transfer through a conducting medium in the corrosion phenomenon is essential in the determination of corrosion behaviour. The migration of the respective species leads to a variety of corrosion behaviours, many of which are thoroughly depicted in literature. One of the major problem in the boiling unit operation is pitting corrosion (Imran, 2014). Occurring at a localized spot on the metal surface, pitting corrosion poses a threat to the structural integrity and efficiency of the boiler. Studies have shown that the presence of chloride ions initiates and accelerates pit formation (Li & Sagues, 1999). The present study focuses on understanding the influence of varied concentrations of chloride on 304 stainless steel (SS304). The sample SS304 was immersed in different chloride concentrations; 3.5% NaCl, 7% NaCl and 14% NaCl, and the corrosion behavior studies. A three electrode electrochemical cell was used in the present study. Open Circuit potential was monitored to observe the free corrosion behavior of the SS304 in the respective electrolyte solution. Polarisation scans were conducted to determine the corrosion resistance and thus corrosion rate under the assumption that the cathodic and anodic reactions follow the Stern-Geary equation. Pitting resistance equivalent number (PREN) was used as a predictive measure to assess the expected localized corrosion behavior of the SS304 sample. PREN showed SS304 to be more susceptible to pitting corrosion when compared to SS316. SEM revealed stable pits after 3 days of submission in chloride solution. Electrochemical Impedance Spectroscopy was used to attain the electrolyte resistance and assess the passivation film formation with respect to time. Passivation was observed as expected. Corrosion occurred at a faster pace when the concentration of the chloride ions was increased.

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A Novel Organosilicon Groups Functionalized Ionic Liquid Electrolyte Boosts the Performance of Dendrite-Free Lithium Batteries

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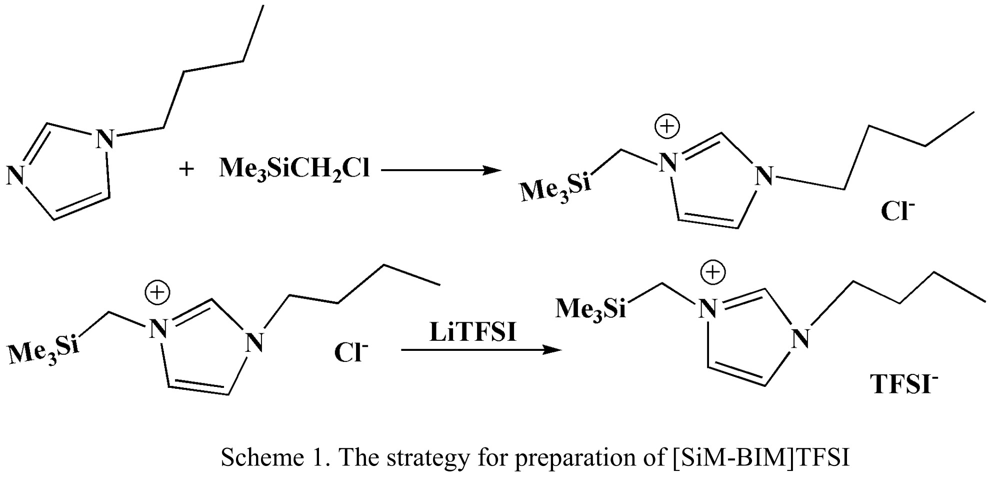
A new organosilicon groups functionalized ionic liquid, 1-trimethylsilylmethyl-3-butylimidazole bis(trifluoromethylsulfonyl)imide ([SiM-BIM]TFSI), was designed and synthesized. The infrared absorption peak between 750 and 850 cm^{-1} confirms the presence of the $-Si(CH_3)_3$ group in the [SiM-BIM]TFSI ionic liquid. The viscosity of the [SiM-BIM]TFSI ionic liquid is 73.5 cP and much lower than that of the non-organosilicon groups functionalized 1-neopentyl-3-butylimidazole bis(trifluoromethylsulfonyl)imide ([NP-BIM]TFSI) ionic liquid. The result indicates that the introduction of organosilicon groups can greatly reduce the viscosity of ionic liquid. The ionic liquid prevents the formation of a highly loose lithium corrosion layer, and enables Li/$LiFePO_4$ cycling with a high Coulombic efficiency and greatly enhanced cycling stability. The discharge capacity of a $LiFePO_4$/Li half-cell with 0.6 mol/Kg LiTFSI-[SiM-BIM]TFSI electrolyte achieves 160 mAh·g^{-1} and the Coulombic efficiency is 99.7 % at a 0.1 C rate at room temperature. In addition, ionic liquid is conducive to the battery to maintain a small polarization voltage throughout the cycling, which to some extent reflects its good cycling performance. The SEM images demonstrate that this new ionic liquid electrolyte can help to form passive film on the surface of $LiFePO_4$ cathode. The EDX and XPS results indicate that Si is the main element of the cathode electrolyte interface film. These results explain the high capacity and coulombic efficiency of Li/0.6 mol/Kg LiTFSI-[SiM-BIM]TFSI/$LiFePO_4$ half-cell.



Scheme 1. The strategy for preparation of [SiM-BIM]TFSI

Comparative study of inclusion abilities of methylated and non-methylated β-cyclodextrin immobilized on gold electrodes

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Macrocyclic receptors, such as amino-cyclodextrins (amino-CDs), with -NH_2 groups located at the narrow edge of their structure (in C_6) can be immobilized on gold surfaces, through amide bonds, using linkers that have terminal -COOH. These CDs can be also modified at the wide edge of their structure (in C_2 and C_3), with functional groups other than the secondary -OH of the conventional CD, that is, they can be modified with fewer groups polar as the -OCH_3 (Methyl-CDs, located in C_2 and C_3). This modification can cause changes in the non-covalent interactions of host-guest systems. The CDs form inclusion complexes (IC) with guest molecules that are the right size to interact with their hydrophobic cavity. Among these guest molecules are pesticides such as propanil. The presence of propanil in the rice fields is high since it controls the broadleaf weeds. The excessive use of propanil has a negative impact on the biodiversity of soils and their biological activity, therefore, its determination is a current topic.

In this work, a comparative study was carried out immobilizing amino-CD and Methyl-amino-CD (with -NH_2 in C_6) on gold electrodes. Two types of CDs were used: (i) 6-monoamino-6-monodeoxy-β-cyclodextrin hydrochloride (CD_1) and (ii) 6-monoamino-6-monodeoxy-per-methyl-β-cyclodextrin hydrochloride (CD_1Me) using the strategy described by *M. García et al.* [1]. Briefly, gold electrodes were modified with self-assembled monolayers (SAMs) of 4-mercaptobenzoic acid (MBA). The -COOH of MBA form amide bonds with the -NH_2 groups of CD_1 and CD_1Me.

Each stage of the sequential modification of the gold electrodes from MBA was corroborated through Raman spectroscopy. In the Raman spectra, the characteristic bands of the MBA are observed, at 1078 cm^{-1} and 1591 cm^{-1} both associated to the tension ν(C-C) of the aromatic ring of the MBA. When the formation of the amide bond occurs, the spectra show two bands at 1765 cm^{-1} and 1405 cm^{-1} associated with the tension of ν(C = O) and ν(C-N) of the amide bond, respectively. The immobilization of both CDs was also evaluated through cyclic voltammetry (CV) using $[Fe(CN)_6]^{3-}$ in phosphate buffer solution (PBS) at pH 8.0 as a redox mediator. Under these conditions a reversible process (Fe^{3+}/Fe^{2+}) was observed on Au-naked with a $\Delta Ep = 65 \pm 2$ mV (vs. $Ag/AgCl_{(1M)}$). The surfaces Au-CD_1 and Au-CD_1Me showed a more irreversible redox process with $\Delta Ep = 182 \pm 2$ mV and $\Delta Ep = 151 \pm 12$ mV, respectively. Besides, the response showed a decrease in the cathodic peak current (j_{pc}) of 29 and 30%, respectively. These results are attributable to a coating on the surface.

The effect of the different functional groups of CD_1 and CD_1Me immobilized on the surface upon host-guest interactions was evaluated using propanil in solution ($1 \cdot 10^{-3}$ M) through differential pulse voltammetry (DPV) in PBS at pH 9.0 with an accumulation time of 20 min. In both electrodes Au-CD_1 and Au-CD_1Me an anodic peak was observed at a peak potential (E_p) 780 ± 2 mV associated with an irreversible oxidation process that occurs in the nitrogen atom of propanil. The same E_p was observed for the Au-naked, with a current density (j_p) 18.66 ± 0.65 $\mu A\ cm^{-2}$. However, j_p increased 72% (32.15 ± 0.00 $\mu A\ cm^{-2}$) and 110% (39.35 ± 0.13 $\mu A\ cm^{-2}$) for the Au-CD_1 and Au-CD_1Me electrodes, respectively. We also have determined the association constants (K_a) of the CDs/propanil IC in solution by DPV in PBS at pH 9.0. Higher K_a values were obtained for the IC propanil/Methyl-CD (468 M^{-1}) with respect to the IC CD/propanil (228 M^{-1}). These values show that the -OCH_3 groups, produce a more stable IC, since the polar nature of the environment of the Methyl-CD cavity is reduced favoring hydrophobic interactions [2]. Based on the differences in the K_a values shown in solution and the results showed before, the presence of -OCH_3 groups give advantage to encapsulation phenomena with immobilized CD on gold.

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Cytidine Nucleolipid Supported on Gold (111) electrodes as Biomimetic Membranes: A Photon Polarization Modulation Infrared Reflection Absorption Spectroscopy Study

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Characterization of the adsorption and molecular recognition between complementary nucleoside base pairs at electrode surfaces is key in the development of biosensors for DNA recognition, which is essential in cancer diagnosis and drug delivery technologies. The use of *in situ* spectro-electrochemical methodologies provides structural information and the determination of molecular interactions under the influence of electric fields [1-4].

In this communication, photon polarization modulation infrared reflection-absorption spectroscopy (PM-IRRAS) is used in combination with electrochemical measurements to study the orientation and conformation of a cytidine nucleolipid film, the 1, 2-dipalmitoyl-*sn*-glycero-3-cytidine diphosphate monolayers, deposited on the gold (111) electrode as a function of electrode potential. It is shown that the lipid tails are predominately in the gel phase at potentials more positive than –0.2 V adopting a tilt angle of ~30° with respect to the surface normal. At negative rational potentials, a progressive detachment of the monolayer takes place inducing an increase of the tilt angle of the acyl chains that indicates a more disordered monolayer.

The effect of the electric field on the cytosine head group was also monitored. The PM-IRRA spectra are interpreted on the base of DFT calculations of the frequencies of vibration modes and the results suggest that the plane of the cytosine moiety assumes a small angle of ~20° with respect to the surface normal when the lipids are in the gel state, while in the disordered state, the cytosine moiety rotates and the angle between the plane of the cytosine head group and the surface increases. These changes are explained by the interaction between the permanent dipole of cytosine and the surface charge. In the ordered gel state, the positive pole of the cytosine permanent dipole moment is repelled by the positively charged gold surface. When the applied potential is negative, the cytosine moiety rotates and tilts towards the metal surface due to the attraction between the positive pole of the cytosine permanent dipole and the negatively charged metal surface.

The conclusions reached are crucial in the understanding and development of electrochemical sensors for the molecular recognition of the complementary DNA base of the cytidine nucleolipid film, the guanine.

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The Mechanism of Li_2O_2-Monolayer Formation and Reoxidation – the Effect of Electrode Roughness

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In Li – O_2 batteries, there are two reaction paths leading to lithium peroxide: In one, initially formed dissolved Li – superoxide disproportionates to the peroxide, in the other, the superoxide is reduced to the peroxide at the surface. This latter forms an atomically thin layer, which largely blocks it and largely inhibits further oxygen reduction.[1-3]

We have now studied in detail the role of roughness on this reaction on Au and Pt electrodes (including single crystals) using differential electrochemical mass spectrometry (DEMS) and the rotating ring-disc electrode (RRDE). This allows separation of the contribution of the different reaction paths. We thus confirmed that for all roughness factors the maximum coverage is a full monolayer; reoxidation requires indeed two electrons in all cases. The absolute rate of Li_2O_2 - adlayer formation increases with the roughness factor, however, the blocking of the surface is much delayed.

One of the key quantities in kinetic studies is the Tafel slope, which is related to the apparent transfer coefficient alpha. It often allows to draw a conclusion on the rate determining step in multi step reactions. We have recently introduced a method to determine this value also for a surface limited reaction.[4,5] This method involves measurement of the ac voltammogram, under certain conditions the ration of ac current and the dc current and the ac voltage is proportional to the reciprocal of the Tafel slope:

$$\alpha' = \frac{RT}{nF}\,\frac{1}{i_{\mathrm{dc}}}\,\frac{i_{\mathrm{ac\text{-}re}}}{u_{\mathrm{ac}}}$$

We have now applied this method to determine alpha for the reoxidation of the Li_2O_2 – adlayer and could conclude that the first electron transfer is the rate determining step in the reoxidation of the thin Li_2O_2 - adlayer.

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Novel reactive barrier concept coupled to electrokinetic remediation to remove Pb^{2+} from soil

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In this work, a novel, original and ecological alternative to treat soils contaminated with lead was proposed. Coupling two well-known technologies, electrokinetic remediation and permeable reactive barriers (PRBs), the depollution efficiency was evaluated; however, the originality of PRBs concept is the use, for first time, of cork as the main barrier were composition. The barrier was placed into the soil near the anodic compartment to favor the retention and adsorption of Pb^{2+} due to the migration/diffusion effects promoted from soil to the anode during the electrokinetic remediation (ER). For this purpose, NaNO3 and citric acid were used as supporting electrolytes into the cathodic reservoir, while in the anodic compartment; a solution of 0.1 M $NaNO_3$ was used. Additionally, the influence of direct current (DC) and reverse polarity (RP) approaches for applying electrical fields were evaluated for removing Pb^{2+} from the soil. Results clearly indicated that, the novel PRBs concept was efficient when coupled with ER because higher Pb^{2+} removals were achieved. Nevertheless, Pb^{2+} removal by adsorption in cork is influenced by the pH conditions, as observed in adsorption tests. During ER coupled to cork barriers, it was observed that the use of citric acid and RP contributed positively to the transport of Pb^{2+}. At the end of the 14 d of depollution treatment, it was possible to observe that the integration of two technologies resulted in 80% associated to pH control in the cathode reservoirs. The cork contributed to increase the removal efficiency of Pb^{2+} due to adsorption phenomena. Therefore, this technology provided a global treatment to soil without following treatments of the contaminated effluents. Finally, electrokinetic and cork barrier associate to citric acid in the cathodic reservoirs was possible decreasing the cost for soil remediation.

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Electrochemical Study of Titanocene Dihalides in Non-aqueous media

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One of the first complexes where anti-tumor activity was found is "cis-platin" [*cis*Pt$(NH_3)_2Cl_2$][1]. It is still considered as one of the most potent and most used cytostatics. Nevertheless, its toxicity and generated resistence of cancer cells limit its use. Therefore in last years increasing interest is observed in development of new generations of cytostatics containing no platin.

Metalocene dihalides represent one of such types of complexes. These organometallic compounds are based on organic ligand and transition metal (Ti, Zr, Hf). The first metallocene dihalide showing anticancer activity[2] and being tested in hospitals was titanocene dichloride Cp_2TiCl_2, where Cp = η^6-C_5H_5 [3].

In order to understand the molecular mechanism of this activity and to describe the processes occurring in the tissue, the investigation of redox properties of various metallocene dihalides is necessary together with studies of reactivity following the primary electron transfer.

Our research follows on from the previous work on $(C_5H_{5-n}Me_n)_2TiCl_2$, where n = 0 to 5, performed on mercury electrodes in tetrahydrofuran[4] and currently our investigation is focused on various titanocenes with halide ligands, like Cp_2TiX_2 and $Cp^*{}_2TiX_2$, where Cp* = η^6-C_5Me_5 and X = Cl, F.

All electrochemical experiments were performed in non-aqueous media on Hg, Pt and glassy carbon electrodes and it was confirmed that the electrode material does not influence the redox potentials and the follow-up reaction pathways. Both oxidation and reduction reactions were followed and discussed.

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Suppressing lithium dendrite formation using electrolyte additives

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Currently, Lithium batteries present the most promising solution for energy storage in many applications, from electronic devices to electrical vehicles and electrical network power storage. In recent years, to meet the technology developments and the human's living standards, the rechargeable batteries, are regarded as increasingly appealing alternatives to be applied in both grid electrical energy storage and electrical vehicles. Lithium-sulfur (Li-S) battery is widely researched due to its higher theoretical specific capacity and theoretical energy density in comparison with lithium-ion battery. The lithium anode is absolutely necessary for lithium-sulfur battery, which plays an important role for the electrochemical stability and the security of the battery. Lithium metal is regarded as a preferred electrode material for the anode of lithium-sulfur battery, which is mainly attributed to its excellent performances such as low gravimetric density (0.59 g cm−3), high theoretical specific capacity (3860 mAh g−1) and fine negative redox potential (−3.040 V vs. standard hydrogen electrode). So the lithium metal plays a indispensable role for the next generation high-performance energy storage systems The working mechanism for Li anode is Li+ plating/stripping from the anode instead of intercalation/de-intercalation in graphite anode during charge/discharge process. During the repeated charge-discharge cycling, the continuous uneven deposition and stripping of lithium induce uncontrollable growth of lithium dendrites, which not only breaks solid electrolyte interfacial (SEI) film and leads to the generation of "dead Li" with low Coulombic efficiency (CE), but also induces safety hazards (like internal short circuit, combustion/explosion of full cells) since it can penetrate through the polymer separator and form micro-short circuits between the positive and negative electrodes, causing the serious safety issues including fire and even explosions. The aim of the present work is to avoid formation of lithium dendrites by adding additives in the electrolyte. The electrolyte was based on LiTFSI 0.5 M and LiNO3 0.25M in 1,2-dimethoxyethane(DME)/1,3-dioxolane (DOL) 1:1 with different additives. The electrochemical behavior was studied by means of Li/Cu cells and Li/Li cells by charge-discharge cycles at different current rates, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). Lithium before and after cycling was also characterized by scanning electron microscopy (SEM).

Electrowinning from WEEE Bioleachate

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Printed circuit boards (PCBs) are a necessity for electronic equipment to function. From a PCB in your smart phone to PCBs in medical devices they are what makes electronic equipment operate. The sophistication possible with modern electronic and microelectronic devices depends ultimately on the materials they are made from. Metals have assumed a vital role in electronics at every stage in their evolution. PCBs are rich in base and precious metals and can be considered as a secondary resource [1]. Bioleaching is a green and sustainable method for metal recovery from electronic equipment and the process generates dissolved metal ions which need to be removed from solution. Several technologies are available [2], but we have focused on metal recovery using ion exchange to concentrate the metal ions and electrowinning to recover the metals from solution.

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Final Glycerol electrooxidation on low index Pt single crystals in alkaline media. Effect of the surface structure

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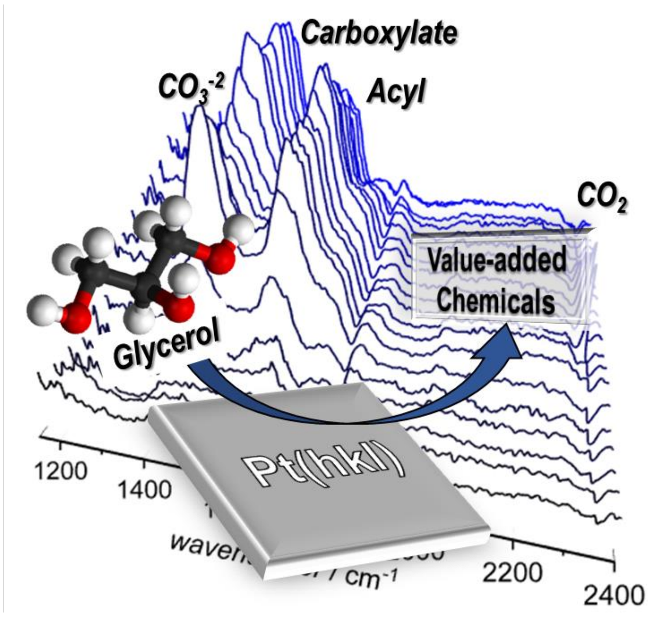
Glycerol adsorption and oxidation reactivity at platinum single crystal electrodes in alkaline media using electrochemical and Fourier transform infrared (FTIR) techniques are reported. The behavior of Pt(100) and Pt(110) for the glycerol electrooxidation reaction (GEOR) were compared and analyzed altogether with those previously reported for Pt(111).[1] The voltammetric profiles confirm the structure sensitivity of GEOR as well as the role of the surface atoms orientation on the electrocatalytic activity. The Pt(100) surface has shown to be less prone to poisoning during multiple potential cycles in contrast to Pt(110) which suffers an accentuate deactivation at the first positive-going scan. Spectroscopic results show that the GEOR on all three surfaces is characterized by the presence of two broad bands, centered circa 1400 cm^{-1} and 1600 cm^{-1}. This provides evidence that GEOR mechanism undergoes, through glycerol dehydrogenation, to alkoxydes followed by formation of aldehyde intermediates adsorbed as η^1(O)-aldehyde and η^1(C)-acyl geometry, respectively. The surface atomic arrangement induces different selectivity in the oxidation process.



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Application of Electrodeposited Gold-Poly (Propylene Imine) Dendrimer on Expanded Graphite for the Voltammetric Detection of Lead (IV) in Water

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Abstract

In this work, a simple experimental procedure was reported for the electroanalytical detection of Pb (II) based on novel gold nanoparticles-poly (propylene imine) dendrimer platform. The sensor was prepared by co-electrodeposition of gold nanoparticles and generation 3 poly (propylene imine) dendrimer on an exfoliated graphite electrode which was prepared by intercalation and exfoliation of graphite material. The electrochemical properties of the bare and modified exfoliated graphite electrode were interrogated using cyclic voltammetry. The electrodeposited gold-poly (propylene imine) dendrimer expanded graphite electrode displayed increase in the electroactive surface area and in the faradaic current of $[Fe(CN)_6]^{3-/4-}$ in comparison with the expanded graphite electrode. The optimisation parameters employed for this study include 0.1 M H_2SO_4 as supporting electrolyte, pre-concentration time of 210 s, deposition potential of -0.6 V and pH of 1. A linear regression of Y (μA)= 1.340X+209.44 and a detection limit of 0.15 ppb was obtained. More so, Cd(II), Hg(II) and Cu(II) were the three cations that interfered in the analysis of Pb(II) ion. The sensor was employed for the quantification of Pb (II) ion in real sample water analysis and the results obtained was validated with inductively coupled plasma optical emission spectroscopic method (ICP-OES).

Key words: Gold, poly (propylene imine) dendrimer, lead, electrochemical sensor, expanded graphite

Combined dip-spin Coating Technique: a Feasible Approach of Preparing Hematite Thin Films for Photoelectrochemical Water Splitting

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Abstract

In this work, hematite films were prepared using dip, spin and combined dip-spin coating techniques on Florine doped tin oxide substrates. The films prepared were characterized using FE-SEM, XRD, Raman spectroscopy and UV-Vis spectroscopy. FE-SEM studies showed spherical nanoparticles with some agglomeration of individual particles into small larvae shape nanostructures. XRD studies of the films revealed prominent peaks for hematite at (104) and (110) planes with weak reflections at (012), (113), (024), (122) and (310). Raman spectra of the films revealed seven symmetrical optical phonon modes (two A_{1g} and five E_g modes) of hematite. XRD and Raman spectra analysis both suggest good crystallinity for films prepared by dip and combined coating techniques over the one prepared by spin coating. UV-Vis spectroscopy studies of films prepared using combined coating technique showed enhanced light absorption over the one prepared by spin coating at wavelengths below 485 nm. Better absorption properties and crystallinity of thin films prepared using combined coating techniques over spin coated films indicates that they can be suitable photoanodes for photoelectrochemical (PEC) water splitting. The results suggest that aside dip coating, the combined dip-spin coating could be a feasible approach of preparing hematite films for PEC water splitting.

Results

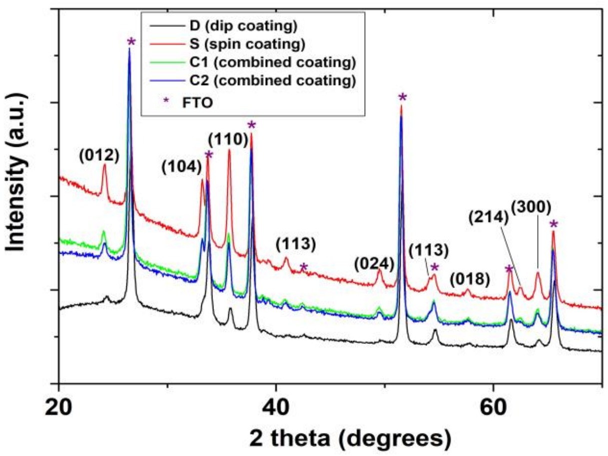

Fig. 1: XRD spectra of hematite thin films prepared using dip, spin and combined dip-spin coating techniques

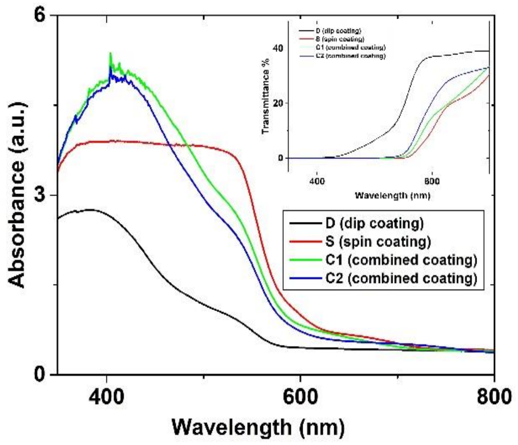

Fig. 2: UV-Vis absorption spectra of hematite thin films prepared using dip, spin and combined dip-spin coating techniques with inset showing its transmittance

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Investigation of Ternary Catalysts as Anode Catalysts for Direct Methanol Fuel Cell

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The factors controlling the activity and the stability of electrocatalysts based on PtRu/CNT and ternary catalysts PtRu-X/CNT (X=W,Mo,Ir) were examined. .Pt-Ru catalyst is a promising anodic catalyst for direct methanol fuel cells (DMFCs) but the slow reaction kinetics reduces the performance of DMFCs. Therefore, this study attempts to improve the performance of PtRu catalysts by adding iridium (Ir), molybdenum (Mo) and tungsten (W) thereby discovering which ternary catalysts, Pt-Ru-X is capable of reducing the cost of anode catalysts for DMFCs by up to a satisfactory extent compared with Pt-Ru. Active area of the ternary catalyst was increased using multiwalled carbon nanotubes (MWCNTs). Electrochemical analysis techniques such as high resolution transmission electron microscopy (HRTEM), energy dispersive X-ray spectrometry (EDX), X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM) were used to characterize the kinetic parameters of the hybrid catalyst. Cyclic voltammetry (CV) was used to investigate the effects of adding Ir, Mo and W to the binary catalyst on the reaction kinetics. Additionally, chronoamperometry tests was conducted to study the long-term performance of the catalysts for catalyzing the methanol oxidation reaction (MOR). Electrochemical impedance spectroscopy was conducted to investigate reaction mechanism. Finally the polyol method produced elctrocatalysts of best stability. The impregnation method produced hybrid catalysts of best kinetics to the methanol oxidation reaction.

The modified polyol method gave electrocatalysts of best activity towards methanol oxidation. The HRTEM analysis results indicated that well-dispersed PtRu particles are formed on the MWCNTs.

Key word: Anodic catalyst, ternary catalysts, electrochemical analysis, kinetic parameters.

Pd/CB-CeO_2 as Efficient Electrocatalyst for Alcohol Fuel Cell

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Palladium nanoparticles supported on carbon black (Pd/CB) has been recognised as a viable catalyst by many papers previously published. [1,2] Although it has not been at the pinnacle of the list, it serves as a great starting point and tens and hundreds of derivatives are tested to this day. The negative aspect of the core palladium supported on only vulcan carbon or carbon black (CB) is the instability of the catalyst formed and average HOR kinetics in a basic or alkaline medium. CeO_2 has already proven to diminish this negative trait and produce a viable electrocatalyst – for the main purpose of ethanol (or alcohol) detection. [2]. According to Miller *et al,* the presence of CeO_2 results in an increase in anode performance nearing five times of regular Pd/CB. STEM and other morphology techniques indicate a dispersion of Pd over the ceria particles – favoured over the carbon duo support. This results in a weakening of the Pd-H bond and assists with OH_{ad} transport from CeO_2 (an oxophilic compound) to the palladium core. It was also shown to have an expressively higher activity following the same reasoning. [1]

To further illustrate the positive effects CeO_2 provides to the electrocatalyst, we compared various alternatives of palladium catalysts and the CeO_2 added counterparts. Using identical synthesis processes, the BET surface areas were 1,59 $m^2.g^{-1}$ and 5,97$m^2.g^{-1}$ and average pore size of 138nm vs 59nm for Pd/CB and Pd/CB-CeO_2 respectively. XRD patterns show a slight shift in the carbon (002) peak from 29^o to 33^o with the addition of cerium oxide as well as a diminished palladium peak @ 47^o. LSV data also shows that onset potential has shifted to the left from -0,44V to -0,65V along with producing current peaks nearly 6 times greater. Although quantitative EIS data are not fully analysed yet, a quick comparison does indeed indicate lower resistance experienced by the ceria aided catalyst.

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Challenges for processing of cathodes for all-solid-state batteries: From liquid to solid system

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With continuously growing demands for energy storage systems and an increasing field of application for batteries (e.g. EVs, grid energy storage or portable devices), next-generation battery technologies gain enormous interest in academia and industry. Therein, the all-solid-state battery (ASSB) is a promising candidate to replace the state-of-the-art lithium ion battery (LIB). A potentially higher energy density (Wh/L) compared to LIBs could enable longer driving ranges for electric vehicles [1]. However, the processing of an ASSB is quite challenging and differs strongly depending on the materials used [2]. Up to now, only single parameters or components of the ASSB have been investigated and optimized showing a good performance on the material level but severe difficulties at transferring the technology to the electrode or cell level.

This study focuses on the integration of the oxide based solid electrolyte (SE) lithium aluminum titanium phosphate (LATP) into the composite cathode (results in a catholyte). Thus, in order to understand the Li-transport in the porous catholyte, the study starts with the investigation of a state-of-the-art liquid system in a LIB regarding the influence of the electrode microstructure (porosity, tortuosity) on its electrochemical performance (impedance measurement). To successfully add LATP into the standard suspension-based processing of the cathode, the in-depth understanding of interface and possible other side reactions as well as changes in the electrode microstructure are key to comprehend the ion transport and resistances in the all-solid-state system. However, only a few interactions and side reactions (e.g. at the interface of SE and active material) are understood and even fewer are solved in the literature [3]. Especially using Ni-rich (like $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$) active materials (AM) increases the issues considering thermal and electrochemical stability.

To decrease the porosity and increase the contact area between the SE and AM particles, different methods for densification are investigated. Using only ceramic SE particles, sintering of the cathode can be necessary to decrease the grain boundary resistance and further increase the contact area of the cathode components. Therefore, the thermal stability of the SE and the AM is studied with and without the other cathode components at different temperatures, in inert and ambient atmosphere. The reactions are monitored by changes in the particle morphology (SEM), composition (EDX), crystal structure (XRD) and surface chemistry (XPS). Furthermore, with regard to an improved stability, protective coatings on the AM particle surface are studied. Additionally, the porosity and microstructure of the catholyte were investigated using mercury porosimetry, helium pycnometry, nitrogen adsorption, SEM/EDX and LSM. This way, deviations induced by the measurement technique can be deduced to provide a distinct determination of these crucial parameters and their influence on the possible Li ion pathways in the catholyte.

The influence of the diverse modifications on the microstructure in the solid-state catholyte and their influence on the electrochemical performance are investigated in Li-metal cells using a conductive separator with sufficient stability against the lithium anode and the catholyte components.

The results of this study enable a first insight into the processing of ASSB with ceramic SE and a better understanding of interfaces, reactions and Li-transport in the solid-state system.

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Wireless Electrochemiluminescence at Nafion-Carbon Microparticle Composite Films

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ABSTRACT: Thin films of a composite of nafion and carbon microparticles have been deposited on non-conducting substrates and their conductivity as well as their ability to generate electrochemiluminescence investigated. The films exhibit very low conductivity (< 6×10^3 S m^{-1}) for low particle loadings but once the percolation threshold is reached (volume percentage of 71±8% carbon particles), the conductivity increases dramatically and a maximum conductivity of $2.0 \pm 0.1 \times 10^7$ S m^{-1} is achieved. The electrochemical properties of the composites, including heterogeneous electron transfer rates, were probed using cyclic voltammetry. Significantly, bipolar, or wireless, electrochemiluminescence can be generated with films that contain >65% (by volume) carbon particles where $[Ru(bpy)_3]^{2+}$ is the luminophore and tri-propyl amine as co-reactant, at an electric field of 14 V cm^{-1}. Under these conditions, the complete film is sufficiently conducting to become polarized in the external electric field and the electrochemiluminescence intensity correlates strongly with the film conductivity. These results demonstrate the usefulness of particle arrays for the wireless generation of electrochemiluminescence at relatively low electric field strengths.

Elimination of Pharmaceutics from Municipal Wastewater by Nanofiltration Coupled to Electrochemical Advanced Oxidation Process as Complementary Treatment

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Occurrence of pharmaceutical micropollutants in the effluent of municipal wastewater treatment plants (MWWTPs) has been raising concern amongst different stakeholders in the field of environment and ecology. More and more pharmaceutical substances traceable in the wastewater have been categorized as emerging pollutants due to their recalcitrance and potential toxicity to living organisms [1]. Hence, in the objective of elimination of persistent pharmaceutics in aquatic environment, additional treatment to the effluent of MWWTPs seems obligatory. A variety of tertiary treatment has been proposed across literature and the majority of them are based on the fundamentals of chemical oxidation where strong oxidants are involved in the degradation of pollutants. Classical processes such as chlorination, ozonation and advanced oxidation processes (AOPs) such as ozonolysis, peroxonation, heterogeneous photocatalysis and (photo)-Fenton processes are to some extent well established to degrade effectively contaminants in aqueous media [2]. Nevertheless, their efficiency comes with firstly high price tag and secondly the prerequisite of adding chemical reagents into the treating media. Electrochemical advanced oxidation processes (EAOPs) have also been reported to remove organic and pharmaceutical pollutants [3]. A huge boost to the AOPs is that EAOPs do not necessarily require the addition of chemical reagents since strong hydroxyl radical oxidants ($^{\bullet}OH$) are electrogenerated continuously in-situ. Owing to the development of diamond-based anodes, higher degree of electrochemical oxidation of organic compounds has been attained. Furthermore, the application of microfluidic reactor within the framework of EAOPs has spurred the capability of wastewater treatment. The average ionic conductivity of effluent of MWWTPs (~1 mS cm^{-1}) is apparently too low for conventional macroreactor of EAOPs in–which the distance between electrodes is in the range of 1-4 cm [4]. Hence, supporting electrolyte reagent is very often added to compensate the low value of conductivity as to avoid huge ohmic drop in-between electrodes. Meanwhile, the micrometric interelectrode gap within microfluidic reactors allows the mineralization of pharmaceutical pollutants without additional supporting electrolyte while concurrently enhances mass transfer of organics towards the electrodes. On a separate note, membrane filtration has been widely applied to produce clean water. It does not require the addition of chemicals and its efficiency has been well established. However, membrane is technically a filter. It is prone to fouling and concentrated effluent containing organics and very likely toxic compounds are separated in the retentate stream. Thus, in this research work, synergy between nanofiltration and EAOPs is investigated. Separated retentate effluent, which is a nuisance to the membrane filtration process, is on the contrary an advantage to the EAOPs. The conductivity and the concentration of pollutants are higher, both favoring better operating conditions as well as faradic yield of EAOPs. To date, the application of EAOPs to treat the concentrate of membrane separation techniques has already been reported in literature. However, no report has been found on the coupling of nanofiltration with microfluidic reactor moreover to treat the effluent of MWWTPs. As prevalently acknowledged, the efficiency of degradation of organics by EAOPs depends on various parameters and they behave differently in microfluidic reactors relatively to the macros. Therefore, throughout this study, the influence of different initial concentration of pollutant (1 µg L^{-1} to 1 mg L^{-1}), applied current density (1-30 mA cm^{-2}), interelectrode distance (50-1000 µm) and flow rate (0.1-1 L min^{-1}) is investigated. Experimental results of degradation of pharmaceutics are accompanied with mathematical modelling taking into consideration the enhancement of mass transfer of organics, of kinetic of the redox reactions at electrodes and of flow behavior with microfluidic reactor.

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Highly Sensitive Electrochemiluminescence Signaling of Cardiac Troponin I based on Bipolar Electrochemistry

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Acute Myocardial infarction (AMI) remains one of the major causes of death in people with cardiovascular disease [1]. Development of fast, sensitive and low cost detection strategies are of utmost importance when dealing with ultra-low level concentrations of analyte during early stages of disease progress.

The present study focused on the development of a wireless detection strategy using electrochemiluminescence as signal readout. Here a sandwich-type immunoassay for troponin, an important biomarker for AMI [2,3], was fabricated by modification of the anodic pole of indium tin oxide (ITO) bipolar electrode with a capture antibody, antigen and a secondary antibody conjugated to a synthesized ECL luminophore. The modified ITO bipolar electrode was placed between two driving electrodes and an external voltage was applied. The proposed wireless system showed excellent performance with ECL readout at very low troponin levels. This detection strategy has much promise as a developing tool for multi-analysis as well as real time diagnosis.

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Detailed 3D Reconstruction and Quantification of Graphite Anodes from Lithium-Ion Batteries using Laser Tomography

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The performance of lithium-ion battery (LIB) electrodes is closely related to their microstructure. For the analysis of LIB cathodes, commonly focused ion beam - scanning electron microscopy (FIB-SEM) tomography is used due to its high resolution in the nm-range and excellent contrast mechanisms [1-2]. In recent years, also X-ray tomography or even correlative approaches combining both techniques are applied on LIB cathodes, in order to additionally benefit from the larger volumes analyzable by X-ray tomography [2]. For LIB anodes containing graphite, FIB-SEM tomography is not feasible as the energy from the ion source is not sufficient to adequately mill the graphite. Hence, all anode reconstructions reported in literature are based on X-ray tomography. These studies allow the analysis of large volumes with resolutions in the range of several hundreds of nm. However, due to the lower resolution and the lower contrast mechanism of X-ray compared to FIB-SEM tomography, details of the graphite structure cannot be observed from X-ray tomography analysis.

In this work, a novel method for the 3D reconstruction of graphite anodes is presented. It is realized using a TriBeam system [3], which has integrated an ultrashort pulse femtosecond lasers into a FIB-SEM system. In contrast to FIB-SEM tomography, the milling is conducted by a laser beam instead of an ion beam, though the imaging is still be done by an electron beam. Thus the milling is much faster, while the excellent contrast mechanisms and resolution of the consecutive images retain, which so far was characteristic only for FIB-SEM tomography.

The reconstruction of a graphite anode obtained from this new laser tomography method will be analyzed and microstructural parameters such as volume fractions, surface area, particle and pore sizes as well as tortuosity values will be presented. The results gained from laser tomography will be compared to results obtained on the same anode using X-ray tomography. Finally, the differences, possibilities and limits of both methods will be discussed.

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Extraction and separation of REEs and d-metals from Estonian phosphorite using ionic liquids

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In the report "Critical raw materials" (2014) made for the EU, rare-earth elements are associated with the highest long-term supply risks and the highest predicted demand growth. Therefore the analytical and separation technologies for REEs are attracting more and more attention.

Estonia is situated on the southern buried slope of the Baltic Shield where the sedimentary bedrock (sedimentary cover) overlies the Precambrian crystalline basement. The bedrock ranges in thickness from 100 m near the coast of the Gulf of Finland to 800 m in southern Estonia.

Estonia is not very rich in minerals, but it has some georesources remarkable in the European context:
1. Oil shale. The Estonia deposit is the largest commercially exploited and best-studied oil shale deposit in the world. 2. Peat. Estonia is considered as a country richest in peatlands in North Europe. 3. Phosphorite. The Rakvere deposit (well-studied but not exploited) is the largest phosphorite deposit in Europe. [1] Estonian Shelly phosphorites contain sufficient amount of "light rare earth" (Ce, Pr, Nd and Sm) as well as some "heavy rare earth" elements (Gd, Tb, Dy, Ho, Er) and d-metals (Mo, V etc.). [2]
Ionic liquids (ILs) are electrolytes that are composed entirely of ions and that offer a very wide range of solvent properties [3]. The use of ILs as solvents for extraction of REEs has several reasons: 1. green ILs can replace the volatile and flammable kerosene fraction in solvent extraction processes and high-temperature molten salts (a big saving in energy costs) that are currently used for the separation of rare-earth elements [4]; 2. a rare property of some IL-water mixtures to change the miscibility above a critical solution temperature can be used for the "smart" extraction of metal ions from aqueous solution [5].

To start this project we prepared solutions with the controlled chemical composition in water using Mo and V salts. ILs and some more common organic solvents were used as an organic phase for the extraction/ separation process in order to continue with more challenging phosporite mixtures. Electrochemical methods as well as laser ablation inductively coupled plasma mass spectrometry have been used to analyze the progress of this work.

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Visible-light driven photoelectrocatalytic degradation of ciprofloxacin polluted water treated with WO_3/carbon nanodots heterostructured anode

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Keywords: Water treatment, Photoelectrocatalysis, Photoanode, Organic pollutants, Tungsten trioxide, carbon nanodots

Photoelectrocatalysis (PEC) has been indicated as a promising approach for remediation of wastewater containing organic substances. The most important component of this water treatment system is the photoanode on which the oxidants are generated. Thus, research efforts are being geared towards obtaining anodic materials which are highly effective, sustainable and durable. In this work, we report the fabrication of a heterostructured photoanode compromising WO_3/carbon nanodots (CNDs). The semiconductors were obtained by hydrothermal process and the carbon nanodots was prepared by carbonisation of fructose. The anodic materials and the fabricated photoanode were characterised by XRD, Raman spectroscopy, TEM, FTIR and linear sweep voltammetry, chronoamperometry and electrochemical impedance spectroscopy. Degradation of ciprofloxacin and real wastewater were achieved using the photoanode and platinum cathode in a single-compartment reactor, at an applied potential of 2 V, a near neutral pH and simulated solar light equivalent to 1 sun (1000 W/m2). Significant decolourisation and COD abatement of the polluted water were recorded after 3 h of the process and intermediate study conducted using UHPLC-MS. The outcome of the study showed that the fabricated anode can be used in a photoelectrocatalytic system for the treatment of wastewater and successfully degrade the antibiotic.

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Synthesis and Characterization of F-doped α-MnO_2/Onion Like Carbon (OLC) Composite Cathode Material for Sodium Ion Batteries

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Due to the potential scarcity of lithium resources, increasing cost and low safety may restrict their large scale production of electrical-energy storage devices. For the past decade, many researchers have been focused on alternative batteries such as Na^+, K^+, Mg^{2+}, Zn^{2+} and so on [1]. Amongst, sodium ion battery (SIB) technology is a promising system due to its similar intercalation chemistry to that of lithium, cost effective and abundant resources of sodium. However the electrochemical performance of SIBs is still unsatisfactory owing to its high ionic radius and higher atomic mass, which causes sluggish transport properties and low energy density [2]. Therefore, it is essential to strive for suitable cathode materials for SIBs to enhance the transport properties during insertion and de-insertion process.

The numerous cathode materials for SIBs have been studied such as layered oxides, oilvins, polyanion based sulfates and phosphates and NASICONs. However, manganese oxide based cathode materials has been explored extensively for SIBs due to the abundance, low cost and environmental benign. Moreover, it offers high capacity for SIBs due to its large tunnels causes speedy intercalation and de-intercalation process [3-5]. Therefore, here we reported, fluorine doped α-MnO_2/OLC (F@α-MnO_2/OLC) composite cathode material was synthesized through molten salt method [6]. The XRD, FE-SEM, TEM and XPS characterizations reveal pure phase, Mn valence state and its nano-rod morphology. The electrochemistry performances of F@α-MnO_2/OLC material were demonstrated using Na-foil as the anode and the 1M $NaClO_4$ in EC: PC (1:1, volume ratio) as electrolyte within the potential window of 1.0-4.3 V. The fluorine doped α-MnO_2/OLC exhibits highly stable, better capacity retention and improved rate capability performances compared to pristine cathode materials. It is ascribed to the synergistic effect between the fluorine and OLC coated α-MnO_2 cathode material could enhance the transport properties.

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Pt-free counter electrode for dye sensitized solar cell based on nickel and niobium selenide nanostructure

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Dye sensitized solar cells (DSSCs) are gaining momentum in the world of photovoltaic. They promise technically and economically credible alternatives for harnessing energy from the sun due to their low cost of production and ease of fabrication [1, 2]. However, platinum (Pt) that is conventionally used as the counter electrode (CE) to collect external electrons and reduce I3- in the electrolyte in case of a liquid electrolyte is a noble metal thus expensive. In addition, Pt stability is wanting as it is easily poisoned by the iodine from the electrolyte. As a result, so much attention has been focused in finding alternatives for Pt which include transition metal di/chalcogenides (TMDCs) among other compounds. As transition metal compounds, TMDCs have electronic structures similar to noble metal Pt, with interstitial phases or interstitial compounds, and they show Pt-like behaviour. Consequently they can be considered as substitutes to Pt.

In this project, two transition metal selenide namely nickel and niobium selenide were considered to replace the Pt. The materials were synthesized in nanoscale via colloidal method where the metal precursors were thermally decomposed in oleylamine at temperatures ranging from 200˚C t0 300˚C. The as-synthesized materials were characterized using XRD, TEM, SEM etc to identify the phase and morphology as these features affect the electro-catalytic activity of the material. The materials were then used to make CE by drop casting and spin coating an ink made from the materials in chloroform on FTO, after which the films were annealed at 100˚C for 30 min. Cyclic voltammetry (CV) was employed to characterize the relative catalytic ability of the CEs. CV measurements were conducted using a three-electrode electrochemistry system. Nickel/Niobium selenide CEs under testing were used as the working electrodes, Pt wire as the counter electrode, and Ag/Ag+ as the reference electrode. The scan rate used was 100 mV s^{-1} while the electrolyte was the acetonitrile solution containing 10 mM LiI, 1 mM I_2, and 100 mM LiClO4. Further, a DSSC was fabricated using the as-synthesized materials. The devices performances were characterized by I-V and electrochemical impedance spectroscopy (EIS) measurements. EIS is a useful tool for characterizing important interfacial charge-transfer processes in DSSCs, e.g electron transfer/charge recombination at the TiO_2/dye/electrolyte interface, electron transport in the TiO_2 electrode, electron transfer at the CE, and triiodide transport in the electrolyte [3].

Both the CV and EIS results of Ni/Nb-Se CEs were very comparable to or better than those of the platinum as shown in Fig.1 which depicts mainly data from the CV. Therefore, these materials could be considered for alternatives to Pt. It was also visible that the phase and shape of the nanoparticles affected the outcome of the electro-catalytic activities.

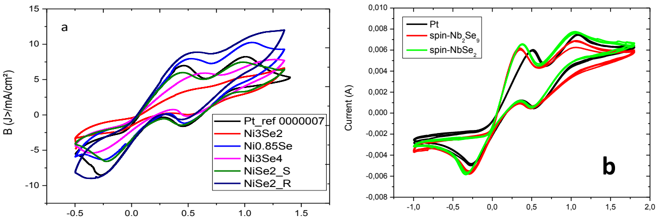

Figure 1: Cyclic voltagrammes for (a) Nickel selenide nanoparticles with S_spheres while R_rods and (b) niobium selenide nanoparticles.

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The Influence of Pt Step Sites Onto Methanol Electrooxidation: An Electrochemical and FTIR Studies

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The methanol electrooxidation (MEO) has been widely studied because of its possible application in direct methanol fuel cell.[1] Many efforts have been devoted to disentangle its oxidation mechanism and how this mechanism depends on the methanol (MeOH) concentration and the surface structure. During the oxidation mechanism onto platinum (Pt) electrodes, parallel pathways is observed simultaneously, which involves, depending on potential, intermediates like carbon monoxide, carbonaceous species (HCO or COH) and soluble intermediates (HCOOH and HCHO).[2] The aim of this work is to determine the influence of Pt step sites over MEO using electrochemical and FTIR techniques. The surfaces used in this work belong to the series of Pt(S)[*n*(111)x(111)] having Miller indices Pt(*n*,*n*,*n* - 2). As usual, *n* represents the number of terrace atoms, which implies that these surfaces had 14, 10, 7 and 6 atom-wide terraces. The cyclic voltammograms (CVs) for Pt(111), Pt(776), Pt(554), Pt(775), Pt(332) and Pt(110) surfaces in 0.5 M H_2SO_4 are shown in the Figure 1, the profiles are in according to the literature. The CVs for MEO using low and high MeOH concentrations are exhibited in Fig. 2.

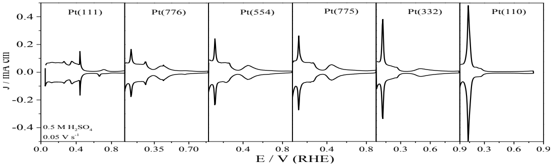

Fig. 1. CVs in 0.5 M H_2SO_4 onto: Pt(111), Pt(776), Pt(554), Pt(775), Pt(332) and Pt(110).

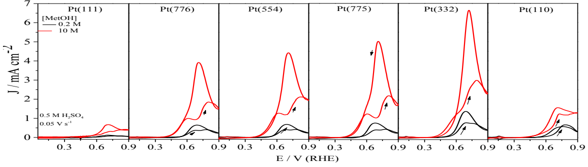

Fig. 2. CVs of MEO (— 0.2 M and — 10 M) onto: Pt(111), Pt(776), Pt(554), Pt(775), Pt(332) and Pt(110).

The CVs of MEO present accentuated differences when the surfaces are modified by adding 'defects' or monoatomic steps. The non-stepped surface, Pt(111), showed lower activity for both MeOH concentrations due to the strong adsorption of sulfate/bisulfate anions, thus inhibiting MeOH adsorption, leading to the reduction of the oxidation rate of MeOH. For stepped surfaces the MEO show a slight enhances as the density of step increases for both MeOH concentrations. However, there is an abrupt decay in the electroactivity for Pt(110). The reverse peak increases considerably when the density of defects increases, indicating a great amount of species formed during the positive scan. Another interesting point is that at high MeOH concentrations, the voltammetric profile changes considerable as compared at low concentration, two separated peaks (0.60 and 0.80 V) are better visualized, indicating changes in intermediates production and promotion of MeOH dissociative adsorption. The FTIR spectra were collected in methanol (0.2 and 10 M + H_2SO_4 0.5 M) using a flat ZnSe window. The sample spectra were recorded after applying successive potential steps of 50 mV in the positive and negative direction from 0.05 to 0.9 V, the surfaces used were: Pt(111), Pt(554) and Pt(110). For Pt(111) (0.2 M) the production of CO_2 occurs at low potential at ca. 0.1 V, and no CO_{linear} was observed for this situation. While at high concentration (10 M), the CO_2 is delayed for potentials close to 0.60 V and CO_{linear} arises in small amounts after 0.40 V. The Pt(554) has 10 atoms terrace, this surface was taken as a representative among the others stepped ones. In this case, the stepped surface produces CO_2 at 0.55 V and CO_{linear} starts at 0.20 V, for low MetOH concentration. For 10 M, CO_2 commences at 0.55 V and CO at 0.20 V, but differently the CO for this surface is generated at all range of the studied potentials, even at high potential, ca. 0.90 V, there is presence of this intermediate. For Pt(110), the MEO is not so active, once CO_2 appears at 0.60 V, CO_{linear} is almost imperceptible and CO_{bridge} is more pronounceable as from 0.70 V. For 10 M, CO_2 arises at 0.65 V and now the CO_{linear} possesses bipolar band at low potential, ca. 0.20 V, also there is the presence of CO_{bridge}, these two species remain to high potentials.

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Nanostructured 2D Ti_3C_2/NiO composite material as electrode for supercapacitors applications

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Abstract

Cost-effectiveness and environmentally friendly nature of the transition metal oxides are some motivating factors for their exploration for use as energy storage devices applications when compared to other electrode materials. This work reports the successful synthesis of Ti_3C_2/NiO nanocomposite for application as supercapacitor electrodes. The as-synthesized material was characterized by various techniques such as, Raman spectroscopy, BET, SEM, TEM and XRD to ascertain the morphological and structural nature of the material. Electrochemical characterization of the composite material performed in a three-electrode configuration using 6 M KOH electrolyte reveals high specific capacity and excellent cycling stability with satisfactory capacity retention for over 2000 cycle.

Electroanalysis of *Aspalathus linearis* and *Musa paradisiaca* mediated zinc oxide nanoparticles against fungal pathogens

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This study describes the single pot synthesis of zinc oxide nanoparticles (ZnONPs) using a mixture of *Aspalathus linearis* and *Musa paradisiaca* against fungi *Candida albicans*. The nanoparticles are known to be one of the most multifunctional inorganic nanoparticles with effective antifungal and antibacterial activities. UV–visible spectroscopy (UV-vis), Fourier Transform Infrared Spectroscopy (FTIR), High Resolution Transmission Electron Microscopy (HRTEM) analyses were performed in order to ascertain the formation of the nanoparticles. The synthesized ZnONPs were characterized by a peak at 290 nm in the UV–vis spectrum while HRTEM confirmed spherical shaped nanoparticles estimated to be 20 -50 nm. The FTIR data clearly revealed that the extracts contained -OH functional groups whose role was capping agents during the nanoparticles synthesis. The antifungal activity of ZnONPs was tested against *Candida albicans* using the standard well diffusion method (The modified Kirby-Bauer method). The maximum inhibition zones observed in the ZnONPs against *Candida albicans* were confirmed to be 24 - 35mm, a clear indication that the synthesized ZnONPs have a great potential to act as effective antifungal agents. The nanoparticles were left at room temperature over a period of four months and remarkable, they still showed a great potency against the fungi. It is therefore confirmed that ZnONPs are capable of rendering high antifungal efficacy and hence has a great potential in the preparation of treatment against *Candida albicans*. Additionally, the cyclic voltammetric studies of the synthesized nanoparticles showed increased electron conductivities an indication of their multifacet applicability particularly in the development of electrochemical sensing platforms.

Density functional theory study of oxygen reduction reaction mechanism on TiO_2 coated platinum electrocatalyst

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Polymer electrolyte membrane fuel cells (PEMFC) have attracted increasing global research interests owing to their advantages of high energy conversion efficiency, low operation temperature and environmental benignity. Platinum remains the most studied and commonly used electrocatalysts for oxygen reduction reaction (ORR) at the cathode in PEMFC due to its high catalytic activity and excellent stability. However, the cost of platinum as well as poor long-term durability and performance under severe acidic operating conditions at the cathode are among the major challenges hindering widespread application of PEMFC. Recently, overcoating metal catalyst with porous metal oxide thin film has been identified as an effective way for improving the durability and selectivity of heterogeneous catalysts. Atomic layer deposition (ALD) is a renowned catalyst coating technique for achieving uniform deposits with precise thickness control at an atomic level. Thus, ALD metal oxide coatings on platinum metal surfaces emerges as a promising technique for designing electrocatalysts with improved durability and activity. In this work, density functional theory calculations are performed to investigate the catalytic activity and ORR mechanisms of titanium dioxide (TiO_2) coated platinum electrocatalyst. The catalytic behavior and ORR mechanism are explained by investigating the adsorption properties and changes in binding energies of two common ORR reaction intermediates, i.e. O_2 and OOH. The results obtained from the density functional theory simulations were compared and correlated with available literature.

Keywords: ALD, DFT, electrocatalyst, fuel cell, ORR, platinum, titanium dioxide

Thermodynamic and kinetic modeling of lithium insertion in graphite- Comparison with experiment

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Lithium-ion batteries are nowadays the most commonly used energy storage devices, with graphite being the material used preferably as an anode. During Li-ion loading and unloading in a graphite anode, it is well known the existence of stable structures called "stages", which can be observed by different types of experimental measurements. The lithium intercalation process in graphite it is still studied exhaustively, because some of its basic features are a matter of discussion. Besides refined experimental studies, theoretical simulations can provide answers to some of these questions. For example, although numerous experiments have been performed, the detailed features of Li ion diffusion in graphite cannot be unambiguously assessed. Something similar can be stated on the behavior of the partial molar entropy in these systems, for which modeling is relatively recent.

In the present talk we address, by means of theoretical tools and computer simulations the thermodynamic and dynamic behavior of lithium storage in graphite, in close comparison with experiments. With this purpose, an effective Hamiltonian is proposed and Statistical Mechanics, Grand Canonical Monte Carlo and Kinetic Monte Carlo simulations are employed to obtain thermodynamic and dynamic information on this system.

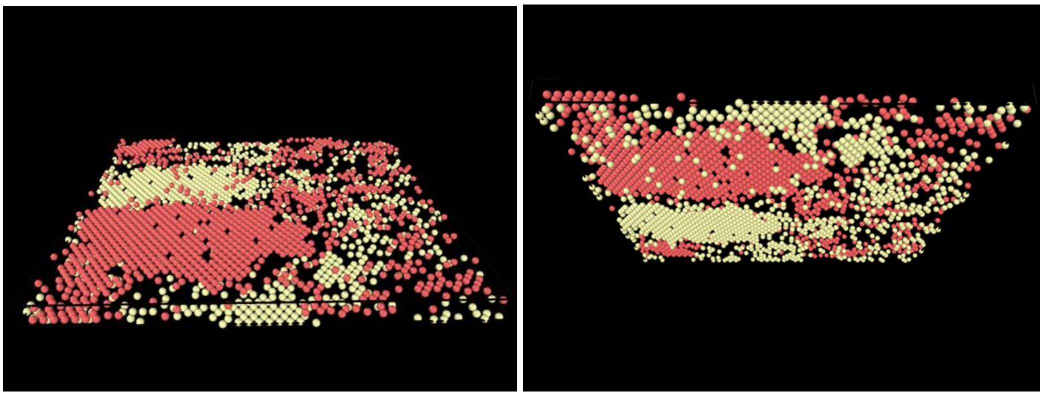

Figure: Occurrence of defective Stage II structures for Li-ions insertion in graphite, as simulated by KMC. Red and yellow spheres represent lithium ions in different layers. Left: top view. Right: bottom view

A Glassy Carbon Electrode Modified with Nitrogen-doped Graphene for Selenium Detection

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Sensitive detection of selenium (IV) in environmental matrixes such as water from dams, rivers, and ground is very essential due to its toxicological effects at elevated levels. This work reports on a simple experimental procedure for the electroanalytical determination of selenium (IV) using a glassy carbon electrode (GCE) modified with nitrogen-doped graphene (NG). The NG was synthesized from graphene oxide (GO) through thermal annealing of GO in the presence of ammonia. Raman spectroscopy, field emission scanning electron microscopy (FESEM), High Resolution Transmission Electron Microscopy (HRTEM), CHNS analyzer and Fourier Transform Infrared Spectroscopy (FT-IR) were used for the physicochemical characterization of synthesized NG. The electrochemical properties of the bare GCE and GCE-NG were determined using cyclic voltammetry and electrochemical impedance spectroscopy. The obtained results indicated that the GCE-NG exhibited a more enhanced electrochemical performance than bare GCE. Square wave anodic stripping voltammetry (SWASV) was employed for the quantitative determination of Se(IV) under the following optimized conditions, 0.1 M $HClO_4$ supporting electrolyte, -0.8 V deposition potential, and 50 s deposition potential. The observable linear range was from 1 to 120 ppb with a detection limit of 0.92 ppb. The electrochemical sensor was successfully applied to selenium (IV) quantification of real water samples and the results were validated with inductively coupled plasm-optical emission spectroscopy.

Keywords: Electrochemical sensor; selenium; nitrogen-doped graphene; square wave anodic stripping voltammetry.

Challenges and advances in organic electrosynthesis: combining building blocks in electrochemical reactions.

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The energy transition from fossil fuels to renewable materials, based on solar, wind and biomass sources, offers new opportunities for many industrial sectors and will help to make the chemical industry more sustainable by using building blocks, such as water, carbon dioxide, nitrogen, and biobased platform molecules, for making chemicals and fuel. The implementation of large-scale electrification by many industrial sectors faces various challenges related to the development of new electrochemical technologies, scaling-up issues and fundamental challenges related to limited efficiency of some chemical transformations and the still relatively limited scope of electrochemical synthesis. Developments are necessary to design new electrochemical materials to steer the activity and selectivity of desirable electrochemical reactions. In this work, I will talk about the challenges in organic electrosynthesis, more specifically in combining building blocks in electrochemical condensation reaction, that is CO_2, CO or NH_3 with biobased building blocks in electrocarboxylation, electro-hydroformylation and electrochemical amination, and the advances in redox reactions of biomass-related organic compounds, such as 5-hydroxymethylfurfural oxidation and electrodimerization of glyoxylic acid in aqueous and non-aqueous solvent.

Our studies go from fundamental to more realistic conditions involving continuous flow electrolysers.

Importance of Mixed-Conducting Mechanism for High-Temperature Fuel Cell Applications

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In many electrochemical devices, mixed ionic/electronic conduction have received great attention. For instance, oxygen transport membrane (OTM) based on $(Ba,Sr)(Co,Fe)O_3$ perovskite exhibit unique hole/oxygen ion mixed conduction behavior for oxygen separation application.

Moreover, composite electrodes/electrolytes consisting of electronic and/or multiple ionic conductors have received great attention for high temperature fuel cell application. For example, enhanced conduction was observed when the oxygen ion conductor, doped ceria was directly mixed with Li/K carbonates. The electrical conduction of composite electrolyte was contributed by the migration of oxygen ions in solid state and carbonate ions in liquid state. It was observed that the two-phase electrolytes exhibit coionic ($O^=/H^+$) conductors during fuel cell operation under the H_2/ air atmosphere. It is believed that highly mobile ions at the interface between doped ceria and carbonates may contribute to the high conductivity of the composite electrolyte. In other words, the super-ionic phase might exist at the interface between doped ceria and carbonates, where the defect concentrations are high. Similarly, mixed conducting electrodes based on composite electrode (e.g. LSM/SDC, LSM/YSZ) also show improved SOFC performance in comparison to conventional electrode. However, to optimize the mixed conduction, the materials/microstructure designs play an important role.

Thus, the objective of this work is to conduct (1) fabrication/design of MIEC and composites (2) microstructure development, (3) characterization of conduction/interfacial kinetics for electrodes/electrolytes in high-temperature fuel cells. High-resolution SEM, XRD, and Electrochemical Impedance Spectroscopy are employed to conduct microstructural, structural and impedance analyses. The electrical conduction behavior of composite electrode/electrolytes will be rationalized based on the pore size, pore distribution and interface area.

Synthesis and properties of chain-like carbon nano-onions via a flame assisted pyrolysis technique using different oils

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The stumbling block in the applications and processability of carbon nano-onions (CNOs) produced from readily available carbon sources has always been the encapsulated metal catalysts from the synthesis procedures [1]. This study reports the synthesis and characterization of catalyst-free chain-like graphitic CNOs using two different oils, namely castor oil and paraffin oil. The synthesis of these carbon materials was achieved through the pyrolysis of the oils in ambient air without any need for a catalyst [2]. The collected pristine CNOs were then subject to heat treatment through annealing at different times (i.e. for 1h, 2h and 3h) in a horizontal chemical vapor deposition technique at 900 °C in Argon gas. While gram scale yields of CNOs produced from both oils were similar, the carbon nanomaterials displayed different chemical and structural properties.

Morphology studies were done using transmission electron microscopy (TEM) for all the materials; and TEM images showed linked chains of quasi spherical layered particles. The particle size distribution of CNOs synthesized from castor oil ranged from 19 to 35 nm ± 7 nm with an average width of 28 nm while those made using paraffin had sizes ranging from 24 to 50 nm ± 9 nm with an average width of 37 nm. For both CNOs synthesized from castor oil and paraffin oil there was a continuation of the closed cage structure towards the core surrounded by layers of nested concentric shells. The CNOs derived from castor oil were on average smaller than those synthesized using paraffin oil and displayed more disordered outer layers with a denser core while castor oil CNOs have inner and outer layers that are more uniform.

Thermal stability analysis was done using thermogravimetric analysis (TGA). Results showed that TGA profiles for the castor oil CNOs differ from those paraffin oil CNOs. In particular, paraffin CNOs have multiple decomposition peaks which are broad while castor oil CNOs show single, sharper peaks. For castor oil CNOs the highest decomposition temperature is that for the pristine CNOs. Annealing decreases the temperature which indicates that defects are introduced during the annealing process. Increasing the annealing time steadily increases the maximum decomposition temperature which shows that annealing orders the CNO shells and making them more graphitic. The decomposition peaks also get narrower with longer annealing time which can be due to an increase in the long range order of within the shells.

Raman analysis was done for the structural characterization of the CNOs. For both CNOs obtained from the different oils there was a decrease in ID/IG ratio with increasing annealing time, showing that annealing does help increase the ordering of the CNO shells, which also correlates to the TGA results.

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Treatment of Antibiotic by Heterogeneous Electrochemical Fenton's based Process using Chalcopyrite as Sustainable Catalyst

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The potential impacts of pharmaceutical residues in the environment have been an emerging research area worldwide. Among pharmaceuticals products, antibiotics are probably the most successful family of drugs so far developed for improving human health. The large application made antibiotics to be released in large amount in natural ecosystems. The primary source of these contaminants in the environment is known to be through wastewater treatment plant effluents, not designed to remove these recalcitrant contaminants[1]. The limitations of conventional methods reflect the need for the complete removal of pharmaceuticals and their metabolites from aquatic systems to avoid their potential toxicity and other possible dangerous health effects. Over around the past two decades, research efforts have been focused at developing more effective technologies to totally remove persistent organic pollutants from wastewater. In this context, electrochemical advanced oxidation processes (EAOPs) acquired high relevance. EAOPs are based on the in-situ production of highly reactive hydroxyl radicals ($^{\bullet}OH$) that non-selectively react with most organics. Fenton's based processes are the most attractive and popular EAOPs. In electro-Fenton process (EF), the oxidizing power of electrogenerated H_2O_2 is strongly enhanced by the addition of a catalytic amount of Fe^{2+} ions, which promotes the generation of homogeneous $^{\bullet}OH$ via Fenton's reaction. EF process is improved by irradiating the treated solution with UVA lamp, which photoreduced $Fe(OH)^{2+}$, regenerating more Fe^{2+} ion and producing more $^{\bullet}OH$, and photodegraded Fe(III) complexes with generated carboxylic acids. Fenton's based EAOPs are very promising but they have some critical limitations such as the need of operating at pH 3 for an optimal run and the loss of soluble iron catalyst as hydroxide precipitate[2].

In this work, a study on the degradation of Cefalexin antibiotic by Fenton's based EAOPs using chalcopyrite as sustainable catalyst to overcome the aforementioned limitations of classical Fenton's based processes has been investigated. Preliminary characterization of chalcopyrite was performed. XPS has been used to determine the oxidation state of Fe and Cu in the mineral. XPS Fe 2p collected from chalcopyrite show peak ranging across reported binding energies of 706.6-712.2 eV corresponding to Fe2p1/2 and Fe2p2/3. The binding energy is characteristic for Fe(III) in the form of Fe-O-OH. XPS also show the presence of Cu(I) and Cu(II) in different form. Evaluation of the amount of Fe^{2+} ions released from chalcopyrite dissolution under continuous stirring and air feeding was performed by spectrophotometric complexometry with 1,10-phenantroline. The concentration of Fe released is proportional to the concentration of chalcopyrite. In all cases, a spontaneous regulation of solution pH to an optimum value for the Fenton's reaction was reached. The treatment of 100 mL of Cefalexin solutions in 0.050 M Na_2SO_4 has been investigated by EF and photoelectro-Fenton (PEF) processes in an open and undivided cell equipped with a RuO_2 based anode and an air-diffusion electrode (ADE) as cathode. Heterogeneous EF and PEF were carried out using chalcopyrite and homogeneous EF and PEF using Fe and Cu salt. The performance of each treatment was assessed by TOC, HPLC and GC-MS analyses. EAOPs based on Fenton's reaction using chalcopyrite were more efficient than conventional EAOPs based on Fenton's reaction. PEF process was the most effective technology for the degradation and mineralization due the additional production of $^{\bullet}OH$ and the photodegradation of iron complex with organics. The effect of some relevant operation parameters such as the applied current, the concentration of chalcopyrite on the PEF process efficiency and the formation of intermediates was thoroughly evaluated.

Acknowledgements

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Adsorption of Sulfonyl-group based Anions from Ionic Liquids: an *in situ* STM and Impedance Study

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Adsorption of particles, such as molecules or ions, is an important basis for many everyday phenomena, such as corrosion inhibition or chromatographic separation. With regard to electrochemical technology, it provides a basis for energy storage in supercapacitors as well as helps to mitigate many important faradic processes via the formation of the electrical double layer (EDL). However, in many cases, the particles themselves adsorb at the surface by chemical bonding, thereby contributing to an effect called specific adsorption, which means that the adsorbed species can no longer be considered as components of the diffuse phase at a solid|liquid interface. Therefore, as part of the solid interface, they contribute strongly to the interfacial properties, such as energy storage, reactivity and interaction with other interfaces. It is of interest to look at such systems whereby there are no neutral particles within the liquid phase, such as ionic liquids (IL). Composed of ions, ILs constitute a large variety of liquidous electrolyte media that can be specifically tuned for an application in mind. This allows ILs to have a varied range of applications, such as electrolytes for energy storage, separation of ionic or organic species and catalytic media for organic synthesis.

Although the formation of the EDL in ILs has been in the scientific focus for over a decade, there is still a lack of understanding with regard to the specific interaction of ions at IL|metal interfaces [1]. This is partially due to the difficulties in describing such interactions from a modelling perspective, as well as the complexity of the systems in electrochemical experiments.

To overcome these problems, both classical electrochemical methods (cyclic voltammetry and electrochemical impedance spectroscopy) as well as *in situ* scanning tunneling microscopy (STM) method have been applied to observe the interfacial structuring at electrode|IL interfaces. Single crystal bismuth electrodes have been chosen as the working electrodes due to their variable metallic properties and stable surface structure. Three sulfonyl-group based anions - triflate (OTf), mesylate (Mes) and bistriflimide (TFSI) have been chosen for their potential ability to chemically bond to the surface through the sulfonyl groups, which has been demonstrated in aqueous solutions, but not ILs. These anions have been combined with aliphatic imidazolium cations that are generally thought to not specifically adsorb at the metallic electrodes. It is observed that sulfonyl-group anions show a largely different adsorption behavior at Bi electrodes compared to that of halide anions studied in our previous paper: adsorption of OTf, Mes and TFSI anions is a very slow process and the adsorbed layer acts as a dielectric at the surface, therefore considerably lowering the amount of charge that can be stored. OTf and TFSI anion containing ILs also demonstrated wider electrochemical stability ranges compared with halide ion based ILs, which averaged to 2.3V opposed to the 1.4V of halide-based systems, while Mes anion based ILs did not.

It should be noted that adsorbed sulfonyl-anions form two stable polarization regions (electrostatic and dielectric chemisorbed regions) that can be switched between by varying the applied potential value, possibly contributing to a new electronic memory type system.

Acknowledgements

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Oxygen-Deficient Perovskite-Related $(Nd_{0.4}Sr_{0.6})_2Ni_{0.8}M_{0.2}O_{4-\delta}$ as Oxygen Electrode Materials for SOFC/SOEC

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Perovskite-related $Ln_2NiO_{4+\delta}$ (Ln = La, Pr, Nd) nickelates with layered Ruddlesden-Popper combine redox stability with noticeable oxygen stoichiometry changes, yielding enhanced mixed transport and electrocatalytic properties. These unique features are promising for applications as oxygen electrodes with good electrochemical performance in reversible SOFC/SOEC (solid oxide fuel/electrolysis cell) systems. To date, most efforts were focused on oxygen-hyperstoichiometric $Ln_2NiO_{4+\delta}$-based phases, whereas nickelates with oxygen-deficient lattice remain poorly explored. Recent studies demonstrated that the highest electrical conductivity in $(Ln_{2-x}Sr_x)_2NiO_{4\pm\delta}$ series at elevated temperatures is observed for the compositions containing ~ 60 at.% of strontium in A sublattice [1,2]. The present work was focused on the characterization of $(Nd_{0.4}Sr_{0.6})_2Ni_{0.8}M_{0.2}O_{4-\delta}$ (M = Ni, Co, Fe) nickelates for the possible use as materials for reversible oxygen electrodes.

The ceramic materials were prepared by Pechini method with repeated annealings at 650-1200°C and sintered at 1250-1300°C for 5 h under oxygen atmosphere. Variable-temperature XRD studies confirmed that all studied compositions retain tetragonal K_2NiF_4-type structure in the temperature range 25-900°C. The results of thermogravimetric analysis showed that the prepared nickelates has oxygen-deficient lattice under oxidizing conditions at temperatures above 700°C. Partial substitution of nickel by cobalt or iron results in a decrease of *p*-type electronic conductivity and the concentration of oxygen vacancies in the lattice (Fig.1), but also suppresses dimensional changes associated with microcracking effects (due to anisotropic thermal expansion of tetragonal lattice). Electrochemical performance of porous $(Nd_{0.4}Sr_{0.6})_2Ni_{0.8}M_{0.2}O_{4-\delta}$ electrodes in contact with $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ solid electrolyte was evaluated at 600-800°C employing electrochemical impedance spectroscopy and steady-state polarization (anodic and cathodic) measurements.

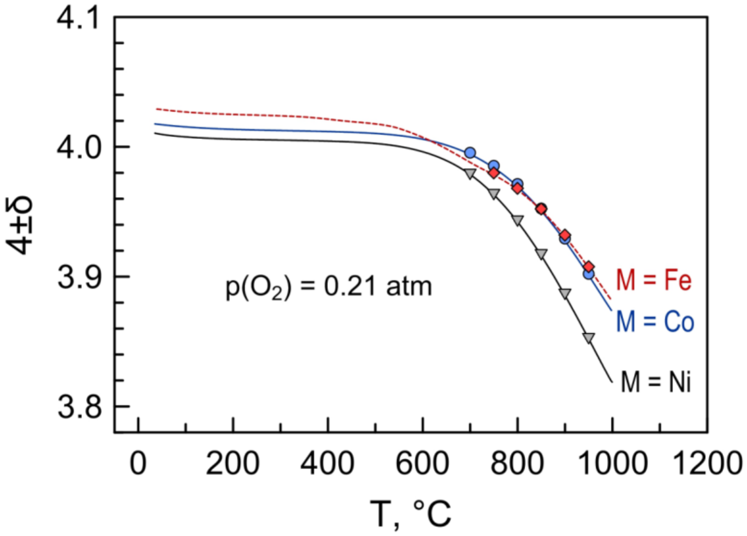

Figure 1. Oxygen nonstoichiometry of $(Nd_{0.4}Sr_{0.6})_2Ni_{0.8}M_{0.2}O_{4-\delta}$ in air. Lines correspond to the data obtained in dynamic cooling regime (2°C/min), and symbols correspond to the equilibrium values.

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First principles calculations on potential addivtives in Li-ion batteries to prevent thermal runaway

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The ongoing challenge to integrate and balance renewable energy sources have created the need for innovation in energy storage. Lithium ion battery (LIB) received much attention in recent years as a high density energy store. This is mainly because of the lightness and relatively high density of the used intercalation compounds paired with large voltage differences. That makes them ideal for portable devices, such as laptops.

However, Li ion technology faces significant safety challenges for larger scale apllications, such as in electric vehicles, etc., due to the increasing energy content and associated increased risk associated with failure modes in these batteries. Failure modes due to thermal, mechanical, and electrical abuse may lead to thermal runaway, with potentially lethal consequences.

In this work, we perform first principles calculations on potential additives for Li-ion batteries, that show a positive temperature coefficient of resistivity (PTCR) effect. It is expected that these additives can be used to prevent the excessive temperature rise due to abusive electrochemical charge/discharge and act as a cut-off mechanism physically preventing thermal runaway phenomena, thus improving safety of these devices.

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Role of Defect Reaction on Electrochemical Behavior of Electrode Materials for Li Batteries

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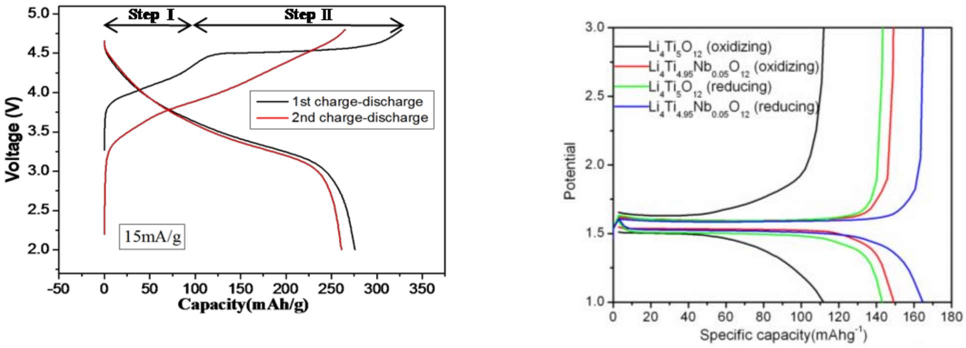
Defect reactions have played important role on improved electrical properties of many oxides. For lithium batteries, functional oxides with desired defect structures also show interesting electrochemical properties.

For examples, Li-rich layered cathode formulated as xLi_2MnO_3-$(1-x)LiMO_2$(M = Mn, Ni, Co, etc.) during 1st charging process was found to exhibit oxygen oxidation, vacancy formation. In the following discharging, Mn reduction (or activation) occurred. As a result, a reversible capacity as high as 250 mAh/g was observed (Fig. 1(a)). Such redox reactions in 1st charging may be illustrated by defect chemistry including oxygen extraction, the formation of oxygen vacancies and electron release. In the next discharging, electrons was accepted through valence changing of Mn^{+4} to Mn^{+3}.

Furthermore, the anode oxide $Li_4Ti_5O_{12}$ (LTO) shows little volume change during charging/discharging cycles with potential for high rate applications. However, as-received $Li_4Ti_5O_{12}$ shows conductivity as low as 10^{-9} S/cm and then causes high interface polarization and low rate capability. With proper processing under low pO_2, the electron conduction and electrochemical properties of LTO was significantly improved as seen in Fig 1(b). Such property enhancement may be well illustrated by defect reaction under low pO_2 environment. In other words, lattice oxygen near surface of LTO tends to be removed under very low pO_2. Consequently, positively charged oxygen vacancy is formed and then charge-compensated by the creation of two negatively charged electrons. These electrons are eventu ally associated with tetravalent Ti ions. The fast electron pathway is established by the coexistence of Ti^{+3} and Ti^{+4} in Ti cation sublattice.

It is known that typical electrochemical reactions are highly dependent up movement of electrons and ions. With understanding of defect reaction during materials processing and charging/discharging, advanced electrode materials with much improved electrochemical and/or stability may be developed.



(a) (b)

Figure 1. 1st Charge/Discharge Curves for (a) $Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ at 0.05 C; (b) Undoped and doped $Li_4Ti_5O_{12}$ tested at 1C rate

Development of Carbon Supports for Direct Methanol Fuel Cells

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Palladium catalysts supported by multi-walled carbon nanotube, graphene oxide, reduced graphene oxide, nitrogen-graphene oxide, reduced nitrogen-graphene oxide and carbon nanofibers have been synthesized in this work. The carbon nanotube was commercial while the graphene oxides and their reduced counterparts were obtained through modified hummer's method and thermal reduction using hydrazine hydrate respectively. The catalysts were synthesized using modified polyol method. The structures were examined using Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The FTIR showed that the surface of the carbon supports exhibit oxygen containing functional groups (carboxyl, nitrosyl and hydroxyl) which serve as the anchor sites for metal deposition while the XRD revealed the formation of the catalysts. The dispersion of the metal nanoparticles and their morphology were determined using high resolution transmission electron microscopy (HRTEM) while the surface area analysis was done using BET. The electrocatalytic activities of the catalysts as anode catalysts in direct methanol fuel cells were determined using cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy.

Keywords: multi-walled carbon nanotubes, graphene, carbon nanofibers, palladium catalyst, methanol oxidation, oxygen reduction, direct methanol fuel cell.

Design of Glucose Oxidase-Coupled Polymeric Film of Dendrimer and Its Use as Amperometric Biosensor

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AIM

The aim of the research is to design a glucose –oxidase based amperometric biosensor. This is achieved by forming a polymeric film of the dendrimer-glucose oxidase composite on glassy carbon electrode, via electropolymerization.

DESIGN AND METHODOLOGY

Dendrimers were prepared by a divergent method using the reagent excess method by using Ethylene diamine (EDA) as starting material by consecutive Michael addition and ester amidation reaction previously reported. Electrochemical study of 0.0 generation of poly amido amine (PAMAM) dendrimer was done by dipping the mirror polished glassy carbon, the counter and reference electrodes into a cell containing the dendrimer solution in methanol with 0.1 M Tetrabutylammonium perchlorate (TBAC) as supporting electrolyte at a scan rate of 100mVs^{-1} vs Ag/AgCl. This was done using BASi Epsilion EC- Version voltammetric analyzer (Bio-analytical Systems, USA). Formation of polymer films of 0.0 G PAMAM dendrimer on GCE was done by repetitive cyclic voltammetry scanning of the bare electrode in 10 mM solution of the dendrimer in methanol containing 0.1 M TBAC supporting electrolyte, the process showed a reversible peak at -0.8V Vs Ag/AgCl attributed to the presence of Nitrogen atoms. Glucose Oxidase-dendrimer composite was synthesized by adding 10 mg of glucose oxidase to 4 ml of DMF. Dicyclohexylcarbodiimide (DCC) (1 mg) was added to the resulting mixture to convert the carboxyl groups of the enzyme to active carbodiimide esters. The mixture was stirred under Nitrogen for 72 hours. Thereafter, 10 mg of 0.0 G PAMAM dendrimer was added to the resulting solution and then stirred for a further 72 hours. Nucleophilic reaction between the activated COOH of glucose oxidase and the tertiary amine of the dendrimer resulted in the formation of amide linkage.

Result and Discussion

Glucose oxidase-dendrimer composite showed a reversible redox process with reduction peak at – 0.52 V and oxidation peak at +0.52 V which could be attributed to presence of oxidizable nitrogen atoms. The formation of polymeric films of glucose oxidase-dendrimer composite glassy carbon electrode was further elucidated by repetitive scanning of the electrode, the gradual shift in the redox potentials confirms the stability of the entrapped enzyme's improved mechanical stability which minimized enzyme leaching. Furthermore, the stability of the polymeric film was confirmed by cyclic voltammetry of 10 mM of 0.0 G PAMAM in pH 7.0 buffer, the reduction peak was observed at a potential of -0.378 V and a higher reduction peak current 4.9 µA which may be attributed to stability of the composite on the electrode surface.

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Synthesis and Electrochemical Study of Fe-Ni Hofmann-type Polymers

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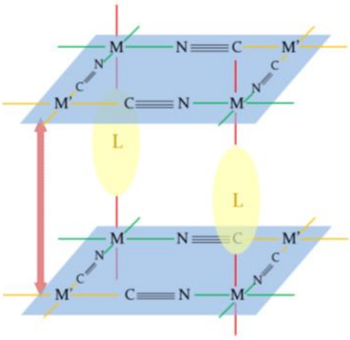
Coordination polymer is referred to any crystalline material obtained by the link between transition metal ions (M) through organic ligands (L) forming extended arrangements of varied dimensionality (commonly 2D or 3D). The Hofmann-type coordination polymers [1] {ML[M'(CN)$_4$]} (L= organic ligand with N substituents, as pyridine or pyrazine derivatives, M= Fe, Co, Mn, Cu, Zn, among others, and M'= typically Ni^{II}) [1] include the 2D extended structures in which M adopts an octahedral coordination environment, and [M'(CN)$_4$] a planar geometry. The latter act as bridges between the M-L entities (see Scheme 1). Both important structural properties of these materials, dimensionality and porosity can be modulated by the length and coordination capability of L, which remains within the polymer linked to the M atom in the apical position of the octahedral. Additionally, their electronic versatility is directly defined by the type of the M atoms, which oxidation state defines their unpaired electrons and therefore their electronic properties, being the most studied the magnetic ones [2]. Despite the attractive structural and electronic properties of these kind of compounds, their use as catalytic materials or precursor to obtain active materials is unknown.



Scheme 1. Representation of the structure of the Hofmann-type polymers.

In this work the synthesis and structural characterization of four {FeL[Ni(CN)$_4$]} Hofmann-type polymers (L= 3-CNpy **(1)**, 4-CNpy **(2)**, 3-Brpy **(3)** and 4,4'-bpy **(4)**) are presented, including the study of their electrochemical behavior. A thermal treatment under N_2 atmosphere was applied to all the polymers in order to study their capability of forming M-N-C type catalytic materials. The electrochemical behavior of the final pyrolized materials was compared with the non-pyrolized precursors. Finally, the catalytic activity for the non-pyrolized and pyrolized materials were also tested, to which a relationship with their structural properties is expected.

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Application of new graphite-polyurethane screen printed electrodes modified with magnetite and chitosan-coated magnetite nanoparticles in the determination of epinephrine

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In this work, graphite-polyurethane screen printed electrodes were modified with magnetite nanoparticles (Fe_3O_4, MNPs-SPE) and chitosan-coated magnetite nanoparticles (CHMNPs-SPE) in the 5.0% (*m/m*) optimized proportion. The MNPs and CHMNPs morphologies were evaluated by TEM (Transmission Electron Microscopy). The crystalline structure and thermal behavior were studied respectively, by XRD (X-ray Diffractometry) and TG/DTA (Thermogravimetry/Differential Thermal Analysis). The electrochemical performances of both electrodes regarding epinephrine (EP) determination were evaluated. EP was chosen as a probe once it is an important neurotransmitter in mammalian which electrochemical response is well-known among several studies in the literature. [1] EP electrochemical behavior was studied by Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV).

Initially, chronocoulometric data were obtained in order to evaluate the electroactive areas of MNPs-SPE and CHMNPs-SPE. The resulting values were, respectively, 0.053 and 0.044 cm^2. The decrease in electroactive area in comparison to the geometric value (0.0707 cm^2) can be explained due to the presence of polyurethane resin, a non-conducting agglutinant material. In both cases, diffusional mass transport was found from linear curves obtained in log ν *vs* log I_p plots. [2]

Therefore, some parameters regarding EP analytical determinations by DPV at MNPs-SPE and CHMNPs-SPE were optimized, such as: pulse amplitude (a), scan rate (ν) and pre-concentration time (t). Better peak definition and higher peak currents were observed for $a = 50$ mV, $\nu = 10$ mV s^{-1} and $t = 10$ s, for both proposed electrodes. In sequence, an analytical curve was obtained for the MNPs-SPE and CHMNPs-SPE, from 0.10 µmol L^{-1} to 1.0 µmol L^{-1} for MNPs-SPE, following the equation $Ip = 1.24x10^{-6} + 1.31\ C_{EP}$, with a LOD of $1.68x10^{-8}$ mol L^{-1}. For CHMNPs-SPE, a linear relationship was obtained in the 0.10 – 0.60 µmol L^{-1} concentration range, following the equation $Ip = 1.77.10^{-5} + 1.55\ C_{EP}$, with a LOD of $1.35.10^{-8}$ mol L^{-1}. Although the CHMNPs-SPE linear range obtained was narrower, this electrode presented higher sensitivity and a lower LOD value.

Next, the applicability of MNPs-SPE and CHMNPs-SPE was evaluated by EP quantifications in synthetic cerebrospinal fluid (CSF) and synthetic urine (SU). For MNPs-SPE, recoveries in the 98 - 109% and 99-103% range were found for CSF and SU, respectively. The recoveries found for CHMNPs-SPE in CSF and SU were ranged between 97 - 100% and 96 - 101%, respectively. Interference tests were performed with dopamine, uric acid, creatinine and tryptophan revealed interference in the potential working window. Finally, repeatability tests were carried out with both printed electrodes, using two MNPs-SPE and two CHMNPs-SPE. An average RSD of 5.0 % and 4.4 % was obtained for each one, respectively, indicating that the proposed disposable electrodes present satisfactory signal stability and are capable of achieve good repeatability in EP sensitive quantifications.

Aknowledgements:
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Functionalisation of Graphite Electrodes towards an artificial Solid Electrolyte Interface

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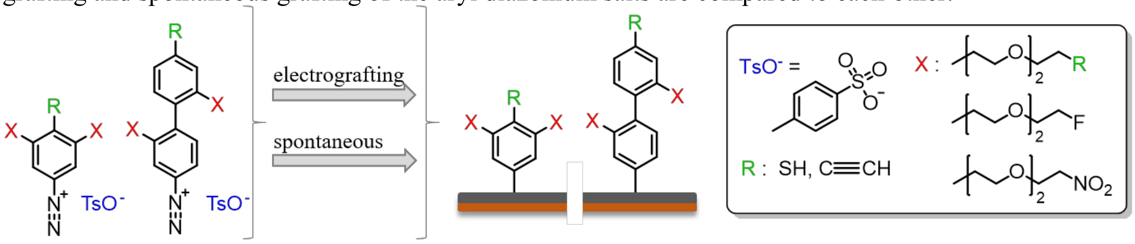
One of the main reasons for battery aging in lithium ion batteries (LIBs) is the formation of a solid electrolyte interface (SEI). SEI formation results in capacity loss and power fading due to irreversible electrochemical decomposition of electrolyte. However, the SEI protects the negative electrode from further parasitic surface reactions with the electrolyte. To avoid irreversible capacity loss due to electrolyte decomposition we aim to create an artificial SEI layer. Therefore, a sequence controlled molecular network is grafted onto the negative electrode surface.

The artificial SEI is realised on graphite electrodes which are commonly used as negative electrode material in LIBs. The graphite electrode is modified with anchor groups that feature functional groups for further layer growth via thiol-yne/ene click chemistry on the substrate. In this work we use aryl diazonium salts as anchor groups for electrode modification. The influence of different functional groups attached to the aryl diazonium salt on the electrochemical properties is investigated. Furthermore, differences between electrografting and spontaneous grafting of the aryl diazonium salts are compared to each other.



To prove the successful grafting of the aryl diazonium salts on the surface X-ray photoelectron spectroscopy (XPS) and Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is used.

Financial support of the German Research Foundation (DFG) within the project B2 of the Collaborative Research Centre (SFB 1176) is kindly acknowledged.

Amperometric Detection of H_2O_2 using Fe-N-C pyrolyzed catalysts

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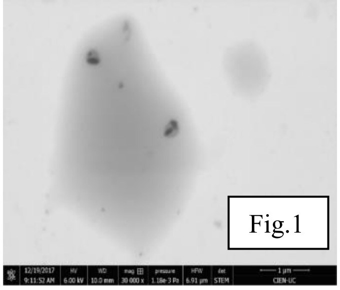
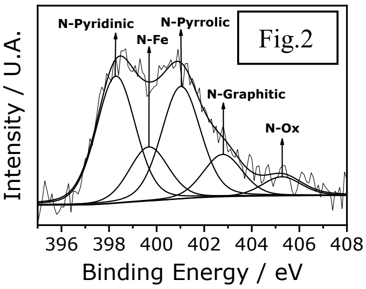
Carbon nanomaterials have been studied extensively in recent decades due to their interesting properties, such as high electrical and thermal conductivity, high mechanical stability, as well as catalyzing several chemical reactions of interest (Wang *et al*, 2005). Within this group of materials, pyrolyzed Fe-N-C catalysts have shown high activity and stability for conversion energy reaction (Masa *et al* 2016), however, there is a lack of knowledge about their use as sensor.

In the present work, the Nitrogeneous Base Adenine in the presence of different percentages of Fe were pyrolyzed, by heating the mixture at 1000 °C at N_2 atmosphere, then an acid leaching was performed, and finally a second heat treatment in a NH_3 atmosphere was carried out. The obtained material was characterized by FESEM, BET analysis, XPS and electrochemical techniques, to finally study the hydrogen peroxide reduction in neutral media using the pyrolyzed material.

The FESEM and BET analysis showed that after the first pyrolysis a mesoporous structure is obtained, with a presence of 40-50 nm metallic nanoparticles covered by a graphitic matrix (Fig. 1). The XPS showed different nitrogenous sites, which are produced in the heat treatment, it was observed a high contribution of N-pyridinic sites (34.59 %), followed by N-Pyrrolic (32.58 %) and N-Fe (15.11 %), which confirms the presence of iron in the material after the heat treatment. In lower proportion N-graphitic and N-Ox sites were detected (Fig. 2). A Fe(III)/Fe(II) faradaic process was observed using cyclic voltammetry which corroborates the XPS results. A shift towards more positive values of this process was detected with each step of the pyrolysis process. The catalysis of the H_2O_2 reduction starts with the Fe(III)/Fe(II) faradaic process potential. The highest potential was are obtained with 3.44% of initial iron load and with the NH_3 pyrolyzed material, where a higher N-doping is achieved.

At neutral pH, a high linearity and sensibility between the hydrogen peroxide and the current response was observed, even at high potentials (0.0 V vs Ag/AgCl) (Fig. 3) compared with similar materials (Xu *et al*, 2010).





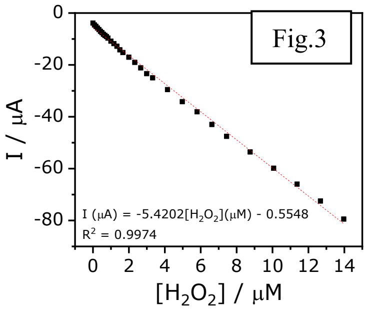


Fig. 1. FESEM obtained for Adenine with 6.88% of Fe after the heat treatment.
Fig. 2. XPS Spectra of the material with a 6.88% of Fe after the heat treatment.
Fig. 3. Calibration plot obtained for the H_2O_2 reduction using the pyrolyzed material in neutral media. E = 0.0 V vs Ag/AgCl

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Application of different cathodic modifiers in Single-Chambered Microbial Fuel Cells versus H-type Microbial Fuel Cells for wastewater treatment

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Microbial fuel cells (MFCs) are promising technologies for wastewater treatment. This study presents the operation of an air-cathode single-chambered MFC (SCMFC) in the presence and absence of a proton exchange membrane, comparing performance to conventional double-chambered (H-type) MFCs. These MFCs were operated using reinforced clostridial medium (RCM) as the anodic substrate, *Enterobacter Cloacae* as a biocatalyst, and carbon paper as the cathode and the anode.

Operational performance of SCMFCs were improved by electrode modification using carbon black at anode electrodes and carbon black/iron(II)phthalocyanine (FePc) modifiers at cathode electrodes in H-type fuel cells. To function as proton exchange membranes, modification of the cathode using either a carbon black/FePc/Nafion composite or carbon black/FePc/sulphonated-polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene composite were examined for cathode modification in membrane-less SCMFCs. The effect of electrode modification for these MFCs was investigated using cyclic voltammetry and electrochemical impedance spectroscopy and compared to the performance of the MFCs.

MFCs performance was further characterized by nutrient remediation in RCM using phenol-sulphuric acid carbohydrate and Folin-Lowry protein assays before and after operation. To visualise attachment of the bacteria and modifiers at the electrode surfaces, scanning electron microscopy (SEM) images were captured. The H-type MFCs generated high power densities compared to SCMFCs while the presence of the proton exchange composites resulted in SCMFCs producing comparable power densities to those lacking these composites.

LLZO-Polyester Based Composite Electrolytes for Solid-State Li-ion Batteries

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Due to their flammability, liquid organic electrolytes currently used in lithium-ion batteries (LIBs) exhibit potential safety issues, which render their application in high energy and power batteries problematic [1]. Garnet $Li_7La_3Zr_2O_{12}$ (LLZO) constitutes one of the most promising solid-state electrolytes for all solid-state Li-ion batteries (SSLBs). This is due to its attractive properties such as high ionic conductivity, excellent stability against Li-metal anode, negligible electronic conductivity and wide electrochemical window of operation [2]. The lack of intimate contact between the LLZO electrolyte surface and the electrodes - especially for Li-metal anodes – however results in large interfacial resistances and potential dendrite formation [3]. The poor physical contact also leads to inhomogeneous and non-optimal current distribution in the cells. These problems with interfacial contacts are mainly caused by the rigid ceramic nature of the garnet oxide, and possible presence of impurities due to LLZO instability when exposed to air and moisture [4]. To address this challenge, polymer-ceramic composites are prepared here with the aim to improve the contacts between the bulk LLZO electrolyte and the electrodes (cathode and anode) in order to reduce the interfacial resistance of the LIB cells.

Recently, polyester-based polymers such as poly(trimethylene carbonate) (PTMC) and poly(ε-caprolactone) (PCL) have shown to be superior to traditional poly(ethylene oxide) based polymer electrolytes since they have higher cation transference numbers and better ambient-temperature ionic conductivities [5,6]. Moreover, the inclusion of the trimethylene carbonate repeating units in a poly(ε-caprolactone) (PCL) host polymer results in an amorphous, mechanically stable and highly ionic conductive copolymer that can also be implemented at room temperature functional cells [6]. Therefore, polymer-ceramic composites based on PCL-PTMC copolymers and Al-doped LLZO are studied in this work, with the ambition of utilizing the advantages of the PCL-PTMC copolymer. Al-doped LLZO is used because it stabilizes the structure of LLZO and increases its conductivity [4]. This presentation will focus on the electrochemical performance and lithium-ion transport in electrolyte composites of PCL-PTMC 80:20 copolymer and Al-doped LLZO for Li-ion batteries. The electrolytes are benchmarked in LIB cells using $LiFePO_4$ (LFP) and Li-metal as cathode and anode, respectively.

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Electrocatalytic Studies of Mono- and Binuclear Copper Complexes for ORR by using Scanning Electrochemical Microscopy (SECM)

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Scanning Electrochemical Microscopy (SECM) is an effective electroanalytical tool that facilitates the fast selection of active electrocatalysts by determining the kinetics and the mechanism for a given reaction, the identification of the reaction products and the durability estimation of the catalytic material [1]. This technique has been widely used in the fast-screening of nanomaterials such as metal nanoparticles and alloys for oxygen reduction reaction (ORR) in the generation/collection mode where O_2 is electrochemically generated at the tip of an ultramicroelectrode (UME) [2-4]. However, the electrogeneration of O_2 requires high overpotentials and the metal tip can be oxidized and deposited on the substrate interfering with the analysis. In this case and for those analytes that can't be generated electrochemically, the UME is replaced by a micropipette that controls release of the analyte in the media while the surface is scanned [5].

In the present work the electrocatalytic activity of different mono- and binuclear copper complexes obtained from a series of 3,5-di-substituted-1,2,4-triazole ligands was evaluated by means of the scanning electrochemical microscopy in a new mode named "Pumped micropipette delivery – Substrate collection" (MPD-SC) which an O_2 saturated solution is injected into the supporting electrolyte through a micropipette connected to a microflow pump, so when the micropipette scans a catalytic spot where the copper complex is located, an increase in the substrate current is registered. Figure 1 shows an image of the glassy carbon substrate modified with three copper molecular catalyst supported on carbon Vulcan (1-3) and the carbon Vulcan blank (B). Through these images coupled with other analysis techniques such as the i-t curves, the catalytic activity of these copper complexes for ORR was evaluated at different applied potentials and the reaction mechanism was determined. The results were compared with conventional electrochemical techniques such as polarization curves and amperometry showing a good correlation.

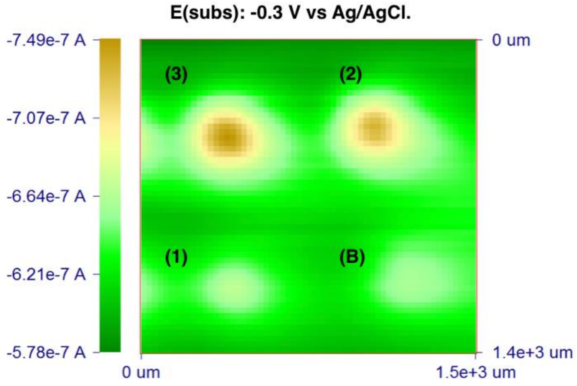

Figure 1. SECM image of glassy carbon substrate modified with three cooper complexes for ORR. Buffer Britton-Robinson, pH 5.

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Electrochemical sensor based on crown ether/polymer/carbon nanotubes composite for simultaneous determination of levodopa, uric acid and tyrosine in biological fluids

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Parkinson's disease is one of the most common neurological diseases in elderly people. In the early -60's of the last century, they found that levodopa (L-dopa) can be used for the treatment of patients with this disease [1]. Hence, a new insight is presented in the fabrication of a reliable electrochemical sensor for determination of L-dopa in presence of uric acid (UA), and tyrosine (Ty); Ty is a precursor for the biosynthesis of L-dopa; which have been considered as important biological compound in human body to diagnosis some psychiatric and neurological disorders diseases [2]. The conductive sensor is based on modifying the glassy carbon electrode with successive stacked layers, multi-walled carbon nanotubes (CNT), poly-hydroquinone (PHQ) and benzo-12-crown-4 (CE); GC/CNT/PHQ/CE. Each component possesses a unique feature that contributes to the remarkable electro-catalytic activity of the sensor. Crown ether allows excellent host-guest recognition and binding ability [3]; PHQ has high electrical conductivity and stability; and CNT has large surface area and mechanical strength. The proposed sensor was successfully applied for electro-oxidation and separation of ternary mixture of L-dopa, UA, and Ty into three well-defined peaks. The separation of these compounds in real human blood serum samples was also successful. Also, the layered sensor showed highly electro-catalytic activity for simultaneous determination of these compounds in very low concentration ranges. Moreover, anti-interference ability of the layered sensor for simultaneous determination of these compounds was successfully achieved in presence of common interfering compounds.

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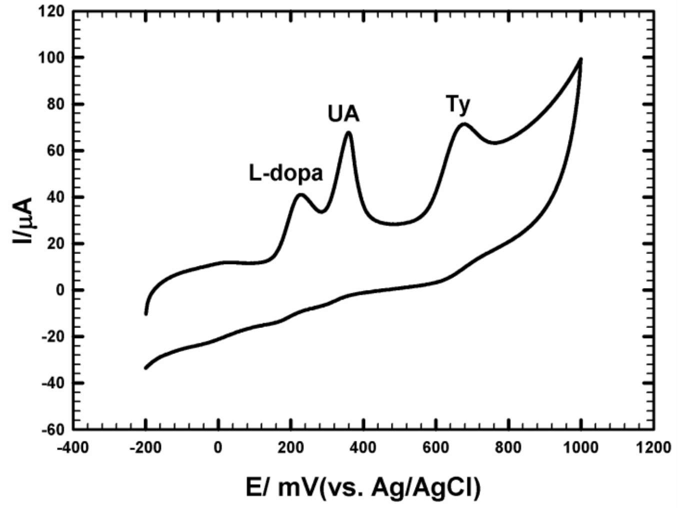

Figure: Cyclic voltammetry of a mixture of: 10 µmol L^{-1} L-Dopa, 15 µmol L^{-1} Uric acid and 50 µmol L^{-1} Tyrosine at GC/CNT/PHQ/CE electrode in phosphate buffer (pH: 7.40); Scan rate 50 mV s^{-1}.

Boron Doped Diamond Electrodes for Metal Recovery from Spoil Banks as well as for Water Treatment

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Boron doped diamond (BDD) electrodes offer, compared to conventional electrode materials, technologically important advantages as high corrosion stability and wide potential window for redox reactions. Because of their ability to produce Hydroxyl Radicals and Peroxides, BDD electrodes are a promising material for numerous applications. The DECHEMA-Forschungsinstitut (DFI) is working on different applications of BDD electrodes for more than 10 years.

We developed and patented an electrochemical method (DE102015110179B3) to dilute and recover metals, e.g. copper, zinc and nickel from spoil banks as well as from waste incineration ashes and slags. Significant improvement of the dissolution of the metals has been achieved by per-acids produced in situ from inorganic acids using BDD electrodes. The diluted metals can be recovered by electrochemical deposition at the cathode; this allows also the regeneration of the employed acid (Fig.1).

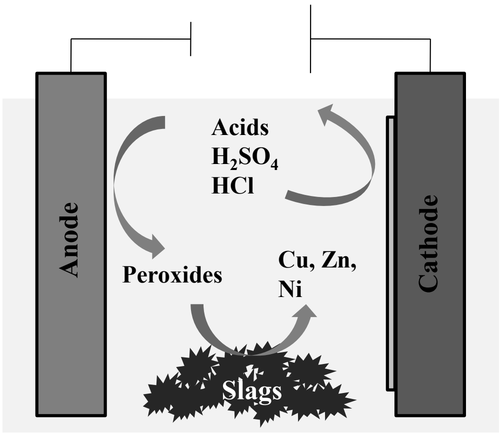

Fig.1: Scheme of electrochemical method for recovery of metals from slags

Another focus is on the application of BDD anodes for water treatment. Pharmaceuticals from surface water and water treatment plants as well as phenolic compounds from contaminated ground water have been oxidized and decomposed.

In situ X-Ray Spectroelectrochemical Investigation on a Ru-based Water Oxidation Catalyst

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In recent years, a great deal of attention has been directed towards the development of clean and sustainable energy solutions. A promising direction in this regard are photoelectrochemical cells (PECs), which can utilize solar energy to perform the water splitting reaction. In such a device, O_2 and H_2 are produced in separated compartments, which can subsequently be recombined in fuel cells to afford a green energy source.[1] To optimize the performance of PECs, efficient catalysts are needed to help overcome the half-reaction's high energetic requirements. The most difficult component to optimize is the water oxidation catalyst (WOC), due to the mechanistic complexity of the water oxidation (WO) reaction. Ever since the first discovery of a WOC,[2] Ru complexes have appeared as good candidates to perform the WO reaction.[3] Nevertheless, in spite of the abundant literature on the field, there are no clear guidelines that allow rational design of economically accessible and more efficient WOCs. In order to do so, a deep understanding of the reaction pathway is paramount and thus a profound geometric and electronic structural characterization of the intermediate species arising in the catalytic cycle is necessary.

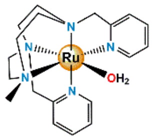

Fig. 1.Molecular structure of the WOC of interest.

To this end, an investigation of a monomeric Ru-based WOC is pursued: $[Ru(L^5)(H_2O)]^{2+}$ (Fig. 1), (where $L^5 = (CH_2Py)_2Me[9]aneN_3$).[4] Computational analysis of the catalytic cycle suggests the O-O bond formation as the rate-determining step, which occurs upon formation of the highly electrophilic $[Ru^V(L^5)(O)]^{3+}$ species. The starting compound and the intermediates species bearing Ru^{III} and Ru^{IV} metal centers have been characterized experimentally (UV-vis spectroelectrochemistry and mass spectrometry). Nevertheless, a comprehensive geometric and electronic structural characterization of these intermediate species is lacking. In this regard, X-ray spectroscopies offer a promising perspective for a detailed characterization of these different species, particularly to allow direct insights into the O-O bond activation for Ru bonded oxygen intermediates. The combination of *in situ* electrochemical measurements with X-ray spectroscopy has already shown to be useful for heterogeneous systems; yet its exploration in homogeneous conditions has so far been seldom explored.[5] The use of a custom-made *in situ* electrochemical cell allowed us to characterize the starting compound $[Ru^{II}(L^5)(H_2O)]^{2+}$ and the subsequent intermediate species that arise in the catalytic cycle in aqueous medium: $[Ru^{III}(L^5)(HO)]^{2+}$and $[Ru^{IV}(L^5)(O)]^{2+}$, by means of X-ray absorption spectroscopy. The XANES region of the spectra show broad features due to the natural broadening of the lines in a heavy atom like Ru, that provide however unique insight into the electronic structure of the species. A shift in the rising edge upon oxidation is noticeable, as a result of the increased effective charge of the photoabsorber atom. This shift reduces between the most oxidized species due to enhanced covalency effects that partially masks the charge increment in the metal. Moreover, the modelling and fits of the EXAFS region of the spectra provide the evolution of the Ru-O bond lengths throughout the catalytic cycle, showing distinctly how it shortens upon oxidation, in agreement with the DFT optimized geometries. Together, the XANES and EXAFS spectra offer a deep insight into the electronic structure of the species arising in the catalytic cycle. These experiments were likewise complemented with EPR spectra collected in an *ad hoc in situ* electrochemical cell in aqueous medium. Additional efforts focus on an unambiguous characterization of the catalytically active species $[Ru^V(L^5)(O)]^{3+}$ through *operando* EPR and X-ray spectroscopy in organic medium.

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Electroorganic Synthesis of Bio-based Carboxylic Acids

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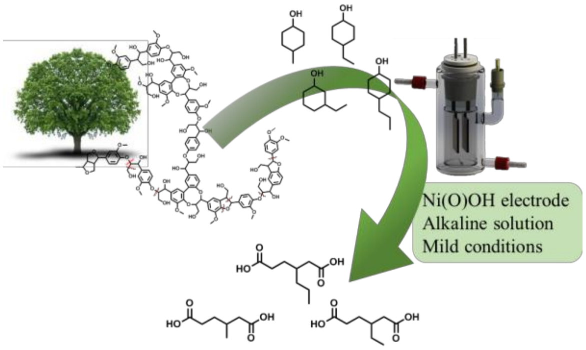
Presently, the main feedstock for organic chemicals is still provided by oil and gas. Limited fossil resources and a growing awareness for the environment require sustainable alternatives. A promising feedstock for renewable raw materials is wood, which is abundant and avoids food competition. In the pulping process of wood to cellulose, large amounts of lignin accumulate as a by-product. With the holistic use of these waste streams in mind, lignin represents a potential source for carbon building blocks [1].

Lignin can be converted into a variety of alkylated cyclohexanol derivatives via catalytic reductive fractionation. One early approach for catalytic hydrogenolysis of hardwood lignin was carried out 1938 by Adkins et al. [2]. By using copper chromite, they could obtain 4-propylcyclohexanol in 11wt% yield. This compound and other lignin-derived alkylated cyclohexanols can be oxidized subsequently to biogenic dicarboxylic acids, which are applied for example as starting materials for polyesters and -amides. For a fully sustainable process, the valorization of biomass goes hand in hand with the demand for a further green chemical method, such as electrosynthesis [3].

The oxidation of alkylated cyclohexanols to bio-based dicarboxylic acids is successfully performed by electrocatalytic conversion. To establish this transformation as a green method, we developed a simple protocol for the anodic oxidation at nickel oxidehydroxide anodes in caustic soda.



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Photovoltaic harvesters integrated with electrochemical double layer capacitors: novel approaches

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Here we present our latest works related to the integration of dye sensitized solar cells/modules (DSSCs/DSSMs) and electrochemical double layer capacitors (EDLCs).

In particular, we propose the integration of a W-type 4 serially connected DSSM and an EDLC employing N-butyl-N-methylpyrrolidiniumbis(trifluoromethanesulfonyl)imide ($Pyr_{14}TFSI$) as electrolyte. The connection of the two sections enables to obtain the highest voltage ever attained to date for a photo-capacitor [1]. The same compact harvesting and storage (HS) device structure is also obtained employing an all solid state electrolyte for the EDLC section, namely a mixture of polyethylene oxide (PEO) and $Pyr_{14}TFSI$ [2].

These two HS devices are the only examples present in literature dealing with stable and reliable high voltage (2.45 V) photo-capacitors.

Then, we propose the utilization of a novel polymer-based platform for the fabrication of an innovative self-powered device integrating energy harvesting and storage sections. The multifunctional polymeric layer, fabricated with two ethoxylated sections and a perfluorinated segment in between, acting as barrier, is obtained by oxygen-inhibited UV-light crosslinking procedure [3].

The resulting photocapacitor present a planar architecture significantly simplified if compared to other recently proposed solutions. The overall conversion and storage efficiency is 3.72%, which is a notable value for DSSC-EDLC harvesting-storage devices literature.

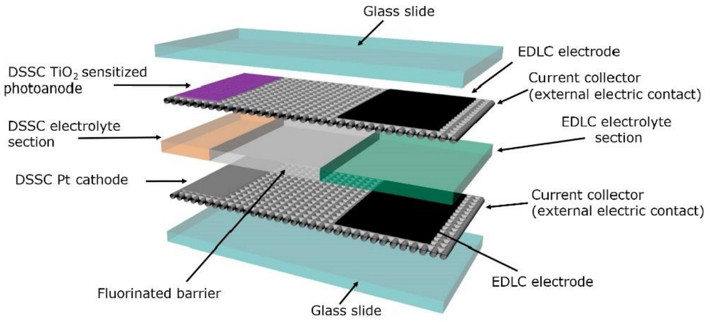

Figure 1: 3D representation of the multifunctional membrane-integrated harvesting and storage device.

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Anodic Stripping Voltammetry analysis of Lead and Cadmium in Fruit Juices using Bismuth Modified Glassy Carbon Electrode

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Key words: anodic stripping, lead, cadmium, bismuth, juices

Heavy metals occur naturally, in trace amounts they are essential for life as nutrients. However, in large amounts can be toxic. Their toxicity is complex as a result of metals potential to accumulate in organisms. Hence, presence of these materials in food and environment has resulted in serious problems on human metabolic systems, kidney failure as well as skin problems. Presence of a number of heavy metals in fruit juices has been reported. However, they are no reports on grape juices. The study focuses Pb and Cd metals in Apple and grape juices (red and white). The analyte choice was due to levels of metals found in South Africa environment as well as the metal toxicity.

The anodic stripping technique was optimized and the optimum. Optimum conditions in acetate buffer pH 4 as supporting electrolyte were a deposition potential of -1 V, deposition time of 90 s and a scan rate of 50 mV. Concentrations of Pb and Cd metals were assessed using normal calibration and a standard addition method. Standard addition method ranges were 1.40-3.40 µM for Cd, 0.70-2.60 µM for Pb while for calibration method values ranges were 2.10-3.40 µM for Cd 2.10-6.30 µM for Pb. A t-test at 95 % confidence level indicates that the methods are the same except for the determination of Pb in white grape juice. All values obtained were within the permissible limits of SA water as well as other countries limits in Juices. Therefore, it is safe to say that the South African juices analyzed do not pose any harmful hazards, hence they are safe for consumption.

Electrocatalytic Properties of Suspended Graphene Oxide in Flow

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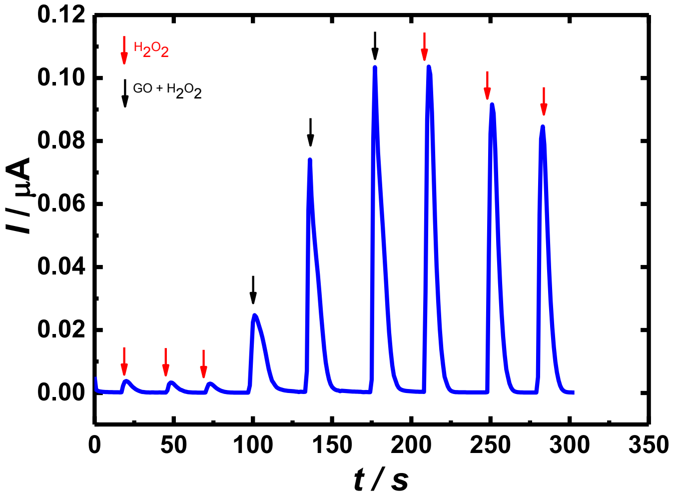
The nanoobjects have already found a numerous applications due to their unique electronic, optical, thermal, and chemical properties [1]. Not surprisingly their global production increases every year [2]. Nowadays, graphene and and related materials are one of the most popular two-dimensional nanomaterials. Their physicochemical properties are intensively studied and explored in the area of energy-storage materials, ‘paper-like’ materials, polymer composites, liquid crystal devices or electrocatalysis [3]. Recently, attention of some researchers has recently turned to the substrate used to obtain graphene, namely graphene oxide (GO) [4]. Recently we have demonstrated that it is possible to detect electrochemically GO suspended in aqueous solution [5-7].

GO is known to exhibit electrocatalytic properties together with other (nano)materials, for example nanoparticles decorated GO (2 odnosniki). Here we will present results of our research on electrocatalytic behaviour of graphene oxide (GO) in a fluidic system. We have used H_2O_2 as a substrate of electrocatalytic reaction, and we will show that presence of GO promotes electrocatalytic oxidation of H_2O_2. With flow injection system, where the samples of GO suspension and H_2O_2 solution are injected, the significant increase of anodic current at the working electrode (at 1.0 V) is observed. Such simultaneous injection results in more than one order of magnitude increase of the peak current as compared to the absence of GO. This indicates electrocatalytic H_2O_2 oxidation. The shape of the signal indicates that GO has tendency to adsorb at the ITO electrode.



One may conclude that flow analysis system will allow continuous, fast and simple graphene oxide detection in the presence of H_2O_2..

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Electrochemical Behaviour of Chalcopyrite Oxidation in Chloride Solutions

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Chalcopyrite ($CuFeS_2$) has proved to be challenging in the leaching process, mainly related to its refractory nature, slow kinetic rates of dissolution and the formation of an inhibiting product layer on its surface, during leaching. This study will focus on chalcopyrite leaching in acidic chloride system, which has been reported as a feasible alternative to conventional sulphate media in heap leaching. It is known that chalcopyrite dissolution depends strongly on the solution redox potential as well as the composition of the product layer that may form on its surface. The chloride ions in solution support the Cu(II)/Cu(I) couple as the primary oxidant, as they can form complexes with the cuprous ions formed, which increase the dissolution rate. Additionally, these ions increase the potential range where chalcopyrite can be oxidized. The behaviour of chalcopyrite using different chloride concentrations in the presence of cupric ions is characterized at different scanning rates to understand the dependence of this parameter on the potential.

Electrochemical experiments have been carried out to investigate the behaviour of mixed potential by open circuit potential (OCP) measurement for 30 minutes using sulphuric acid at 0.05 M under nitrogen. The effect of chloride was analysed at 20, 50 and 100 g/L in presence of cupric ions from 0 to 50 g/L. The potentials obtained were used to carry out potentiostatic tests for a period of 30 minutes in absence of cupric ions. The mixed potential did not show a significant difference with an increase in cupric concentrations in the absence of chloride. However, increased mixed potentials and current densities was observed at higher chloride and cupric concentrations. The potentiostatic measurements at those potentials were used to construct a voltammogram trace which was compared with the anodic polarization at 10mV/s. The scanning rate evaluated on the chalcopyrite electrode showed that a higher sweep rate (mV/s) increased the current densities with more pronounced peaks that prevent the formation of the product layer during the leaching.

Electrocatalytic Activity of Carbon Nanohorn Film Electrodes with Silane Molecules for Oxygen Reduction Reaction

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1.Iintroduction

Fuel cells and solar cells are new energy devices that have been developed to solve problems such as depletion of fossil fuels and global warming due to CO_2 generated during power generation. Although many of these devices use platinum as a catalyst, but platinum is expensive and resources are limited.

Therefore, the development of materials that replace platinum is required. Previously, we have prepared high-performance Single-Walled Carbon Nano Horn (SWCNH) film electrodes using a silane coupling agent for various electrochemical energy devices from the viewpoint of stability and catalytic activity. In this study, the application of these electrodes to catalysis for oxygen reduction reaction(ORR) is investigated[1]. In this presentation, the influence of silane molecules in the film electrode on electro catalytic acitivity for ORR reaction is discussed in more detail by the charge transfer resistance.

2. Experiment

The electrode in this study was prepared by a dropping method. At first, 0.02 wt% of surfactant (Sodium Dodecyl Benzene Sulfonate: SDBS) and 0.13 wt% of SWCNH was added to 10 mL of acetone, and it is mixed carefully by ultrasonic (30 min) and magnetic stirrings (30 min). Then, 2 wt% of each silane coupling agent was added to this solution, then the solution was mixed again by magnetic (30 min) and ultrasonic stirrings (30 min). After that, 5 µL was taken out from this solution and dropped on a glassy carbon disk electrode (electrode diameter: 3.0 mm) and dried for 24 h to produce a SWCNH film electrode. Linear sweep voltammetry (LSV) was measured in 0.1 M KOH at scanning speed of 0.01 V / sec for the catalytic activity evaluation for ORR. Electrochemical impedance spectroscopy (EIS) was measured from 10 MHz to 0.02 Hz at several potentials ±5 mV mainly for measurement of charge transfer resistance. These electrochemical measurements were carried out with three electrode cell, where working electrode is the prepared film electrode, counter electrode is Pt, and reference electrode is Ag/AgCl.

3. Results and discussion

Fig.1 shows the representative LSV of the electrode prepared with silane coupling agents of different functional groups. After the repeated experiments, the SWCNH film with triethoxymethylsilane (Methyl) is revealed to be the most active, i.e., large peak current density and noble onset potential. Moreover, EIS analysis revealed that the charge transfer resistance is the smallest as compared with other systems. Detail discussion will be in the presentation.

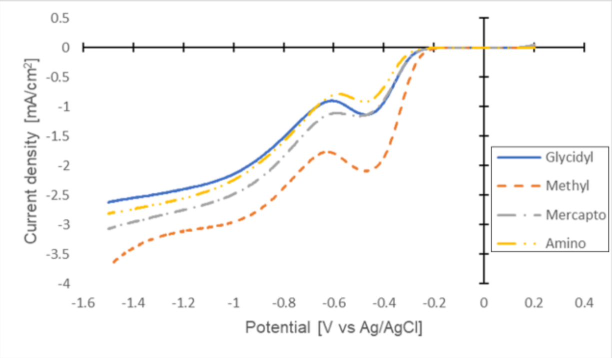

Fig.1 Linear sweep voltammograms of the SWCNH film electrodes with different silane molecules. (Electrolyte: 0.1 M KOH, Scanning speed: 0.01 V / sec, Rotation speed: 1600 rpm, Electrode: SWCNH film electrode.)

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Electrochemical performance metrics of a mixed-assembly activated carbon-based capacitor

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In this study, the electrochemical performance of a mixed assembly device based on porous activated carbon from different sources is investigated. The device was designed from activated carbon (AC) prepared from biomass and polymer material. These ACs materials were obtained using an environmentally friendly, mild-alkaline potassium based activating agents (AAs). The fabricated mixed-assembly device had an extended operating potential window of 1.70 V, exhibiting a relatively remarkable stability after 10 000 constant galvanostatic cycles. An 82% capacitance retention and 100% coulombic efficiency were recorded for the mixed device. The device showcased an improvement in specific capacitance after being subjected to a voltage holding ageing test for 80 hours (capacitance increase from 94.4 $F \cdot g^{-1}$ to 219.5 $F \cdot g^{-1}$). From these results, it is clearly demonstrated that the mixed-assembly device displayed relatively better stability metrics and better energy storage capabilities as compared to the symmetric devices assembled with electrodes adopted the individual AC materials.

This provides a pathway into designing hybrid electric double layer capacitors where the unique materials properties from each carbon-based material can be fully harnessed into one operating system.

Rotating Disc Electrode vs. Electrochemical Flow Cell – New Pathways for Electrocatalyst Characterization

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The rotating disc electrode (RDE) is a widespread and useful technique in electrocatalysis research[1]. However, the RDE technique is restricted to circular-geometry and certain techniques to prepare catalyst samples on electrode tips, usually made of Pt, Au or glassy carbon. Therefore, evaluation of electrocatalysts prepared on different deposition substrates, with diverse synthesis techniques, under various conditions, requires a more flexible alternative. An electrochemical flow cell (EFC) introduces new possibilities compared to the RDE, where instead of rotating the electrode, the electrolyte flows over the electrode. Different flow cell configurations are in use in the state-of-the-art electrocatalysis research, including high throughput analysis and spectro-electrochemistry. However, an EFC is a non-standard setup, developed in individual labs for desired reactions with different configurations and sizes.[2]

Here, we compared the RDE technique with two rationally designed EFCs for the oxygen evolution reaction (OER). For a proof of concept, we compare the EFC designs with a standard RDE setup on commercial catalysts. By combining the EFC with an Inductive Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) setup, we additionally prove the ability to analyze and quantify electrode corrosion and electrolyte impurities. The results shed light on to a new pathway to analyze novel electrocatalysts with a higher degree of experimental freedom and the possibility to combine spectroscopy as well as other physical/chemical methods with electrochemistry.

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Electro-reduction of Nitrobenzene to Aniline Over Pt Catalyst: Density Functional Theory Studies

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Aniline ($C_6H_5NH_2$) plays significant roles in industry and daily life and is synthesized via the catalytic hydrogenation of nitrobenzene ($C_6H_5NO_2$) over transition metals; however, the investigations of reaction mechanism in heterogeneous catalysis are still lacking. In this work, we calculated the nitrobenzene reduction reaction over the Pt(111) model catalyst using density functional theory (DFT) for fundamentally understanding the mechanism at atomic and molecular levels. It was found that the double H-induced dissociation of N-O bond is the preferential path for the activation of nitro group with a much lower reaction barrier than the direct dissociation and single H-induced dissociation paths. The overall mechanism identified is: $C_6H_5NO_2^* \rightarrow C_6H_5NOOH^* \rightarrow C_6H_5N(OH)_2^* \rightarrow C_6H_5NOH^* \rightarrow C_6H_5NHOH^* \rightarrow C_6H_5NH^* \rightarrow C_6H_5NH_2^*$. The overall barrier of the nitro group reduction was calculated to be 0.75 eV, which is much lower than the barrier of the benzene reduction (1.08 eV). Our DFT data elucidates clearly why the major product of nitrobenzene reduction reaction is aniline. Furthermore, the adsorption/desorption of phenyl group was found to have significant impacts on kinetic barriers. Generally, in the hydrogenation process (N-H or O-H bond), the phenyl group prefers to adsorb on surface, but in the dissociation process (N-O bond) it prefers to desorb transiently at the transition state and adsorb again when the dissociation is completed. This work also provides a solid theoretical insight into the selective catalysis towards the large aromatic compounds.

Electrochemical detection of Pb (II) at PAN/Ag Modified Au Electrode

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Abstract

Silver nanoparticles (AgNPs) have received significant interest worldwide due to their antibacterial, stability, and tumour inactivation property. The recent study will report on a cheap and pollution free green method used for fabrication of silver nanoparticle derived from sweet orange (Citrus Sinensis) peel extracts. The green mediated nanoparticle was functionalized with polyacrylonitrile in order to synthesize stabilized PAN/Ag nanofibers by electrospinning. Furthermore, characterization of the nanocomposites was archived by using spectroscopic, electrochemical, and other techniques such as fourier transform infrared (FT-IR) spectroscopy, ultraviolet-visible (Uv-Vis) spectroscopy, x-ray diffraction (XRD) spectroscopy, scanning electron microscopy (SEM), EDX, and transmission electron microscope TEM were used to characterize the synthesized Ag nanoparticles and PAN/Ag nanofibers. Moreover, thermal stability of the nanostructures was investigated through thermogravimetric analysis. Electrochemical characterization investigated using cyclic voltammetry in 0.1 M Ferricyanide buffer, reveals that PAN/Ag modified Au electrode gave a higher anodic and cathodic current response as compared to the bare Au working electrode. Electrocatalysis studies in 0.1 mM Pb (II) solution in all the modified electrodes bare Au, Au/PAN, and Au/PAN-Ag reveals that electrode with PAN-Ag gave a very high anodic current of about 3 times greater than the bare, Au and PAN modified Au electrode as shown in Figure 1.

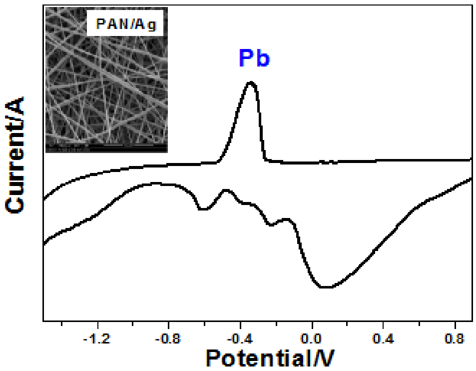

Figure 1: Cyclic Voltammetry of 0.1 mM Pb (II) at PAN/Ag modified Au electrode

Results showed that the nanocomposite can be used for concentration detection of Pb at pH buffer 3 by using square wave voltammetry. Further studies will be conducted on the reproducibility, stability and interference properties of the modified electrode.

Effects of Deposition and Annealing Conditions on Properties of Thermochromic VO_2 Films

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Abstract

Vanadium dioxide films were prepared on soda lime glass substrate at room temperature using DC magnetron sputtering of vanadium target in argon atmosphere. The working pressure and argon flow rate was $5.2 - 5.6\,x\,10^{-3}$ mbar and 76 ml/min, respectively. The films were thereafter annealed in low vacuum environment at different temperatures. The XRD results confirmed that all films annealed at different temperatures and time were VO_2 except for films annealed at a temperature of 300 ^oC. The average grain size as determined by AFM was found to increase from 374 nm^2 to 1107 nm^2 and 290 nm^2 to 548 nm^2 with an increase in annealing temperature and time, respectively. Four point probe indicated that films obtained after annealing had resistivity change between the semiconducting to metallic phases of one order of magnitude. The transition temperature was estimated to be between $\sim$ 58 ^oC to 63 ^oC. Hall Effect measurements showed that films conductivity and carrier concentration were decreasing with increasing annealing temperature and time consisted with formation of semiconducting VO_2 films as confirmed by XRD results. The highest peak transmittance of the annealed VO_2 films was 53% at 2500 nm for film thickness of 44 nm. Film with thickness of 44 nm and annealed at 400 ^oC showed best optical switching of about 18% evaluated at 2500 nm, from 53% transmittance for semiconducting phase VO_2 at room temperature to 12% transmittance for metallic phase VO_2 at 100 ^oC sample temperature.

Synthesis and fabrication of Lithium–Ion Battery Anode via a Novel Graphene-Based Carbon nanofibre Material

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ABSTRACT

Efficient and cost-effective energy storage is essential for universal adoption of alternatives to the current fossil fuels. Lithium-ion batteries are a promising technology for energy storage, and future development of sustainable cathode is critical to developing Li-ion batteries. This research has successfully explored the advantage wrapping-up graphene oxide sheet large specific surface area to form a new sample with nanofibres morphology via a force-driven reflux technique, thereby creating channels for more directional Li-ions diffusion in battery technology. The assembled anode material displays an excellent cycling stability with good capacity retention over 100 cycles within an operating voltage of 0V to 3V. The graphene-based nanofibre material could deliver a significant performance that is comparable to some polymer-based electrodes in the literature. The nanostructure material has provided adequate electrode-electrolyte contact with short lithium ion diffusion distance comparing with some other nanostructures.

Inhibition Potentials of Acridine-based Thiosemicarbazones for Mild Steel Corrosion in Acidic Medium: Experimental and Theoretical Studies

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Mild steel remains in high industrial demand owing to its superior mechanical properties and low cost as compared to other metals of industrial interest [1]. However, the persistent problem of susceptibility when mild steels are exposed to acidic environment is a subject of concern to both the academia and industries [2, 3]. The application of corrosion inhibitors has been found to be a practical, effective and cheap means of mitigating corrosion among other corrosion control methodologies [4]. The search for green corrosion inhibitors in acidic media has led to exploiting acridines as corrosion inhibitors.

This present study reports the inhibition effect of two newly synthesized acridine-based thiosemicarbazones, 2,2'-((1E,8E)-3,3,6,6-tetramethyl-9-(p-tolyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-diylidene)bis(N-phenylhydrazine-1-carbothioamide) (IAM-NP) and 2,2'-((1E,8E)-9-(3-hydroxyphenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-diylidene)bis(N-(2-fluorophenyl)hydrazine-1-carbothioamide) (IAH-NF) as inhibitors of mild steel corrosion in 1 M HCl at 298 K using electrochemical, quantum chemical and surface morphology techniques. The synthesized acridines were tested for mild steel corrosion using open circuit potential (OCP), potentiodynamic polarization (PDP), and electrochemical impedance spectroscopy (EIS) measurements. The morphology of the tested mild steel samples were examined in the presence and absence of the studied inhibitors using scanning electron microscopy (SEM). Quantum chemical calculations were employed to elucidate the structural and electronic parameters of the studied compounds.

The results obtained from electrochemical studies showed that the acridine-based compounds retarded mild steel corrosion in 1 M HCl solution. PDP results revealed that the acridine-based compounds inhibited corrosion at both the anodic and cathodic branches, thus acting as mixed-type inhibitors. EIS results suggested that the corrosion reaction is controlled by a charge transfer process. The mode of adsorption of the inhibitors follows the Langmuir adsorption isotherm. SEM analysis confirmed the formation of a protective film on the mild steel sample. Theoretical studies provided good insight about the adsorption and the inhibition mechanism of the inhibitors. The results obtained from the different techniques are in good agreement.

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Optimization of Bismuth Vanadate Layers Synthesis for CO_2 Reduction by Photocatalysis

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CO_2 reduction is an interesting route for renewable fuel obtaining, such as formic acid, methanol or ethanol [1]. The chemical recycling of carbon dioxide has another beneficial effect: minimizing the harmful environmental effect of excess CO_2 in the atmosphere [1]. Bismuth vanadate ($BiVO_4$) layers were described as a highly efficient and durable CO_2 photocatalyst for methanol production [2]. However, few papers describe the photo and photoelectro behavior for CO_2 reduction reaction (CO_2RR). In this study the synthesis of $BiVO_4$ laminar was optimized by a factorial experimental design, where the variables time and temperature were evaluated. In this procedure $BiCl_3$, CTAB and Na_3VO_4 were added to ethylene glycol. The synthesis was assisted by microwave system (Anton-Paar®). Experimental conditions and named samples are presented at Table 1. For the photocatalysis and photoelectrocatalysis the used conditions were similar to the literature [2], with 0.3 $g_{catalyst}$ for 220 mL of 0.1 mol L^{-1} $NaHCO_3$ (pH 8.0). The detection and quantification of methanol, ethanol and acetone products was performed by GC-FID chromatography [3]. The laminar structure was obtained for all synthesis condition, as seen at Fig.1a, which shows the scanning electron microscopye (SEM) for sample 5. All $BiVO_4$ obtained lead to methanol production and the results from photocatalysis is observed at Fig. 1b. The best condition was the material synthetized at 160 °C and 15 min of reaction. The production of methanol. For this condition, the methanol production raised until 120 min and decreased at the following reaction period. Probably the produced methanol could have been oxidized at holes at the catalysts or continued to react, resulting in by-product formation [3]. Differences of methanol amount seen at Fig.1b are probably related to the crystallographic patterns of the material. The presence of Bi_2O_3 or another $BiVO_4$ crystallographic phase could be affecting the efficiency of the material. The local environment around the Bi^{3+} can promote a more stable anchorage of CO_3^{2-} to the Bi^{3+} sites on the surface, through a weak Bi--O bond, so that they can efficiently receive the photogenerated electrons from the V 3d-block bands of $BiVO_4$ [4]. The presence of different species, besides presenting the same catalyst morphology, affect the $BiVO_4$ for CO_2 reduction reaction.

Table 1. Experimental condition of $BiVO_4$ lamellar synthesis.

Sample	Temp. / °C	Time / min
1	120	5
2	160	5
3	120	15
4	160	15
5	140	10
6	140	10

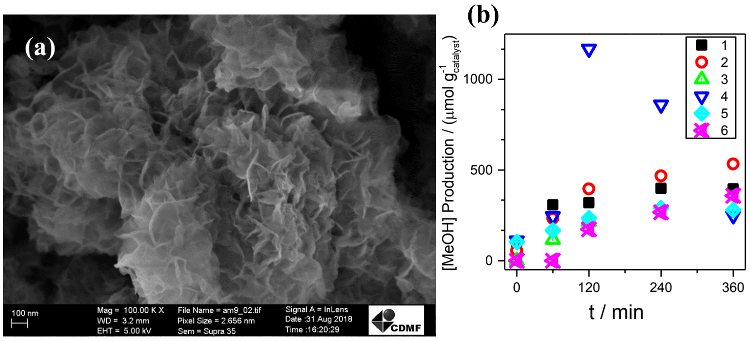

Figure 1. (a) SEM of sample 5. (b) Methanol production for $BiVO_4$ obtained materials, at 0.1 mol L^{-1} $NaHCO_3$ (pH= 8.0), and 5 °C.

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Optimization of aptamer immobilization parameters to improve sensitivity of impedimetric histamine aptasensor

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Different technological systems have been employed to quantitatively monitor histamine due to its negative effect on both food quality and human health.[1] Direct detection of histamine in foodstuff is difficult to establish due to presence of interfering biogenic amines compounds.[2] Thus, a quantitative technique that can improve the sensitivity and specificity of detecting histamine in suitable matrices is essential.

This research group has previously developed aptamers that binds specifically to histamine, through systematic evolution of ligands by exponential enrichment (SELEX) and generated an aptamer-based impedimetric biosensor using these. In order to improve the sensitivity of those early prototype aptasensors, different immobilization techniques of aptamers on the tranducing element were investigated.

This work shows a variety of immobilization methods trialed and their effect on the resultant sensor's capability to detect histamine. Changes in the aptasensor response was observed by monitoring the change in the modelled charge transfer resistance (R_{ct}) using Electrochemical Impedance Spectroscopy in the presence of 10 mM $[Fe(CN_6)^{-3/-4}$.

The H47 aptamer showed more sensitivity towards the detection of histamine as compared to other aptamers tested. Co-immobilization of 5'- thiolated H47 aptamer and mercaptohexanol (MCH) in a 1:1 ratio produced a sensor with extremely favorable sensor kinetics. Experiments were also conducted using QCM-D modelling in order to investigate fabrication of this aptasensor on gold electrode and subsequent changes to the film upon proximity with histamine.

Modelling the sensors' impedimetric responses using a Langmuir adsorption isotherm, a K_M^{app} of 3.78 ± 1.43 µM and a maximal response (ΔR_{ct}) of 5.25 ± 0.31 kΩ was observed, a detection range appropriate for histamine detection in many foodstuff products.[3] The response of the sensor to histidine as a control molecule showed negligible interaction. Analysis of the aptasensors' ability to detect histamine in diluted red wine matrices showed that 40 µM histamine was detectable at a ratio of 1:100 (wine:PBS).

In conclusion, sequential improvements in sensor assembly allowed the resultant H47 aptasensor to achieve a suitably sensitive detection of histamine in both buffer and complex matrices.

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Towards the mechanism of the solution mediated ORR by benzoquinones in metal-O_2 batteries

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Due to its theoretical high specific energy Li-O_2 systems have generated much interest within the electrochemical community [1]. One of the bottlenecks in Li-O_2 batteries is the film like growth of Li_2O_2 on the electrode surface during discharge leading to early cell death [2]. To tackle this problem Bruce and coworkers introduced 2,5-Di-*tert*-1,4-benzoquinone DBBQ as a redox mediator which leads to a particle like growth of Li_2O_2 and therefore enhances the discharge capacity of the Li-O_2 cell [3]. In the last years, much effort has been devoted to understand the solvent properties and electrode material impact in Li-O_2 cells without a redox mediator (also by ourselves [4-7]). At this point only very little is known about the mechanism of O_2 reducing redox mediators.

Therefore, in this study we focused our research on the mechanism of redox mediation in the ORR. It is known that benzoquinones are prone to undergo in their reduced form ion-pairing with the cations of the supporting electrolyte. This ion pairing is affecting the reduction potential of the benzoquinone. We investigated Li^+, K^+, TBA^+, Mg^{2+} and Ca^{2+} as cations in TEGDME and DMSO as solvent. There we found out that there is a direct correlation between the ORR activity of DBBQ and the ion pairing of DBBQ with the cation of the supporting electrolyte: Only if DBBQ is strongly associated with the cations of the electrolyte it will reduce oxygen in the electrolyte. We are the first to show that DBBQ is also working as ORR mediator in Mg^{2+} and Ca^{2+} containing electrolyte. There DBBQ is shifting the ORR potential 260 mV and 360 mV positive, respectively. Increasing the Li^+ concentration in the electrolyte also shifts the ORR potential to more positive electrode potentials. In addition to DBBQ, other benzoquinone derivatives were also tested for their ORR activity. As experimental techniques, we are using Differential Electrochemical Mass Spectrometry (DEMS) and Rotating Ring Disc Electrode (RRDE). Moreover, we are describing a new experimental approach to investigate the kinetics of the homogenous ORR via time resolved mass spectrometry. We will describe the new experimental approach by discussing the time dependent concentration profiles in the cell, derived for finite-difference simulations.

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Bi Electrodeposition on WO_3 Photoanode to Improve the Photoactivity of the $WO_3/BiVO_4$ Heterostructure to Water Splitting.

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The most common photoelectrochemical (PEC) systems to generation of solar fuels are the photocatalytic water splitting and carbon dioxide reduction [1]. For the photocatalytic water splitting, the PEC devices are usually nanostructured semiconductors, which by absorbing sunlight promote the generation of electron-hole pairs, which provides the separation of water into hydrogen fuel and oxygen [2]. Thereby, the energy of sunlight is stored in the hydrogen molecule, which can be introduced in a hydrogen based economy [2]. However, the energy solar-to-hydrogen conversion efficiency (STH) is actually low due to charge recombination at semiconductor of PEC device. The strategies to suppression of charge recombination are the use of heterojunctions and the catalysts deposition on semiconductor surface [3]. Here was used electrochemical deposition of Bi on a WO_3 photoanode to produce better $WO_3/BiVO_4$ heterojunction (obtained after heat treatment with NH_4VO_3) and decreases the charge recombination. The WO_3 was deposited by spray on FTO substrate using a $(NH_4)_{10}H_2(W_2O_7)_6$ 0,002 mol L^{-1} dissolved in a mixture of ethileneglycol:H_2O (1:1 – V:V). To spray deposition were kept 1 s of time of spray, 1.5 mL min^{-1} of solution flow and 20 L min^{-1} of air flow while the substrate was kept at 90 ºC (repeated 40 times at intervals of 60 s to each other). Following, the photoanodes with WO_3 was heat treated at 500 ºC for 5 hours. Next, it was electrodeposited Bi on the WO_3 film applying −1.8 V *vs* Ag/AgCl until obtaining a charge density of −50 mC cm^{-2} using 0.02 mol L^{-1} $Bi(NO_3)_3$ + 0.1 mol L^{-1} $NaClO_4$ dissolved in PEG-300, under magnetic stirring (repeated 10 times at intervals of 60 s to each other). The conversion of Bi to $BiVO_4$ was carried out by dropping 50 μL cm^{-2} of 0.2 mol L^{-1} NH_4VO_3 solution on Bi film, which was heat at 500 ºC for 2 hours. The excess of V_2O_5 was dissolved in 1.0 mol L^{-1} NaOH solution. Finally, the co-catalyst CoPi was electrodeposited on $WO_3/BiVO_4$ applying 1.24 V *vs* Ag/AgCl for 60 s using Na_2HPO_4 0.1 mol L^{-1} pH 7 containing 0.5 mmol L^{-1} $Co(NO_3)_2$ (repeated 10 times at intervals of 60 s to each other). The optical characterization shows an indirect band gap of 2.78 eV to WO_3 film and a direct band gap of 2.45 eV to $BiVO_4$. The crystalline structures were evaluated with X-ray diffractometry and were observed diffraction peaks concerning to phases triclinic WO_3 and monoclinic $BiVO_4$. The photoelectrochemical water splitting was performed in 0.1 mol L^{-1} Na_2HPO_4 + 0.5 mol L^{-1} Na_2SO_4 under solar simulated irradiation (Xenon lamp with AM1.5G filter and 100 mW cm^{-2} of irradiation). The pristine photoanodes of WO_3 and $BiVO_4$ containing the co-catalyst CoPi present photocurrents of 10 and 115 μA cm^{-2}, respectively, at 1.23 V *vs* RHE. Notwithstanding, the heterojunction $WO_3/BiVO_4$ obtained with only 10 steps of Bi deposition present the higher photocurrent 2290 μA cm^{-2} (20 times higher than pristine $BiVO_4$ photoanode). The investigation of $BiVO_4$ thickness was evaluated before and after the electrodeposition of CoPi and, interestingly, the photocurrents for water splitting are higher before the CoPi deposition. The ineffectiveness of CoPi in the water splitting could be due to the thick of the co-catalysts layer or the irrelevance of the CoPi because de charge transport is already efficient. Anyway, the higher photocurrent obtained by the heterojunction shows the effective production of heterostructure using low cost techniques based on spray deposition, electrodeposition and heat treatment. Now, this approach could be used to produce photoanodes with high active area, which definitely would increase the photocurrent of the device.

Acknowledgments

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Investigation of charge storage mechanisms in hybrid materials and novel electrolytes for next-generation supercapacitors

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Several approaches have been suggested to increase the energy density of supercapacitors to make them more viable in different applications while maintaining a high-power performance. The most common strategies can be divided into three categories: **(I)** High-voltage electrolytes to widen the potential window and thereby increasing the energy content. **(II)** Adding electrochemically active materials, such as different oxides, to add a faradic contribution to the capacity in addition to the double layer, relying mostly on surface reactions to ensure a good high-power performance. **(III)** Using a battery type electrode on either the anode or the cathode side and a supercapacitor material in the other, creating real battery/supercapacitor hybrids. The two first approaches have been thoroughly investigated separately but very little has been done when it comes to combining the three concepts. In fact, around 85% of all publications on supercapacitors use traditional aqueous electrolytes[1].

The focus of our work lies in the combination of high-voltage electrolytes and high-capacity electrodes, both faradic and battery type electrodes. With the aim to improve both energy density and safety we investigate the applicability of ionic liquid-based electrolytes and highly-concentrated aqueous electrolytes. Understanding the mechanisms of the interaction between the electrode and electrolyte is essential to ultimately maximize the energy density at a high-power out take. Furthermore, next-generation electrolytes and electrodes should have other advantages such as low (or no) flammability, low vapor pressure and generally be more environmentally benign. To facilitate the transition to these new devices the following issues have been investigated: How does high-capacity faradaic electrodes interact with non-aqueous or highly concentrated electrolytes? How is the current response and rate capability of different electrodes affected by the functional groups of the ions in the ionic liquid nature of the highly-concentrated electrolyte?

In this contribution we present results from studies using ionic liquids chosen systematically to probe individual properties and how they affect the electrode interaction. We show that proton donating ability is of importance in order to improve the capacity of metal-oxide based electrodes, but the low conductivity limits the high-power performance at room temperature. Both electrochemical and spectroscopy techniques are used to investigate the reactions and structures in the electrolyte during in-situ cycling and ex-situ analysis of the electrode.

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Electrochemical Reduction of CO_2 Based on Nanocomposite Catalysts

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The increase of CO_2 concentration has become one of the most urgent environmental problems in the world. Capturing, storing and transforming CO_2 into clean energy can not only reduce the environmental problems, but also alleviate the energy crisis[1,2]. Electrochemical reduction is one of efficient methods for CO_2 utilization and recycling, which may be carried out at moderate temperature and atmospheric pressure. It also shows relatively high product selectivity compared with other reduction methods, such as chemical and thermochemical methods. However, the high over-potential for the electroreduction of CO_2 is the critical bottleneck and the main conversion products are CO, CH_4, HCOOH, and C1-related chemicals, but few C2-related chemicals or polycarbons. Herein, we reported several electrocatalysts based on cobalt nanocomposites prepared by hydrothermal method. These catalysts show good catalytic performance in CO_2 reduction reaction, where ethanol is the only liquid production after long time reduction reaction. The faradic efficiency was calculated, and the possible catalytic mechanism on the interface of catalysts. Furthermore, it is the first time at present to combine copper with cobalt catalysts, two widely used electrocatalytic materials, which reach the highest faradic efficiency of 70%. The composite metals indeed play a good synergistic role and are excellent in both morphology and catalytic performance.

Acknowledgments: The work was supported by the National Natural Science Foundation of China (Nos. 21576138, 51572127), China-Israel Cooperative Program (S2016G5243), and the program for Science and Technology Innovative Research Team in Universities of Jiangsu Province, China

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Hierarchically Structured Bimetallic Phosphate Electrodes for Supercapacitors

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With the initiation of electric vehicles and portable electronic devices, human demand for energy has continued to increase. Although there are different types of energy sources that could be explored to power these devices, the renewable sources (such as wind and solar) have been proposed as best option to use due to the low or zero gas emission rate. However, as a result of the intermittent nature of green energy sources, successful exploitation requires reliable and efficient electrical energy storage systems.

Bimetallic sodium-nickel phosphate/graphene foam composite ($NaNi_4(PO_4)_3$/GF) was successfully synthesized using a direct and simple precipitation method. The hierarchically structured composite material was studied to demonstrate a synergistic of conductive Ni cation in sodium analogue in composite of conductive graphene foam. It was noticed that the graphene served as a base for the $NaNi_4(PO_4)_3$ particles to grow, resulting in highly conductive composite material as compared to the pristine material. The $NaNi_4(PO_4)_3$/GF composite electrode measured in a 3-electrode system achieved a maximum specific capacity of 63.3 mAh g^{-1} at a specific current of 1 A g^{-1}, and a wide potential range of 0.0−1.0V using 2 M $NaNO_3$ aqueous electrolyte. A designed and hybrid device based on the $NaNi_4(PO_4)_3$/GF composite as positive electrode and an activated carbon (AC) as negative electrode could operate well in an extended cell potential of 2.0 V. As an assessment, the hybrid $NaNi_4(PO_4)_3$/GF//AC device showed the highest energy and power densities of 19.5 Wh kg^{-1} and 570 W kg^{-1} ,respectively at a specific current of 0.5A g^{-1}, which are in the same order and even better than some recent similar studies in the literature.

Improving Cathode Morphology at Tschudi Copper Mine (Namibia) by Optimising Magnafloc 333 and Chloride Concentrations

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The aim of this work was to improve the copper cathode morphology at Tschudi Copper Mine by optimizing Magnafloc 333 and chloride concentrations. Magnafloc 333 and chloride are added in the electrowinning circuit to improve the quality of cathodes produced. Magnafloc 333 is a non-ionic polyacrylamide which promotes the plating of smooth, dense copper deposits with minimal impurities (Davenport et al, 2002). Chloride is added to promote the growth of dense, fine-grained, low impurity copper deposits on the cathode. During this study a Hull cell was used to determine the optimum concentrations of Magnafloc 333 and chloride. Optimum Magnafloc 333 and chloride concentrations were found to be 10ppm and 25ppm respectively. These concentrations were then used to plate laboratory scale copper cathodes from synthetic- as well as plant electrolyte solutions. Scanning electron microscopy was used to analyse the morphology of the cathodes plated. SEM images revealed that at concentrations such as 10ppm Magnafloc 333 and 30ppm chloride, spherical nodules are observed, while at concentrations such as 25ppm chloride and 10ppm Magnafloc 333, polyhedral deposits are observed. Polyhedral deposits are associated with high quality, smooth plated cathodes.

Electro-oxidation of caffeine and acetaminophen at glassy carbon electrode modified with a sp^3-sp^2 hybrid carbon nanomaterial

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Caffeine is a psychoactive alkaloid found in many substances of plant origin. Owing to its stimulating effect on the central nervous system, it is an important ingredient in some beverages including energy drinks. Consumption of high dosage of caffeine, however, presents health risks such as insomnia, cardiovascular diseases etc. Quantification of caffeine therefore has analytical and clinical significance. In this work, electrochemical detection and quantification of caffeine in standard and real samples were carried out at a nanodiamond-graphene modified glassy carbon electrode (NDG-GCE) using square wave voltammetry. The electrochemical properties of the nanocomposite obtained from cyclic voltammetry and electrochemical impedance spectroscopy revealed that it possesses advantages over the bare, graphene- and nanodiamond- modified GCE for electroanalyis. Well defined and reproducible oxidation peaks were obtained for the analyte on the modified electrode. And the peak current varies linearly with the analyte concentration over the range 10 - 100 µM with excellent correlation coefficient. The effects of supporting electrolyte and pH on the voltammetric response of caffeine were investigated. Simultaneous determination of caffeine and acetaminophen was achieved on the sensor and it was utilised for their analyses in a locally available energy drink and a pharmaceutical sample.

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Metallophthalocyanine-catalysed Electrochemical Advanced Oxidation Processes for cost-effective destruction of Endocrine-Disrupting Compounds

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Advanced Oxidation Processes (AOPs) – the *in-situ* production of oxidizing chemical species – have become increasingly applied and researched as a means of treating non-biodegradable compounds [1]. To date, however, the relatively high operating cost of treating wastewaters using electrochemically-assisted AOPs have limited their widespread application.

Here, we collate and present our research group's investigations into leveraging existing technology to produce cost-effective wastewater remediation solutions, focusing on the degradation of endocrine-disrupting compounds. Our investigated processes made extensive use of hydrogen peroxide (H_2O_2) as an oxidant to initiate radical production.

Using the endocrine-disrupting compound bisphenol A as a model pollutant, we identified that unsubstituted metallophthalocyanine compounds (notably, iron(II)phthalocyanine and manganese(II)phthalocyanine) can act as suitable advanced oxidation catalysts [2]. Selection of these catalysts allowed extremely efficient advanced oxidation processes to occur: the degradation of various endocrine-disrupting pollutants (bisphenol A, estradiol, estrone, coumestrol) could proceed using lowered concentrations of H_2O_2 (under some conditions, sub-mM concentrations) and µM of the catalyst [3], compared to other AOP processes reported in recent literature.

Additional research validates the use of low-cost carbon fiber electrodes as suitable, scalable, supports for the attachment of cobalt(II)phthalocyanine. Cobalt(II)phthalocyanine catalysed the two-electron reduction of dissolved oxygen to form H_2O_2 in aqueous electrolyte. Dispersed across the carbon fibres, this reaction proceeded at a low overpotential (approximately -0.50 V vs. Ag|AgCl) and at sufficient rates to generate > 100 µM of H_2O_2 within 60 minutes of applying a potential of -0.55 V vs. Ag|AgCl.

This study both showcases the versatility of metallophthalocyanines as catalysts within wastewater treatment and makes several strides towards lowering the operating costs of electrochemically-assisted AOPs. The selection of cost-effective organic catalysts and carbon electrode supports, as well as the lowered overpotential (and associated energy costs) and increased AOP reaction efficiency moves this technology closer to widespread application.

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Initial Stages of Metal Electrodeposition on Single Crystal Electrodes from Ionic Liquids with Dicyanamide Anion.

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Air- and water-stable room-temperature ionic liquids (ILs) are an excellent alternative medium for electrodeposition of metals, alloys, and semiconductor materials [1]. They offer great opportunities for improvement of electrodeposition processes that are inefficient or difficult to realize in aqueous solutions or solutions based on organic solvents. ILs possess good intrinsic ionic conductivity, nonvolatility, high thermal stability, and a wide electrochemical window. These features caused vast interest in studying ILs as deposition electrolytes [2], but the fundamental understanding of the electrodeposition processes in ILs is only at a preliminary stage [3]. Here, we focus on the study of initial stages of metallic chromium and copper electrodeposition on Pt and Au single crystal surfaces in ILs with dicyanamide anion. For this study we employed conventional electrochemical techniques in combination with in situ and ex situ scanning probe microscopy (in situ STM and ex situ AFM) and ex situ XPS technique. Cr electrodeposition was tested from Cr(II) and Cr(III) solutions employing low (10 mM) and high (250 mM) concentrations of chromium salts. The microscopic and spectroscopic methods demonstrate the formation of chromium deposit, although the voltammetric responses are not so obvious to interpret. In case of copper electrodeposition from 10 mM Cu(I) solutions, clear voltammetric cathodic waves of copper deposition are observed followed by a peak of metallic copper dissolution on a reverse anodic scan (Fig. 1a). Microscopic investigation shows (quasi)two-dimensional growth of copper on the Au(111) and Pt(111) electrode surfaces at moderate overpotentials (Fig. 1b,c). At high overpotentials copper deposition proceeds via formation of a large number of three-dimensional crystallites. This observation is in agreement with the shape of voltammetric and chronoamperometric responses.

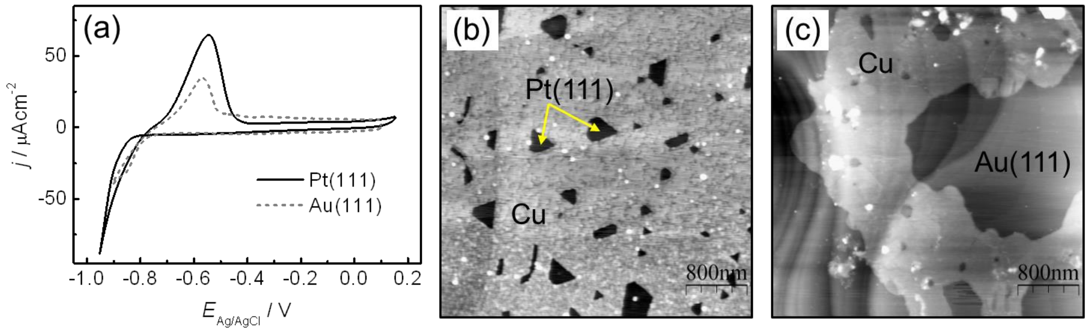

Fig. 1. (a) Cyclic voltammetry of Au(111) and Pt(111) electrodes in 1-butyl-3-methylimidazolium dicyanamide IL containing 10 mM CuCl. Scan rate is 10 mVs^{-1}. (b) Ex situ AFM image of Cu deposit obtained on Pt(111) potentiostatically at –0.94 V (vs Ag/AgCl) for 100 s. (c) Ex situ AFM image of Cu deposit obtained on Au(111) potentiostatically at –0.79 V (vs Ag/AgCl) for 100 s.

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Bienzymatic Biosensor for Phosphoenolpyruvate Determination Based on Pyruvate Kinase and Pyruvate Oxidase Cascade Reaction

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Pyruvate kinase deficiency is a disease with severe symptoms like hemochromatosis. The deficiency of this enzyme causes the failure on the glycolysis metabolic pathway and therefore the accumulation of the intermediate products. Pyruvate kinase is regulated by hormones and dietary factors, adenosine triphosphate (ATP) play a major role in controlling its activity, insulin and glucagon also have influence in its regulation. Diabetic patients have alterations on their levels of phosphoenolpyruvate (PEP) due to effect of insulin. Recently, it was observed metabolic dynamics of phosphoenolpyruvate carboxi-kinase (PECK) in cancer cells, which yields different concentrations of PEP than those observed under homeostatic state [1]. Hence, PEP is of great biological importance and its determination and monitoring by simple, facile and cheap methods presents great interest in biomedical applications and technology. Bienzymatic electrochemical biosensors have been developed with the goal of taking advantage of sequential enzymatic reactions to allow a sensitive determination based on signal amplification of an initial reaction by a second that yields an improved signal [2].

In the presented work, a bienzymatic biosensor was developed for determination of phosphoenolpyruvate based on the cascade reaction of pyruvate kinase and pyruvate oxidase immobilized on a gold electrode. The development of the biosensor was optimized in every step of its construction, enzyme loading and enzyme ratio. Several methods for enzyme immobilization were tested to obtain maximum activity and sensitivity [3,4] The operational conditions like, applied potential, pH, were assed to assure maximum performance in PEP determination as to retain maximum biosensor activity. A study of FAD, Mg^{2+} and ADP concentrations was carried out to optimize co-enzymatic reaction and allow signal amplification for low limits of detection [5].

Cyclic voltammetry and electrochemical impedance spectroscopy were used to elucidate charge transfer process between the electrode surface and the solution, and fixed potential amperometry was used to carry out PEP determination.

Analytical parameters for the biosensor were calculated and the reproducibility and repeatability was determined and the stability of the biosensor over time was studied.

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Improving power performance of microbial fuel cells by the use of supercapacitors

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Microbial fuel cells (MFCs) are bio-electrochemical devices capable of converting the chemical energy of organic compounds directly into electrical energy. This dual scope of degrading pollutants and generating electricity simultaneously makes bioelectrochemical systems promising for both wastewater treatment and small energy systems. Electroactive biofilm forming on the anode is the biocatalyst that degrades organics releasing electrons to the anode electrode via direct electron transfer or nanowire or through catabolites. MFC power output is still too low for practical applications and an effective strategy to boost MFC power is the integration with supercapacitors (SCs), electrochemical energy storage systems of high power density and charge/discharge cycle stability.

SCs can store the energy harvested by the MFC and deliver it back at desired power. SCs can buffer energy fluctuations related to the variability of the bio-electrochemical environment of the MFC. Integrated MFC-SC systems, hence, can play an important role in developing low-cost and low-energy demand strategies for efficient wastewater management.

Here, we report about the performance of MFC-SCs systems featuring a membraneless single chamber MFC integrated with commercial SCs. Particularly, the MFC is composed by a glass jar with a lateral hole in which the cathode is fixed. The empty volume of the jar is 125 mL. Air breathing cathode configuration is used with the cathode fabricated by pressing a mixture of AC and PTFE over a stainless steel mesh. Carbon fibers brush is used as anode electrode. Specifically, we propose a parallel connection of the MFC and SCs of different size and capacitances in the Farad range. We demonstrate that the SCs buffer MFC fluctuations by storing the energy harvested by the MFC. Furthermore, we show that by a proper design, it is possible to achieve discharge currents in the order of 100 mA that are two order of magnitude higher than those featured by the MFC alone and that are of interest for practical pulsed applications.

Acknowledgments

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Organic Molecules for Aqueous Organic Redox Flow Batteries: Synthesis and Electrochemical Investigation

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As renewable energy technologies such as wind turbines and solar cells continue to increase rapidly the need for large-scale environmentally friendly energy storage has never been more urgent. Aqueous organic redox flow batteries (AqORFBS) are a promising technology for a new generation of grid-connected storage devices due to the possibility to decouple power output and capacity, inexpensive active material utilization, cheap aqueous electrolyte and ease of maintenance. A plethora of organic molecules, often belonging to the category of quinones, have been evaluated for this application. So far, however, none have been reported that fulfil the criteria of having a reversible reduction at a suitable potential, high chemical stability, cheap and green synthesis route and high aqueous solubility.

In this work, we present several promising candidates, which were synthesized through low-cost and environmentally friendly synthesis routes. The novel organic quinonoid compounds were tested electrochemically, to assess their applicability as redox-active molecules for AqORFBs. Furthermore, a mechanistical investigation on the electrochemical behavior of the compounds will be presented.

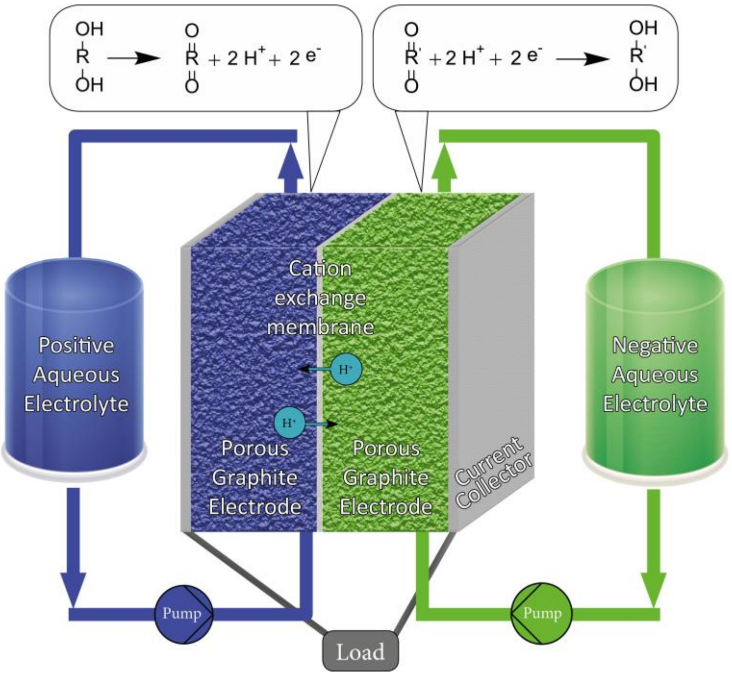

Figure 1: Schematic of organic aqueous flow batteries employing quinonoid active material.

NbeSe$_2$ and Nb$_2$Se$_9$ nanostructures as alternative to Pt electrodes in dye-sensitized solar cells

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Solar cells are amongst the most promising technologies for alternative electricity generation due to the abundance of the sun and their reduced impact on the environment. Among many solar cell designs, dye-sensitised solar cells (DSSCs) have the potential to be used at large scale however there are some disadvantages such as low power conversion efficiency (PCE), poor stability and high cost [1]. As such, researchers have investigated various ways of improving on these disadvantages. In this study, we considered the use of niobium selenide nanoparticles as counter-electrodes (CEs) to replace Pt-CEs in DSSCs with the attempt to lower the cost of the device. Pt is an expensive noble metal with high electrocatalytic activity and stability, so a replacement electrode should be lower in cost while maintaining the high electrocatalytic activity and stability [1]. Niobium selenide nanoparticles were of interest due to their unique and tunable properties such as catalytic, electronic, optical and magnetic [2]. NbSe$_2$ is a 2D-layered material and Nb$_2$Se$_9$ is a 1D material made up of chains, each layer or chain is held together by weak van der Waals forces [2, 3]. Therefore, to solve these problems, two important factors needed to be evaluated; the synthetic route of the nanoparticles and the fabrication of the CE. Colloidal synthesis method was used due to its flexibility, allowance for reaction parameter variation and use of low temperatures and reaction times. NbSe$_2$ nanoflowers were favoured at 320 °C for 120 min in oleylamine (OLA) at a concentration of 0.125 M where NbCl$_5$ was the metal precursor used. On the other hand, Nb$_2$Se$_9$ nanorods were formed when the temperature was decreased to 280 °C and the concentration was increased to 0.500 M, hexadecylamine (HDA) or 1-octadecene (ODE), and NbF$_5$ as a metal precursor were used. The electrocatalytic activity of NbSe$_2$ nanoflowers and Nb$_2$Se$_9$ nanorods were investigated and compared with that of Pt using cyclic voltammetry (Figure 1). The spin-coated NbSe$_2$ CE had a higher current density and electrochemical double layer capacitance than both Pt and spin-coated Nb$_2$Se$_9$ CEs. This was an indication that NbSe$_2$ nanoflowers have a higher electrocatalytic activity than Pt due to high surface area and coverage. As such, it has the potential to produce cost-effective DSSCs by replacing Pt.

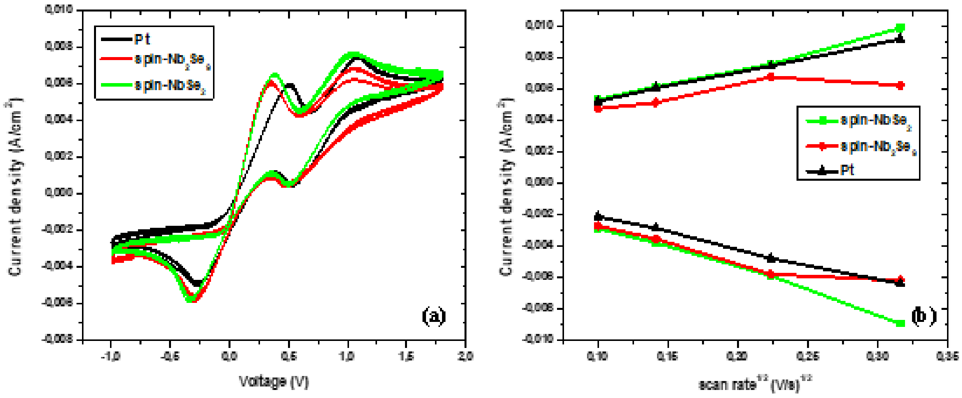

Figure 1: (a) Cyclic voltammograms with the comparison of Pt-CE with the Nb$_2$Se$_9$ and NbSe$_2$ CEs, (b) Linear fitting of the capacitive current densities of Pt compared with the Nb$_2$Se$_9$ and NbSe$_2$ CEs.

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Iridium Oxide Supported on Graphitized Carbon for use as Reversal Tolerant Anodes in PEMFCs

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Potential reversal in PEMFCs occurs when the H_2 supply is insufficient to meet the load requirements of the cell. During cell voltage reversal, carbon oxidation and water electrolysis occur at the anode to maintain the supply of protons and electrons to the cathode. These reactions are non-spontaneous and consume energy from the MEA, causing irreversible damage through carbon corrosion. A material-based approach to prevent or reduce damage to the anode during cell reversal is to include an oxygen evolution reaction (OER) catalyst which will decrease the overpotential for water electrolysis. The addition of the OER catalyst to generate a reversal tolerant anode (RTA) will therefore decrease the occurrence of the carbon corrosion at low cell potentials below -1.2 V.

Due to the harsh conditions of fuel cell operation, the OER catalyst needs to provide both high activity and durability. Studies have shown that among the noble metal electrocatalysts, iridium (Ir) in its oxide form has the highest activity to the OER in acidic media[1]. McCrory et al., (2013) also found that of all their tested metal oxide systems, IrO_x was the most stable under the desired conditions in acidic solutions. IrO_x is an efficient catalyst for the OER but the use of pure IrO_x is limited due to high costs and low surface area in its crystalline form[2]. Researchers have investigated using mixtures with less expensive oxides such as SnO_2[2] or depositing IrO_x on a support material[1]. Ideal catalyst supports used in electrochemical cells need to have porous nanostructure and high electronic conductivity for transfer of electrons through the external circuit.

Carbon remains the ideal support due to its low costs, however, it undergoes corrosion under certain conditions during operation. Carbon blacks are the most used however, graphitized carbon supports have been gaining more attention due to their corrosion resistance and superior electrical conductivity[3]. Therefore, in this study graphitic carbon was selected as the support of choice.

The IrO_x supported on graphitized carbon was synthesized using a polyol deposition technique and then characterized using XRD, TEM and EDX analysis. The nanoparticles were well dispersed and found to be in the range of 8-10 nm. Through XPS analysis the main oxidation states of Iridium were found to be Ir^{3+} and Ir^{4+} which have been proved through previous studies to be the main states responsible for the OER. After comparison with commercial catalysts, it was found to have a good balance between activity and durability.

The characterized supported IrO_x was included in the anode of a membrane electrode assembly (MEA). The design of the MEA included optimization of the ionomer content, desired OER catalyst loading so as not to affect normal operation, choice of coating technique as well as thickness of the OER layer. The MEA's performance was then determined using cyclic voltammetry, polarization curves and electrochemical impedance spectroscopy. The durability of the MEA during reversal tolerance was determined by starving the anode of H_2 while requiring a current density of 200 mA/cm^2 from it. MEA failure was set to when the cell voltage dropped to -1.5 V. The reversal tolerance of the MEA was measured as the time it took for the cell to reach full cell failure.

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Electrochemical and Optical Studies of Organo-chalcogenic Perovskite Nanomaterials with Potential Application in Single Junction Solar Cells

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In this study, chalcogenide anions with lower electronegativities; S (2.58) & Se (2.55), than I_2 (2.66), were incorporated into triiodide perovskite structure; $CH_3NH_3PbI_3$, to prepare organo-chalcogenic perovskite; $CH_3NH_3PbI_2S$ and $CH_3NH_3PbI_2Se$ nanomaterials with lower bandgap energies for potential application in solar cells. X-Ray Diffraction (XRD) patterns demonstrated that the new synthesized organo-chalcogenic perovskite nanomaterials exhibited preferential orientation of prominent peaks towards (110), (112), (220), (310) and (330) planes similar to polycrystalline tetragonal methylammonium lead triiodide perovskite $CH_3NH_3PbI_3$ nanoparticles (as-synthesized) reported in literature. High-Resolution Tunnelling Electron Microscope (HR-TEM) images showed well defined hexagonal crystals. Square Wave Voltammetry (SWV) studies confirmed the presence of chalcogenides (S^{2-} and Se^{2-}) at the oxidation state of -2 confirming a successful preparation of organo-chalcogenic perovskite $CH_3NH_3PbI_2S$ and $CH_3NH_3PbI_2Se$ nanoparticles for the first time. Small Angle X-ray Scattering (SAXS) results showed that the chalcogenides resulted in an increase in particle size (particle size distribution by number) from 47 to 48 to 52 nm for $CH_3NH_3PbI_3$, $CH_3NH_3PbI_2S$ and $CH_3NH_3PbI_2Se$, respectively. Optical studies by Ultraviolet (UV-vis) and Photoluminescence (PL) showed that the chalcogenide ions induced an anticipated redshift in the absorption and emission resulting in lower bandgaps of organo-chalcogenic perovskites, i.e. $CH_3NH_3PbI_3$ (1.9 eV) > $CH_3NH_3PbI_2S$ (1.74 eV) > $CH_3NH_3PbI_2Se$ (1.63 eV) attributed to lower electronegativitites of the chalcogenides. Electrochemistry studies demonstrated that the chalcogenides anions promoted the Highest Occupied Molecular Orbitals (HOMOs) (valence band) to higher energies $CH_3NH_3PbI_3$ (3.78eV), $CH_3NH_3PbI_2S$(3.84eV) and $CH_3NH_3PbI_2Se$ (3.85eV), respectively, indicating that less energy will be required to knock out the electrons from the valence band to the conduction band to create electrical/photocurrent, making organo-chalcogenic perovskites potential candidates for solar cells (photovoltaic cells) applications.

Keywords: organo-chalcogenic perovskites, chalcogenides, electronegativity, Square Wave Voltametry ,red-shift.

Development of an electrochemical immunosensor for the detection of steviol glycosides by experimental and computational methods

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Steviol glycosides are non-nutritive sweeteners widely employed in food industry and their detection has been primarily based on chromatographic techniques. Electrochemical immunosensors provide selective, sensitive and cost-effective detection routes for these widely consumed sweeteners.

In the present work, platinum electrode where its surface was fabricated with graphene oxide (GO), assimilated in Zinc Oxide nanoparticles (ZnO NPs) with multiwalled carbon nanotubes (MWCNTs) decorated with human sweet receptor subunit T1R2, was applied. The electrochemical detection of Reb A was evaluated qualitatively and quantitatively using cyclic and differential pulse voltammetry, respectively under optimized conditions in pH 11 borate buffer from -0.4 V to 0.8 V purged with N_2 (Bathinapatla *et al.* 2016).

The characterization of the GO/MWCNT/ZnO-NPs nanomaterial used on this study was based on different conventional, Field Flow Fractionation (FFF), High Resolution Transmission Electron microscope (HR-TEM), Thermogravimetric Analysis (TGA), Attenuated Total Reflection Mode Fourier transform infrared (ATR-FTIR) and UV-VIS spectroscopy, characterization techniques. Asymmetric flow field-flow fractionation (AF2000) and centrifugal flow field-flow fractionation (CF2000) with UV/VIS at 365 nm and MALs at 90° detectors were used to determine the size of ZnO nanostructures. Field flow fractionation is one of the efficient separation techniques known, and centrifugal flow field-flow fractionation separates different particle sized nanoparticles by density, thus determining size variation within the synthesized batch. The findings on FFF were compared and validated with conventional characterization techniques like transmission electron microscopy (TEM) and thermogravimetric analysis (TGA).

Computational studies were used to supplement experimental results using docking and adsorption methods. Adsorption studies were carried out to better understand the mechanistic aspects between T1R2, the nanocomposite used to modify the platinum working electrode, and the analyte Reb A. Docking studies between T1R2 and the steviol glycosides were used to explore the interaction as a mechanism of the immunosensor detection (Mayank and Jaitak 2015).

The results of this study will contribute to the development of an immunosensor that can potentially be used to quantify steviol glycosides in the food and beverage industry.

Keywords: Steviol glycosides; Rebaudioside A; Zinc Oxide Nanoparticles; Human Sweet Taste Receptor T1R2; Density functional theory (DFT); Molecular docking.

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Amorphous MoP and ∝-WP_2 particles as non-noble electrocatalysts for Hydrogen Evolution Reaction

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The search for cheap and earth-abundant electrocatalysts with efficiencies comparable to platinum has received much attention in recent years. The research has been driven by the need for cheaper alternatives to platinum in hydrogen production. In this study, non-crystalline MoP and ∝-WP_2 microparticles were prepared through colloidal synthesis using $MoCl_4$ and WCl_6 as metal sources, Trioctylphosphine as phosphorus source and 1-Octadecene as both a solvent and reducing agent. The structure and morphology of the microparticles was determined using Powder X-ray Diffraction (PXRD), Transmission Electron Microscopy (TEM) and Energy Dispersive X-ray Spectrometry (EDX). XRD showed that amorphous particles were successfully synthesized from both Mo and W metal salts as indicated by a single broad peak in XRD (Figure 1). Post synthesis high temperature (800 ˚C) treatment of the particles converted the amorphous particles into crystalline materials with prominent diffraction peaks which could be matched to MoP (PDF 03-065-6024) and ∝-WP_2 (PDF 01-076-2365). It was discovered that longer annealing time (2 h) was required for MoP than for ∝-WP_2 (1 h) to improve the crystallinity. Both electrocatalyst showed promising catalytic activity and stability in hydrogen evolution reaction in acidic medium. The high catalytic activity of the ∝-WP_2 over MoP was attributed to the high transfer of electron density from W to P on the shorter W-P bond length, the high electron conductivity and superior charge transfer. Our findings demonstrate that the type of metal is important for electrocatalytic activity.

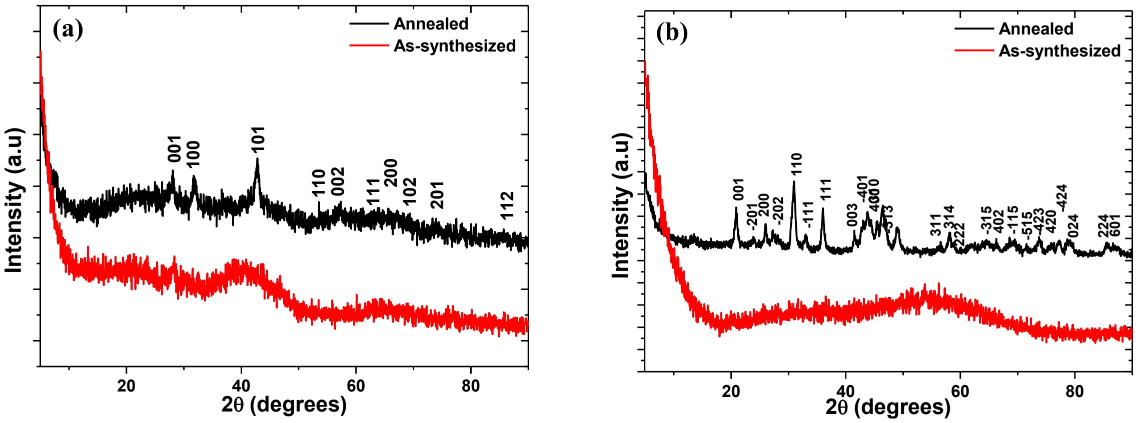

Figure 1: XRD diffractograms for (a) MoP and (b) ∝-WP_2 nanoparticles before and after annealing.

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Copper Telluride Nanoparticles for Solar Cells

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In this work, Copper Telluride nanoparticles (CuTe NPs) were successfully synthesized through wet-chemical reduction. During synthesis, hydrazine monohydrate was used as a reducing agent while mixture of ethylene glycol and water was used as solvent. Transmission electron microscope (TEM) and powder X-ray diffraction (XRD) results indicated that CuTe NPs have hexagonal phase. Comparing the ultraviolet-visible (UV-Vis) spectra showed that after chemical reduction took place; bands from the precursors disappears confirming successful occurrence of reduction for CuTe NPs. Synthesized NPs were incorporated in TiO_2 where they turned to improve absorption properties of the composites. Quenching studies revealed that 99.7% of the TiO_2 intensity was quenched in CuTe/TiO_2, respectively, indicating successful separation of electron-hole pairs. Electrochemical studies showed that CuTe/TiO_2 has lower charge transfer resistance. The results obtained revealed that CuTe/TiO_2 is good for application in solar cells.

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Amorphous Molybdenum Sulfide Deposited on Ti for Hydrogen Evolution Reaction

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The energetic matrix of the world has been based on exploration and use of petroleum, coal and natural gas. The population growth coupled with the use of non-renewable fuels reiterate the necessary development of alternative energy sources. Hydrogen is been highlighted as an environmentally friendly alternative energy source due to the zero carbon emission. Hydrogen gas has high heat conversion efficiency and has been produced by methods like steam methane reforming, an effective production method but does not solve the environment problem because emits carbon dioxide. An alternative hydrogen production method is the water splitting process, in which the hydrogen evolution reaction (HER) occurs on the cathode electrode. In order to increase the HER efficiency a highly active catalyst is necessary. In acidic medium, the best catalyst is Pt, but factors as high cost and scarcity make it a nonviable material to be used in large scale. Molybdenum sulfide is a stable, earth-abundant, nontoxic, low cost material, and an effective electrocatalyst for the hydrogen production. The literature have shown that amorphous MoS_2 are the most active form that can be easily obtaining by a one-step electrodeposition technique in mild conditions such as room pressure and temperature.[1] Some studies report the MoS_2 films growing in conductive glass substrates or in carbon nanotubes. However, it is more interesting to perform electrodeposition on substrates that are economically and chemically stable under acidic conditions. In this context, this work presents amorphous molybdenum sulfide electrodeposition on Ti substrate. The MoS_2 films were electrodeposited by cyclic voltammetry for 25 cycles at 50 mV s^{-1}. The electrolytic solution was prepared from 4 mmol L^{-1} $(NH_4)_2MoS_4$ and 0.1 mol L^{-1} $NaClO_4$ as the supporting electrolyte. The film were characterized by XRD, SEM, and UV-vis, Raman and EDX spectroscopies. The electrocatalytic activity was analyzed in 1.0 mol L^{-1} H_2SO_4 solution by linear sweep voltammetry (LSV) at scan rate of 1 mV s^{-1}. The catalyst´s durability was performed on the same solution by cycling potential during 1,000 cycles at 100 mV s^{-1}. The polarization curve results were used to analyze the overpotential, η in -10 mA cm^{-2} and to obtain the Tafel plot. The cyclic voltammograms deposition is shown in Figure 1(a) and it is possible to see a better definition of the anode and cathode process with increasing cycle number. The MoS_2 resulting film is amorphous, with band gap about 1.1 eV, and composition close to the stoichiometric MoS_2. Figure 1(b) presents the electrocatalytic results and an overpotential of -139 mV was necessary to achieve -10 mA cm^{-2}. The electrodeposition method has been used to synthetized MoS_2 film, which showed good properties for the electrocatalysis of the hydrogen evolution reaction.

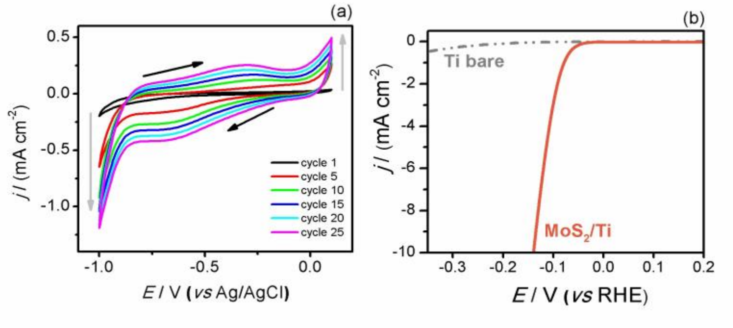

Figure 1. (a) Cyclic voltammograms and (b) polarization curve of MoS_2 film on Ti substrate.

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Enhanced visible light driven activity of p-n heterojunctions for photoelectrocatalysis of pharmaceuticals by electrodeposition of Cu_2O films on anodized TiO_2 nanotube arrays

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Abstract

Pollutants arising from pharmaceutical industries have been adjured to be one of the emerging pollutants that have deteriorating threats to human health and aquatic life thus the need to eliminate them from water using effective method/process. Photoelectrocatalysis provides a valuable means of achieving this. A successful and sustainable photoelectocatalytic process requires photoanodes that are highly active in the visible region of the solar spectrum. In this work, a visible-light active Cu_2O-TiO_2 photoanode was synthesized, characterized and evaluated by the degradation of pharmaceuticals in water. The p-n heterojunction photoanode was synthesised via electrodeposition of Cu_2O on anodized TiO_2 nanotube arrays (NTAs). It was further characterized with XRD, FESEM, EDX and diffusive reflectance UV-Vis. Mott-Schotty plots was carried out to confirm the formation of the p-n heterojunctions between the two electrodes. Photoelectrochemical properties of the synthesised photoanode were also examined followed by photoelectrochemical application in degrading pharmaceutical pollutants. The result from this work therefore suggests the electrodeposited Cu_2O/anodized TiO_2 NTA as a highly efficient photoanode for degrading other emerging pharmaceutical pollutants from wastewater.

Keywords: Photoelectrochemical degradation, p-n heterojunctions photoanode, Copper (I) oxide, Titanium dioxide

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Highly Efficient Three-Dimensional Honeycomb-Like CuCo oxide Nanosheet Arrays Supported by Nickel Foam and as an Oxygen Evolution Electrode

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Herein, we prepare three-dimensional honeycomb-like CuCo oxide nanosheet arrays supported by Ni foam via electrochemical co-deposition of Co and Cu hydroxides on Ni foam followed by thermal oxidation. The co-deposition with Cu considerably changes the morphology of the Co hydroxide deposit to form honeycomb-like nanostructures, significantly decreasing the onset potential for oxygen evolution. Specifically, the CuCo oxide anode displays an exceptionally low oxygen evolution overpotential of 290 mV at a current density of 10 mA cm^{-2} in 1 M KOH, and an anion exchange membrane–based water electrolysis cell employing the above anode achieves a current density of 100 mA cm^{-2} at 1.68 V in 0.1 M KOH.

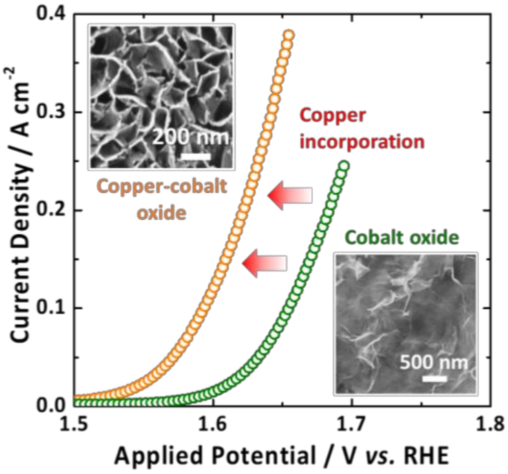

Figure 1. A cobalt oxide nanosheet array supported by nickel foam shows remarkably enhanced catalytic activity for the oxygen evolution reaction due to the incorporation of copper.

Reference

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Visible light driven photoelectrocatalysis of Ciprofloxacin at a FTO/$BiVO_4$/MnO_2 anode

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Abstract

Contamination of water bodies by harmful and recalcitrant organic substances is a global challenge. A promising technique for removing these organics from water/wastewater is photoelectrocatalytic oxidation which combines electrolytic and photocatalytic processes. Herein, we report the degradation of ciprofloxacin at a $BiVO_4$/MnO_2 anode under visible light irradiation via photoelectrocatalytic process. The $BiVO_4$/MnO_2 was electrodeposited on a FTO glass and characterised with XRD, SEM, EDS and diffusive reflectance UV-Vis. The electrochemical properties were studied using linear sweep voltammetry, electrochemical impedence spectroscopy and photocurrent response. The results confirmed the successful electrodeposition of $BiVO_4$/MnO_2 on the glass substrate. The calculated charge carrier density of $BiVO_4$/MnO_2 from Mott-Schotty plot was higher than those of pristine $BiVO_4$ and MnO_2. The binary electrode also gave improved photocurrent response compared with unitary electrodes. Degradation efficiencies of 76% was achieved upon the application of the prepared photoanode (FTO/$BiVO_4$/MnO_2) in PEC degradation of ciprofloxacin dye using a bias potential of 1.5 V within 2 h. The findings of this study suggest the suitability of the prepared photoanode for the photoelectrocatalytic degradation of organic pollutants in wastewater.

Keywords: Bismuth vanadate; manganese dioxide; heterojunction photoanode; photoelectrocatalytic degradation; ciprofloxacin.

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Pt nanoparticles on porous hollow electrospun carbon nanofibers as electrocatalysts for high temperature polymer electrolyte membrane fuel cell (HT-PEMFC) applications

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Fuel cells convert chemical energy directly into electrical energy through electrochemical reactions catalyzed by suitable catalysts, most commonly costly platinum nanoparticles. One specific type of fuel cell is the high-temperature proton exchange membrane fuel cell (HT-PEMFC), which operates at temperatures above 150 °C and thereby offers several advantages, such as higher tolerance to fuel contaminations and enhanced reaction kinetics. Proton conduction is enabled within a phosphoric acid imbibed polybenzimide membrane (PBI), but also by phosphoric acid (PA) within the porous electrodes. In operation, however, water is produced and the proton-conducting phosphoric acid flushed out off membrane and electrodes. This leads to a severe performance loss. One way to overcome this problem is to bind the phosphoric acid more strongly to either ionomer or catalyst surface. Another strategy may be using a porous hollow fiber catalyst, in which the phosphoric acid is confined.

Coaxial electrospinning is a common method to create nanofibers with different structures, such as core-shell, hollow and porous fibers. Hollow fibers can be obtained in various ways, for example, due to the incompatibility of the two polymers, the mixed polymer solution used in the core is separated as continuous surrounding and discontinuous droplet phases. Lee et al. used two polymer solutions consisting of polymethylmethacrylate (PMMA) and polyacrylonitrile (PAN) with polyvinylpyrrolidone (PVP) to flow through a coaxial capillary (double jet) in order to create a core-shell structure. [1] By a subsequent washing or calcination process porous hollow structures are formed from previously electrospun nanofibers. During this process, PVP and PMMA decompose and PAN is transferred to graphitic carbon.

We report here the preparation of Pt nanoparticles on porous hollow carbon nanofibers (CNF) by coaxial electrospinning. Two phase-separated polymer solutions are electrospun, followed by heat-treatment at 1000 °C in an inert atmosphere and a Pt impregnation step. During the electrospinning process, the shell polymer solution (PVP and PAN mixed solution) forms a shell around the core solution (PMMA), resulting in cable-type structures. A hexachloroplatinic acid solution is sprayed onto the CNF and then reduced at 280 °C under Ar/H_2. We studied the oxygen reduction reaction (ORR) in the presence of minute amounts of phosphoric acid and also at elevated temperatures relevant to high temperature polymer electrolyte fuel cells. The evaluation of the activity of our Pt nanoparticles decorated CNF is done in a first step by cyclic voltammetry (CV) and linear sweep voltammetry (LSV) on a rotating disk electrode (RDE). For this purpose, a thin layer of the CNF catalyst is attached to glassy carbon electrode to be examined in home-made fixture. For the electrospun CNF catalysts, higher limiting currents and onset potentials were obtained in the presence of PA compared to their commercially available counterparts. This trend also persists with a temperature increase to 40 °C and 60 °C. A future challenge is to scale-up and implement the Pt-decorated CNF mat into a fuel cell.

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Electrochemical study of the dissolution of platinum group minerals in various potential lixiviants

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The traditional route utilised for the recovery of Platinum Group Minerals (PGMs) in South Africa involves the concentration of ore by flotation, followed by smelting to produce a PGM rich matte, which is then digested hydrometallurgically to solubilise base metals and Platinum Group Elements (PGE). HCl/Cl_2 is conventionally used for PGE dissolution from concentrated material, which is an aggressive reagent associated with high maintenance costs as well as environmental concerns.

Of interest is the study of leaching PGMs directly from mineral ores, low grade concentrates and tailings as a more sustainable alternative. This study investigates the dissolution mechanisms of two PGM minerals (cooperite and sperrylite) in various potential lixiviants (cyanide, thiocyanate and iodide) in the context of an electrochemical study involving OCP, chrono-amperometry and cyclic voltammetry. This approach allows the assessment of leaching characteristics with relative ease, on a small sample to pin-point optimal conditions for more elaborate leach tests.

Effect of Mn doping into $NiCo_2O_4$ towards Oxygen Reduction Reaction in Alkaline Media

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Keywords: spinel oxide, electrocatalyst, cyclic voltammetry, linear sweep voltammetry, alkaline fuel cells

The present work elucidates synthesis and electrocatalytic activity of cobaltites non-platinum group metal electrocatalyst, $Mn_xNi_{1-x}Co_2O_4$ spinel oxide nanostructured particles synthesized by a facile hydrothermal method, employable for oxygen reduction in alkaline media. Electrocatalysts for the oxygen reduction reaction (ORR) with high activity and stability comparable to Pt/C are needed for fuel cell commercialization [1]. Various characterization techniques including TEM and SEM confirmed the successful incorporation of Mn leading to the formation of Co−Mn (Ni)−O mesoporous solid. FTIR, Raman spectroscopy, XRD, TGA, BET and XPS were used to reveal the redox activity of Co^{3+} to Co^{4+}, Ni^{2+} to Ni^{4+} and Mn^{2+} to Mn^{3+}. These redox systems when coupled with oxygen vacancy sites within the spinel cobaltite lattice and their large surface area are crucial for ORR performance [2]. Electrochemical measurements were performed using a standard three-electrode system with 0.1 M KOH electrolyte via cyclic voltammetry and linear sweep voltammetry. The prepared electrocatalyst showed an outstanding electrocatalytic activity towards oxygen reduction in an aqueous alkaline medium with increasing Mn content, giving a more positive onset potential and a high current density relative to the parent spinel $NiCo_2O_4$. Most importantly, the $Mn_{0.5}Ni_{0.5}Co_2O_4$ electrocatalyst showed superior poisoning tolerance levels relative to Pt/C and $NiCo_2O_4$ electrocatalysts. Hence, the facile hydrothermal method can be used to give a high degree of spinel oxide crystallinity having an idealistic cationic stoichiometric ratio of Mn, Ni and Co. Thus, superior behaviour of the cobaltites can be attributed to structural veracity coupled with high surface area and electrical conductivity properties, which facilitated the high catalytic oxygen electroreduction.

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Recovery of Reusable Chemical Elements from Spent Lithium Ion Batteries for the Synthesis of Metal Organic Frameworks (MOFs)

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The world is currently at the verge of embracing the fourth industrial revolution with inclusion of clean and sustainable energy. With such a hurry in creating a sustainable future, many countries have started migrating towards the use of zero emission vehicles powered by fuel cells and Li-ion batteries (LIBs). Electric vehicle (ECs) powered by LIBs are gaining prominence, with China as one of the leading countries and other countries such as United States of America, Japan and Australia already migrating towards ECs [1,2]. This rapid change is helpful in the reduction of CO_2 emission. However, the recycling of spent LIBs is still minimal and hence creates the need for development of new and innovative LIBs recycling technologies. South Africa disposes approximately 50 million spent LIBs annually mostly in the landfills which can be an environmental hazard [3]. Industrial recycling processes such as pyrometallurgical and hydrometallurgical methods are applied in companies such as Umicore, Inmetco, and Toxco [4]. Most of the recovered metals are in the form of alloys or compounds which are later used in various industries. They can also be use in the re-synthesis of cathode materials, supercapacitors and $LiAlO_2$ nanocrystallites. However, there are no records of utilizing the recovered metals for preparation of porous materials such as metal organic frameworks (MOFs). MOFs are porous materials that are made from the bonding of metal units with an organic linker to result in a 3-dimensional porous crystalline framework material. MOFs properties such as large surface area, tunable pore sizes and topologies make them desirable for energy storage applications [5]. The aim of the current study is to create a cheaper and environmentally friendly way for preparing MOFs and hence create a new strategy for recycling of the spent LIBs. The obtained MOFs were characterized using XRD, SEM, TGA, BET surface area measurements.

Key words: Lithium ion batteries (LIBs); metal organic frameworks (MOFs); recycing; cathode material.

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Preparation, characterization and zeta potential studies of polysulfone-blend-poly(styrene-*co*-maleic anhydride) membrane for heavy metal removal from wastewater

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Abstract

The 1,4,5,8-naphthalenetetracarboxylic dianhydride- 4,4'-Diaminodiphenyl Ether-2,2'-disulfonic acid homopolyimides having oxygen, amine and sulfonate chelating motifs were synthesized and characterized from readily available and inexpensive materials considering its tremendous scientific and technological interest. The novel poly(styrene-*co*-maleic anhydride) cumene terminated (PSMAC) polymer was also synthesized by ring opening polymerization using *p*-aminohippuric acid. The structural compositions of the polymers were determined by Fourier transform infrared spectroscopy (FTIR) and Nuclear magnetic resonance spectroscopy (NMR). The thermal stability of the polymers was determined by thermogravimetric analysis (TGA). The physicochemical and mechanical properties of the sulfonated polyimides based blend membranes were studied. The blend membranes revealed improved hydrophilicity, porosity, zeta potential, water uptake and permeability due to the existence of the hydrophilic functional group.

The surface charge of the membrane was determined by zeta potential. Membranes M-0 and M-3 exhibited the negative charge over the entire pH range 4-10, and the absolute ζ-potential value was decreased to acidic pH values. The isoelectric point (IEP) of PSF neat (M-0) membrane was observed at pH 3.0, which is similar to the literature. However, the IEP of M-3 membrane was detected at pH 3.4. The change in the IEP could be attributed to the incorporation of nanoparticles. In addition, the incorporated polymer is negatively charged at pH 6.5. However, the ζ- potential of M-3 was less at pH 7 when compared to M-0 membrane. The reduced ζ- potential could be attributed to the intervention of cation adsorption from background electrolyte (KCl) on the surface, which decreases the negative charge density of the sulfonate group. As a result, the ζ- potential of the polymer becomes less negative, that directly reduces the net charge of the membrane surface. Overall, the as-prepared membrane could exhibit negative charge over the large range of pH.

As there was an increase of hydrophobic alkyl group density, the contact angle was not reduced as desired level. Furthermore, the blend membranes were explored to study their efficiencies for the removal of metal ions from the wastewater. The M-3 membrane has been shown to be remarkably effective in the removal of several toxic and priority metal pollutants from the matrix of an industrial wastewater. The adsorption parameters indicated that the Langmuir isotherm model fits well for selective metal ions adsorption on M-3 membrane. Overall, the preliminary results indicate that M-3 membrane has great potential in advanced wastewater treatment.

The authors gratefully acknowledge the support provided by Deanship of Scientific Research (DSR), King Fahd University of Petroleum and Minerals (KFUPM) for funding this work through internal research grant project No: IN161036.

Plasmonic silver/silver phosphate/methyl viologen/exfoliated graphite ($Ag/Ag_3PO_4/MV/EG$) Photoelectrode for Photoelectrocatalytic Degradation of Diuretic Drug

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Hydrochlorothiazide (HCTZ), one of the most consumed drugs, is recognized for its presence in most receiving waters. HCTZ is diuretic indispensable group of drugs used to treat hypertension, congestive heart insufficiency, renal tubular acidosis, diabetes insipidus, formation of kidney stones, and sometimes hypercalciuria. However, HCTZ is not completely metabolised and about 62.6% of the oral dose is eliminated unchanged by the kidneys in a period of 24 h. HCTZ is thus ubiquitous pollutant in the sewage and receiving water bodies. There is therefore need for novel, robust, and cost-effective methods for removal of HCTZ in wastewater. Photoelectrocatalysis (PEC), which combines both heterogeneous photocatalysis and electrochemical oxidation, is one of the novel hybrid processes for effective treatment of wastewater containing a myriad of emerging pharmaceutical pollutants. In this process, the inherent challenges of photocatalysis and electrochemical oxidation are resolved, with both processes synergistically generating reactive oxygen species. For economic viability of PEC, visible light responsive semiconductors should be considered together with electrochemically active substrate material.

In this work, plasmonic $Ag/Ag_3PO_4/MV/EG$ photoelectrode was fabricated and utilized for the degradation of HCTZ. Prior to its use, the electrode was characterized using FESEM, EDS, TEM, XRD, XPS, FTIR, and UV-Vis DRS to confirm its structural integrity. The UV-Vis DRS results showed that the composite material has huge capacity to absorb visible light. After construction of electrodes, CV, EIS, and LSV were used to characterize the photoelectrode. As shown in **Fig. 1**, the XRD results of the materials confirmed formation of Ag on and around the matrix of Ag_3PO_4, when large quantities of MV were used. The electrode showed high performance (94%) HCTZ removal. The enhanced performance was attributed to the plasmonic Ag, visible light absorbing nature of Ag_3PO_4, MV as electron shuttle, and EG material for its electron transporting properties. The mineralization was evaluated through TOC measurements, while HPLC was used to analyze degradation by-products. Among the intermediate, altizide was observed as a fragment of HCTZ. The electrode could thus be used for degradation of other difficulty- to-degrade organic pollutants in water.

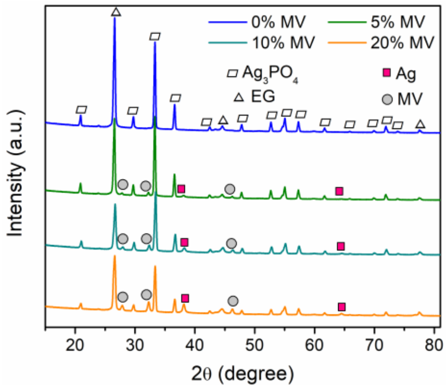

Fig. 1. XRD patterns of Ag_3PO_4/0%MV/EG, Ag_3PO_4/5%MV/EG, Ag_3PO_4/10%MV/EG, and Ag_3PO_4/20%MV/EG materials.

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Quantum dot Impedimetric Phase Angle based Aptasensor for TB biomarker detection

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Tuberculosis (TB) is one of the major infectious diseases that affect the health of people all over the world. Various tests have been used to diagnose tuberculosis infected patients but some of these tests are unreliable as they sometimes give false positive results. Studies have shown that TB related cytokines signaling proteins, such as interferon-gamma (IFN-γ) can serve as biomarkers for the diagnosis of the disease [1]. IFN-γ related test for TB currently in use are antibody-based immunosensing techniques which are very expensive and time consuming. It is thus vital that an alternative detection method for IFN-γ be developed [2]. This presentation deals with the development of a fast, simple and sensitive QDs-based electrochemical DNA aptamer biosensor (aptasensor) for the detection of IFN-γ. The aptasensor consists of novel indium telluriselenide (In_3TeSe_2) quantum dots capped with L-cysteine to produce a DNA aptamer sequence for IFN-γ on a gold electrode. The optical properties of the QDs were characterized by UV-vis and fluorescence (FL) spectrometry which gave an absorbance band at 291 nm and emission band at 320 nm. The structure of the QDs was verified by Fourier transform infrared spectroscopy (FTIR) and high resolution transmission electron microscopy (HRTEM). HRTEM revealed that the QDs consist of 6 nm particles. The electrochemical response parameters of the QDs aptasensor for IFN-γ were studied by phase angle electrochemical impedance spectroscopy (EIS). It was observed that the analytical technique showed good linearity with linear correlation coefficients (R^2) of 0.99 and displayed a high sensitivity of 2.25 Ω/(pg/mL) and wide linear range of 0.25-1.25 pg/mL.

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Carbon nanomaterials as electrode modifiers in electrochemical determination of selected veterinary drug

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Carbon nanomaterials offer an enormous versatility, providing tailored electrochemistry for target applications. This versatility is based on the selection of a target carbon nanomaterial and the chemistry behind its electrochemical behavior, which is going to determine the final electrochemical performance. The excellent properties of carbon nanomaterials, such as large surface–to–volume ratio, high conductivity and electron transfer, have led to numerous advances in electrochemical sensors.

Single-wall carbon nanotubes (SWNTs) are known as one-dimensional materials. They consist of sheets of graphene, rolled up to form hollow tubes with walls one atom thick. They possess extraordinary thermal, mechanical, and electrical properties and are considered as one of the most promising nanomaterials for applications.

Carbon nanohorns (CNHs) are the conical shaped carbon nanostructures sometimes also called as carbon nanocone are in the group of one-dimensional carbon nanostructures. CNHs are considered as a good replacement of carbon nanotubes, due to its great specific surface area, high yield, high chemical stability, high purity, low toxicities, exceptional catalytic properties, superior porosity, and good conductivity.

Graphene quantum dots (GQDs), as a unique category of zero-dimensional carbon nanomaterial. GQDs are featured by ultra-small particle size (<10 nm) which affords many oxygen-containing functional groups on the planar surface that can serve as highly active reaction sites. This carbon nanomaterial is environmentally friendly due to its non-toxic and biologically inert properties, which have attracted worldwide interests from academic and industry.

In this work, glassy carbon electrodes (GCE) modified with different carbon nanomaterials such as SWCNTs, CNHs, and GQDs (SWCNTs–GCE, CNHs–GCE, and GQDs–GCE) were used as a working electrodes for the determination of chosen veterinary drug nitroxinil. Developed sensors were analysed using atomic force microscopy (AFM) and cyclic voltammetry (CV). The voltammetric procedures for the determination of nitroxinil were developed using a square–wave voltammetry (SWV). The proposed methods exhibited acceptable analytical performance in terms of the linearity and the detection limits.

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A High Performance Electrochemical biosensor for the detection of Sucralose in Food Samples

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Abstract

Sucralose, [1,6-dichloro-1,6-dideoxy-β-D-fructofuranosyl-4-chloro-4-deoxy-α-D-galactopyranoside] also known as splenda or sucraplus is generally used as a sweetener and flavor enhancer in foods and beverages. In this study a novel laccase modified nanocomposite electrochemical biosensor was developed for the electrochemical determination of sucralose in different food samples. The electrode surface was fabricated with graphene oxide assimilated with zinc oxide nanoparticles decorated on graphene oxide/laccase. The developed biosensor exhibited a 4-fold enhancement in the differential pulse voltammetry signal carried out at pH 5.0 in a 0.1 M phosphate buffer. Under the optimized conditions, Ip (µA) was proportional to the sucralose concentration in the range of 0.002 – 0.07 mM (R2 = 0.9984) and 0.070 – 1.35 mM (R2 = 0.9979) with a detection limit (S/N = 3) of 0.32 µM. Results of this study revealed that laccase was adsorbed tightly onto the surface of the modified electrode and showed an enzymatic catalytic activity towards the redox peaks at 0.34 and 0.4 V (vs Ag/AgCl). Additionally, the molecular docking simulations predicted a stronger binding affinity of sucralose towards laccase, thus supporting their host-guest relationship. The use of novel electrode materials in this study demonstrates the application of the electrochemical biosensor in the food industry.

Keywords: Sucralose, laccase, Differential pulse voltammetry, Biosensor, food samples

Enhanced Electrochemical Kinetics of Azidomethyl Substituted Poly(3,4-ethylenedioxythiophene) for DNA Sensor Elaboration

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The analysis of specific nucleic acids sequences is of central importance in clinical medicine because of their use for rapid diagnosis of infectious diseases. Detection of bacterial, fungal, or viral pathogen by modern gene-based techniques usually includes a nucleic acid amplification step. However, a variety of electrochemical sensing techniques has been developed that are achieving levels of sensitivity that make amplification unnecessary [1].

DNA sensors require an immobilization of single-stranded DNA onto electrode surface. Usual carbodiimide coupling chemistry is not fully chemoselective in aqueous solvents. Moreover, hydrolysis occurs, thereby lowering the efficiency of the immobilization. To overcome these drawbacks post-functionalization of a novel conducting poly(azidomethylethylenedioxythiophene) (azido-PEDOT) by “click” chemistry with various types of terminal alkynes can be done [2].

Here we present electropolymerization of azidomethyl substituted PEDOT. Screed-printed electrodes were modified in acidic aqueous solution (in contrast to the most of works presenting substituted EDOT polymerization from organic solvents) in potentiodynamic regime. Increase in oxidation current at maximum anodic potential together with increase in charge upon cycling indicated the conducting polymer formation.

Since most of the approaches of nucleic acid detection rely on redox labels or mediators, the electrochemical activity of modified electrodes was assessed. Cyclic voltammetry of ferri-/ferrocyanide redox couple was used for investigating of the electrochemical kinetics of the novel material. Comparison of azido-PEDOT with PEDOT revealed the improved charge transfer of the former resulting in amplified analytical signal (electrochemical rate constant increased by 2 times) and higher faradaic/non-faradaic currents ratio.

Thus, azido-PEDOT was electropolymerized from aqueous solution for the first time. The material exhibits enhanced electrochemical kinetics compared to unsubstituted PEDOT. This approach allows improving the sensor performance since the sensitivity of nucleic acid detection methods is mainly driven by the translation of an interfacial layer change into the electrical current.

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Electrochemical impedance spectroscopy of single nanoparticles

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Electrochemical impedance spectroscopy (EIS) has attracted growing interest in the last years, not only because it is one of the most valuable tools for investigating the electrochemical interface, but also because it provides a promising platform for developing different chemical and biosensors. Although EIS is a powerful electrochemical approach for analyzing a variety of electrochemical phenomena, this approach usually measures the averaged property of the entire electrode surface. However, the electrode surface is often rather heterogeneous and rarely presents an ideal electrochemical behavior, resulting in some difficulties with data interpretation. Here we present a monochromatic dark-field microscopy (DFM) for determining the EIS of single Au nanorods (AuNRs) based on the quantitative dependence of the localized surface plasmon resonance (LSPR) on its electron density. Its capability to measure the surface capacitance of single AuNRs was further demonstrated. Different from the conventional EIS that relies on the recording of electrode current, an optical-to-electrochemical conversion model is proposed here to report the charging current of single nanoparticles from its optical responses. This is based on the fact that LSPR scattering of single AuNRs is regulated by its electron density during non-Faradaic charging and discharging processes. The EIS of single AuNRs is extracted by measuring the scattering intensity response of single AuNRs to the applied sine-wave voltage as a function of frequency. Frequency analysis further allows for distinguishing the pure charging effect and the accumulations of counterions surrounding the nanoparticle, so that the surface capacitance of single AuNRs can be accurately determined by solely considering the charging effect. Both factors were found to contribute to the LSPR band, but their temporal constants were different, leading to different features in the frequency spectrum.

This method is also suitable for studying other types of plasmonic nanomaterials. Furthermore, because the surface capacitance of metal-electrolyte interface is known to be sensitive to the molecular recognition (binding) events, the present work is anticipated to pave a promising way towards single nanoparticle biosensing by measuring the surface capacitance under high-frequency modulation conditions.

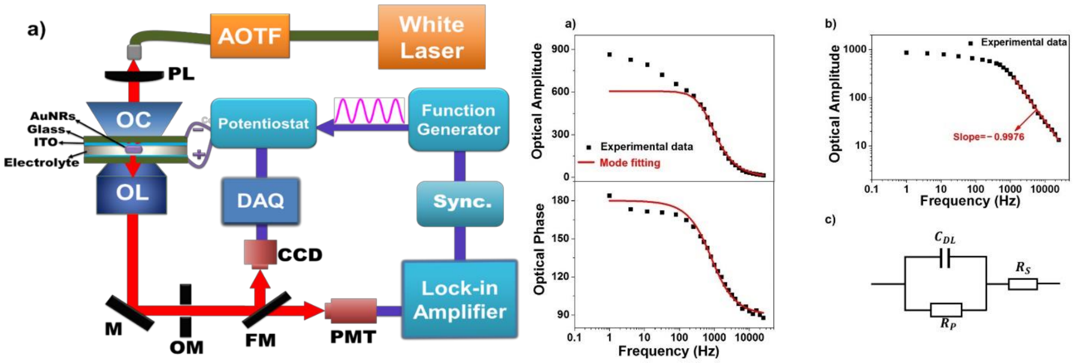

Figure 1. Left: Schematic illustration of optical setup for determination the EIS of single AuNRs using DFM. AOTF=Acousto-Optic Tunable Filter, PL=Plan-convex Lens, OC=Oil Condenser, OL=Objective Lens, M=Mirror, OM=OptoMask, FM = Flip Mirror, CCD=Charged-coupled Device, DAQ= Data Acquisition Board, PMT= Photon Multiplier Tube. Right: a) Semi-log plots and b) log-log (Bode) plot of scattering intensity amplitude and phase of a single AuNR as a function of frequency. The red line is calculated results from model fitting, and the black squares are experimental data. c) Randles equivalent circuit of the electrochemical cell used in the present work.

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Development of a Poly(methacrylic acid)-co-Poly(3,4-ethylenedioxythiophene) Molecularly Imprinted Polymer Sensor for the Electrochemical Detection of 17β-estradiol-An Estrogenic Endocrine Disrupting Compound

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Abstract

The interference of the endocrine system by endocrine disrupting compounds (EDCs) in the daily functions of the endocrine system possesses a threat to the proper functions of the processes that are essential for development, reproduction and the immune system in both humans and wildlife evidenced through morpho-anatomical modifications or expression of femi- nine protein marker in male fish. This study reports for the first time the development and characterization of a molecularly imprinted polymer (MIP) sensor for the detection of 17 β-estradiol an estrogenic endocrine disrupting compound (eEDC), based on the copolymer poly (Methacrylic acid)-co-poly (3,4-ethylenedioxythiophene). The sensor was prepared by chemical polymerization of methacrylic and 3,4-ethylenedioxythiophene monomers in the presence of 17 β-estradiol. The removal of the template molecule from the copolymer matrix resulted in the MIP sensor denoted PMAA-co-PEDOT/Au. The structural properties of the MIP were determined by Fourier transform infrared spectroscopy (FTIR) and high-resolution scanning electron microscopy (HRSEM). The electrochemical behaviour of the MIP sensor was investigated using differential pulse voltammetry (DPV) by comparing the current response between the MIP in the presence and absence of the target analyte. The MIP sensor showed a limit of detection (LOD) of 6 pM, a dynamic linear range (DLR) of 1-10 pM and sensitivity of $1{,}25\times10^{-7}$ µA/nM with a good selectivity for 17 β-estradiol detection.

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Colloidal synthesis of $ReSe_2$ nanomaterials and their carbon nanocomposites for applications in hydrogen evolution reactions

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Transition metal dichalcogenides (TMDs) have been at the forefront of exciting research in the last decade or so. These are layered materials with a general formula MX_2 where the M is a transition metal and X is a Chalcogen. The individual layers are composed of a thin layer of transition metal that is sandwiched between two chalcogen atom layers, the transition metal is covalently bonded to the chalcogen atoms while the layers are connected by weak van der Waals forces [1]. These materials have interesting properties that can be used for applications in energy generation and storage, sensors and in electrocatalysis. They could potentially replace the precious and expensive metal platinum as an electrocatalysts in the hydrogen evolution reaction (HER) which is used to produce hydrogen [2]. Unfortunately, these materials have thus far been difficult to produce at large scale. This is due to the challenges faced in producing these materials using the traditional methods such as exfoliation methods, chemical vapor deposition and hydrothermal synthesis. In this work colloidal synthetic methods are explored for their potential for the large-scale synthesis of these materials. Colloidal synthesis could also be used to design more effective catalyst by altering the properties of the TMD nanomaterials, this is done by altering the reaction parameters such as temperature, surfactant and reagent concentration to control the size and morphology of the nanomaterials. This synthetic method can be used to design TMD electrocatalysts that maximise edge site exposure that have been determined to be the active site for HER. This can be done by synthesizing the electrocatalysts in a morphology that maximizes exposure of the active edge sites. The TMDs $ReSe_2$ was synthesized and characterized for possible application in HER. The $ReSe_2$ nanomaterials of different morphologies was obtained by varying the surfactants/capping agents in the synthesis of the materials. The nanoflower like morphology seen in Fig. 1(a) was synthesized using oleic acid as the capping agent and the nanosheets/nanoplates morphology as seen in Fig. 1(b) was synthesized using oleyl alcohol as the capping agent. The electrochemical performance of the electrocatalyst was evaluated using linear sweep voltammetry and cyclic voltammetry to determine parameters to conclude on the performance of the electrocatalysts such as the onset-potential, exchange current density and Tafel slope.

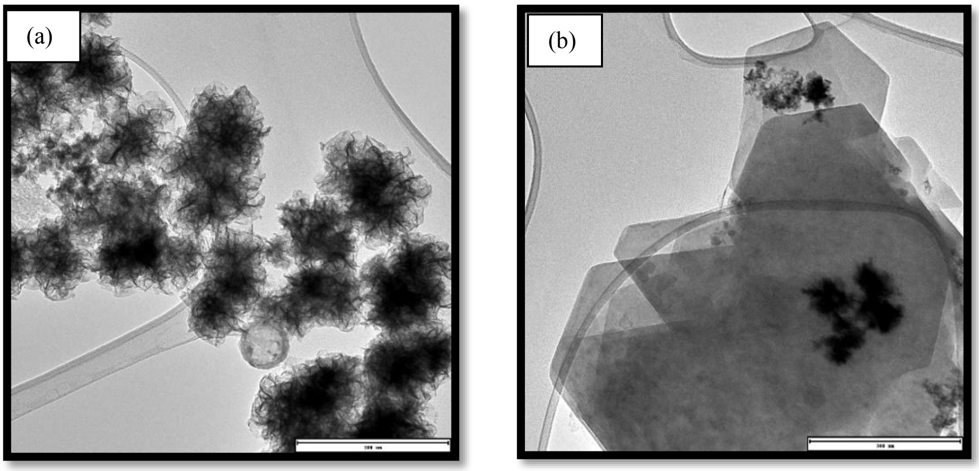

Figure 1: TEM images of $ReSe_2$ nanomaterials with (a) nanoflower like morphology (b) nanosheet morphology.

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Polyhydrazide Architectures for (bio)Sensing Applications

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Versatile platforms for fast screening of polymeric architectures in (bio)sensing applications are required to speed up the discovery process and device development. At the current time, the screening of sufficiently large numbers of functional polymers, that may work either as receptors or as components of the surface interface for biomolecule immobilization is hindered by long syntheses and characterization times. To address these issues we have synthesized different polymeric structures comprising hydrazide side-chains or end-groups and investigated their suitability as scaffolds towards functional polymers for (bio)sensing applications.

Hydrazides are versatile functional groups and can be easily functionalized with a variety of chemistries, particularly "click" chemistry with aldehydes[1,2] and ketones, coupling with carboxylic acids etc. Hydrazides also display an oxidation peak in electrochemical measurements, allowing for the direct use of these scaffolds as sensors for carbonyl groups present in oxidized biomolecules[3].

Herein, polyhydrazide architectures were tested for development of electrochemical sensors for the detection of carbonyl groups in proteins subjected to oxidation by reactive oxygen species. We present the synthesis and characterization of poly(4-ethynylbenzohydrazide) via the rhodium catalyzed polymerization of a Boc-protected monomer (Fig. 1), its reactivity towards a range of aldehydes that can aid immobilization and interaction with biomolecules.

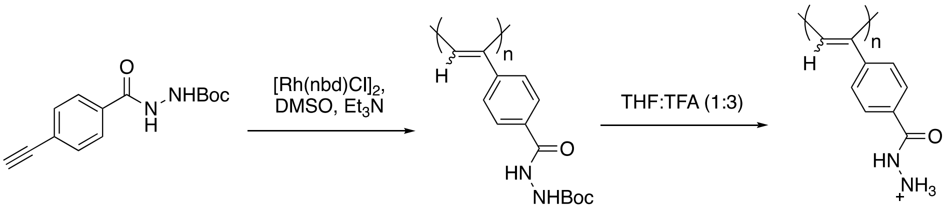

Figure 1: Synthesis of poly(4-ethynylbenzohydrazide)

Electrodes' surfaces modified with poly(4-ethynylbenzohydrazide) and/or some of its derivatives were characterized by electrochemistry, Fourier-transformed infrared spectroscopy, surface plasmon resonance and imaged by scanning electron microscopy. Native and oxidized BSA was used as a model protein in order to investigate the capability of the hydrazide moiety in the polymeric chain to detect some oxidative damages, showing its potential use as a sensor for carbonyl groups.

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Development of Transition Metal Oxides as Possible Photoelectrodes for Fuel Cells

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ABSTRACT

A green and renewable energy generation initiative has sought to have alternative form of energy sources apart from usage of fossil fuels. This is in order to reduce carbon footprint in the atmosphere and thus minimise the effects it has on the climate, most especially global warming. Fuel cell technology is one of the renewable energy sources that helps in the quest to eradicate the adverse effects of fossil fuels. This technology uses hydrogen as its fuel to generate clean energy as it forms water as the product. However, the catalytic components in fuel cells are usually made up of noble metals, which may render this technology expensive to operate. Thus, there is a need to develop catalytic components, which are cost effective while they possess similar catalytic activity as those of the noble metals. These alternative catalytic components include, among others, transition metals and/or their oxides such as titanium(IV) oxide. Metal oxide nanoparticles of CuO were synthesised by following "solvent-deficient" [1] and a modified co-precipitation [2] methods. The CuO nanoparticles were characterised with SEM, XRD, ATR-FTIR and CV techniques. Other metal oxide nanoparticles, which include ZnO, Fe_2O_3, FeO, CoO, MnO, NiO, Cr_2O_3 and WO_3 will be prepared and characterised by the same methods and techniques. In this presentation we will focus on the electrochemistry, spectroscopy and morphology of nanoparticles synthesised by "solvent-deficient" and co-precipitation methods.

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Label-free electrochemical immunosensor for sensitive detection ochratoxin A in coffee

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A novel label-free electrochemical immunosensor for sensitive quantitative detection of ochratoxin A (OTA) was reported. A two-step reaction was elaborated to modify carbon felt electrode (CFE). The electrode was first modified with palladium nanoparticles (PdNPs) by atomic layer deposition (ALD). Anti-OTA was then immobilized on this electrode by the use of carbodiimide chemistry. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used for the characterization of each step of the immunosensor. Electrochemical studies show that PdNPs provide the increased electroactive surface area for loading of anti-OTA and the improved of the electron transport between the anti-OTA and the electrode. Under the optimum condition, the immunosensor showed a linear relationship between 0.5-20 ng/mL ($R^2 = 0.996$) with a low detection limits of 0.096 ng/mL, making it applicable to control OTA in different food product. The developed immunosensor was utilised to detect OTA in spiked coffee samples.

Keywords: Electrochemical immunosensor, ochratoxin A, carbon felts, palladium nanoparticles, Atomic Layer Deposition

Medicinal electrochemistry of biologically active pterocarpanquinones

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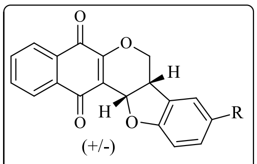
Electrochemical methods are considered useful tools for simulations of biological (i.e. metabolic) redox reactions. In fact, a major bottleneck in metabolic profiling remains, regards the detection and identification of active metabolites in complex mixtures. Metabolically active sites, i.e., positions at which the drug is prone to suffer oxidation or reduction, can be rapidly elucidated through electrochemical/computational investigations and possible metabolites can be directly identified. The majority of these intermediates are formed after oxidation of the parent compound or reduction followed by elimination, to generate an electrophilic intermediate, which subsequently can react with nucleophilic groups in cellular biomacromolecules such as lipids, proteins and DNA.

We, herein, investigated the electrochemical behavior of halogenated and nitropterocarpanquinones, in aprotic media (DMF + $TBAPF_6$), at glassy carbon electrode, in the absence and presence of oxygen in order to obtain data regarding its reduction mechanism, reactivity with oxygen, the analysis of the stability of the electrogenerated intermediate and interactions with biological targets, like DNA. Spectroelectrochemistry was used to shed light into the reduction mechanism. The electrochemistry of LQB118, active against melanoma growth *in vivo* was earlier reported.[1] LQB's 149, 150 and 151 (Figure 1) were shown to be active against human leukemic cell lines (K562 and HL-60), especially LQB-149.[2] LQB-151 is a promising compound for chemotherapy to treat toxoplasmosis. It inhibited *T. gondii* growth in LLCMK2 cells with IC_{50} value lower than 1 μM.[3]

LQB-118, LQB-150 e LQB-151 present similar voltammetric behavior (Figure 2), while LQB149 shows difference, due to the presence of the nitrofuncionality, reduced at the potencial of the second wave. This fact is corroborated by spectroelectrochemistry (Pt electrode), which UV spectrum does not show the characteristic bands of the electrogeneraated quinonemethides (figure 2).[1] The products of the electroreduction of pterocarpanquinones have been shown to react with oxygen (Fig. 3), indicative of ROS generation and explaining, in part, their reported cytotoxic effects.The biological data are correlated with the electrochemical parameters. Computational results also corroborated electrochemical data.



LQB-118- R = H
LQB-149 - R = NO_2
LQB-150 - R = Br
LQB-151 - R = Cl

Figure 1. Structures

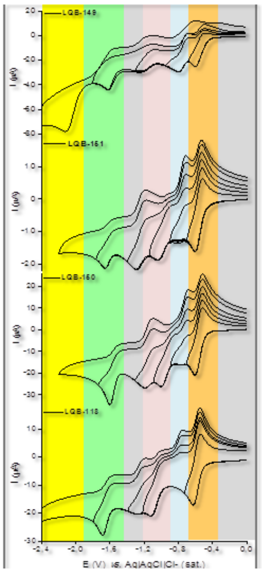


Figure 2. CVs

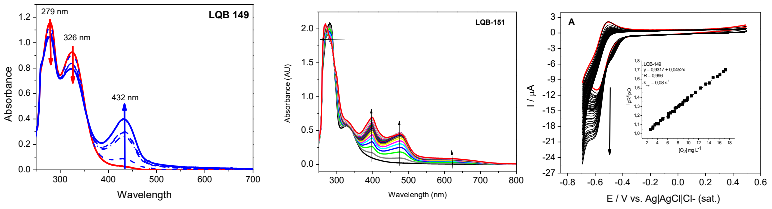


Figure 3. Spectroelectrochemistry and interaction with oxygen.

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P-doped Hive-like Carbon Derived from Pinecone Biomass as Efficient Catalyst for Li-O2 Battery

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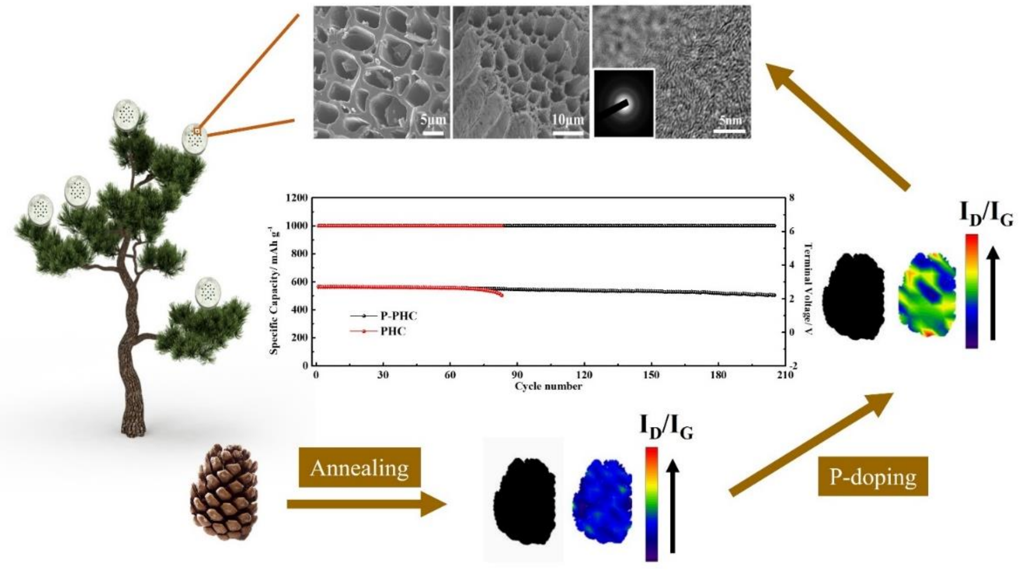
Development of energy storage materials with high energy density to fulfill the demand of next generation batteries is a blistering topic under immense debate. In this content, metal-air batteries walk into the horizon of energy filed. Among them, non-aqueous Li-O_2 batteries attract more and more attentions owing to their exceeding theoretical energy density (3500 Wh/kg), almost 10 times higher than that of traditionally Li-ion batteries. Nevertheless, there is still a long way to achieve practical applications of Li-O_2 batteries in reality, because of many grim barriers including low cycling stability and high polarization, causing the early death of the battery. In a typical Li-O_2 battery, Li metal anode and porous air cathode are separated by separator impregnated with Li salt containing electrolyte. The operation of Li-O_2 batteries depends on the formation of Li_2O_2 via discharging and the reverse decomposition of Li_2O_2 via recharge. Therefore, the performance of Li-O_2 battery depends on the reversibility of Li_2O_2. Moreover, during the discharge/charge process, the reaction among Li^+, O_2 and Li_2O_2 happens on the surface of catalyst. Hence, constructing unique structure and active sites of cathode catalyst would achieve a predominant electrochemical performance.

In this work, discarded pinecones, which collected from the campus, were used as the raw materials for the preparation of metal-free P-doped pinecone-derived hive-like carbon (P-PHC) catalyst for Li-O_2 batteries. This P-PHC has hive-like porous structure which offers enough space for O_2 diffusion and Li_2O_2 deposition. Without P doping, pinecone-derived hive-like carbon (PHC) could only deliver a discharge capacity of 16800 mAh g^{-1} under current density of 100 mA g^{-1} and a stable roundtrip performance of 80 times under a limited capacity of 1000 mAh g^{-1}. After the P doping, the catalytic activity enhanced quite much, thereby obtaining a discharge capacity of 26300 mAh g^{-1} under current density of 100 mA g^{-1} and a durable cycling stability of over 200 times under a limited capacity of 1000 mAh g^{-1} at current density of 0.5 A g^{-1}. Moreover, ex-situ SEM images demonstrate the tubular of P-PHC is not blocked by Li_2O_2 and the porous structure is still remained during the discharging process.

Keywords: Li-O_2 battery; Pinecone-derived; hive-like porous carbon; biomass; P-doping



Bacterial cellulose-based microbial fuel cells

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Microbial fuel cells (MFCs) utilize organics in wastewater as fuel to produce electricity. A plethora of organic molecules simple or more complex have been successfully degraded by MFCs. In principle, MFC is a very low cost technology that can be used to ubiquitously supply energy from cheap resources. However, many efforts are still needed to make MFCs competitive with other fuel cell technologies while keeping the cost of material low.

Electrode materials and binders have the highest impact on MFC cost and delivered power. Initially, electrodes materials and catalysts were inherited by the more mature technologies of proton exchange membrane fuel cells (PEMFCs) or alkaline fuel cells (AFCs) and often platinum was used as cathode catalysts. As the power produced by an MFC is 3-5 orders of magnitude lower compared to PEMFCs or AFCs, the utilization of precious material with extremely high cost is illogical and hinder the potential for large-scale commercialization. Moreover, it has been shown that platinum is easily poisoned in presence of pollutants and its durability is questionable. In the past years, platinum has been substituted with carbonaceous materials or platinum group metal-free catalysts that have been shown to be more durable, have relatively high electrocatalytic activity towards ORR in neutral media and be certainly more affordable. Polytetrafluoroethylene (PTFE) is the most used due to its hydrophobic properties that enhance the three phase interface (TPI) and its capability of binding with the carbon particles on the electrode. Also PTFE is an important cost while preparing large-scale electrodes.

Cellulose as the most abundant material on the planet earth has an extreme potential to be used as a great and cheap precursor of high cost constituents of MFC especially electrodes. In this study, for the first time, we report about binder-free three dimensional composite electrodes based on low cost and highly available bacterial cellulose (BC). The decoration of BC with nanostructured carbons (like carbon nanotubes), conducting polymers (like polyaniline and polythiophenes) is here exploited to design bio-anodes and air-breathing cathodes of membraneless, single chamber MFCs. The results of the electrochemical and morphological characterizations of the proposed electrodes are here discussed. The data are compared with those obtained from conventional electrodes featuring high surface area carbon and Teflon binder. Our work aims at giving new directions for the design of cheap, durable and high performance MFCs.

Acknowledgments

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Molecular Stop-Motions: Unravelling Transient Electrochemical Phenomena at the Millisecond Timescale using EC-MS

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The electrochemical carbon dioxide reduction reaction (CO_2RR) allows the storage of energy in readily available chemicals such as ethylene and other hydrocarbons, while contributing to the abatement of CO_2. Copper is the only pure metal able to perform CO_2RR with appreciable activity and selectivity towards multi-carbon products, especially when the electrode is nanostructured and derived from an oxide. Interestingly, when the Cu catalyst undergoes sudden potential changes, transient phenomena arise showing that the long-term activity and selectivity of the catalyst is not always reflected on the sub-second timescale. The lack of techniques that can probe the electrochemical performance in a time-resolved fashion prevents the detection of phenomena that can give a remarkably different picture of working catalysts. Here, we study Cu electrocatalysts using ultra-sensitive time-resolved electrochemistry and mass spectrometry (EC-MS) to reveal hidden transient phenomena during CO_2RR and HER.

Oxide-derived copper (OD-Cu) electrodes exhibit activity and ethylene selectivity higher than pristine copper during the carbon dioxide reduction reaction (CO_2RR), whereas methane production is suppressed.[1] However, by exposing pristine Cu nanoparticles to gaseous dioxygen (O_2), while resting the working electrode at 0.0 V vs RHE, a reproducible, high transient production of CH_4 is seen at the onset of constant-potential CO electroreduction (Fig. 1).[2] Interestingly, this transient behavior is not observed on H_2 or C_2H_4, which indicates that only the reaction pathway towards single-carbon reaction products is affected. With DFT we show that O weakens the binding for *CO on both kink and step sites, whereas *CHO is stabilized on step sites and destabilized on kink sites. Thereby the kink sites, which were previously inaccessible to CH_4 production, get activated.

In a second experiment, when cycling the potential of a Cu electrode between -0.3 to 0.45 V vs RHE, a surprising double feature appears in the H_2 formation on the electrode. At cathodic potential, H_2 evolves as expected due to HER, while scanning the potentials anodic of the reversible hydrogen potential, a second desorption of gaseous H_2 is observed.[2] This is surprising as the reduction of water to H_2 is thermodynamically prohibited at such anodic potentials. We propose that H_2 may be released through a surface replacement reaction, where adsorbed hydrogen species are replaced with surface adsorbed OH, once the latter becomes more energetically favorable.

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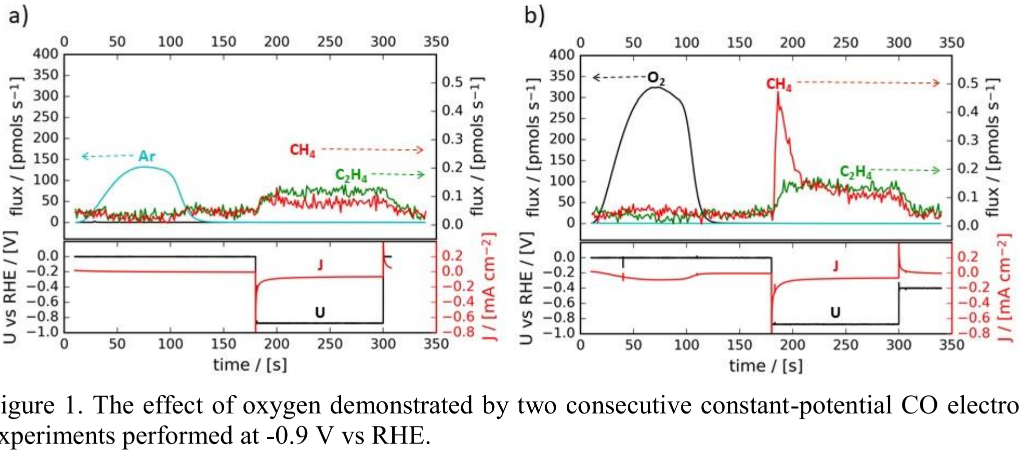

Figure 1. The effect of oxygen demonstrated by two consecutive constant-potential CO electroreduction experiments performed at -0.9 V vs RHE.

Electrochemical Detection of Glucose from Whole Blood using CuS Modified Screen Printed Electrodes

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Blood glucose monitoring has attracted extensive attention because diabetes mellitus is a worldwide public health problem. Glucose is the major energy source in cellular metabolism and plays an essential role in the natural growth of cells. On the basis of the statistics of the World Health Organization, about 300 million people suffered from diabetes in the year 2010; this number is estimated to almost double in 2030 [1]. Therefore, the availability of a rapid, simple, cheap, disposable, easy to use, in-situ whole blood assay testing platform for clinical diagnosis, especially in developing countries, resource limited and remote region, would greatly benefit point-of-care or public health applications. Electrochemistry technology was considered as a replacement for the spectrophotometer, based on the desire to reduce expensive equipment and construct portable near patients devices [2]. Chemically modified screen printed electrode technology provided a new turning point for biochemical determination technology [3]. The non-enzymatic glucose sensor based on direct electrocatalytic oxidation of glucose by chemically modified electrodes would exhibit convenience and advantage, not only to eliminate the problem of maintaining stability during enzyme preservation, but also reducing the cost of supplying enzymes [4].

In this work we report on electrochemical detection of glucose in blood on in house produced screen printed electrodes (SPEs) modified with CuS nanoparticles. Blood was collected using Venipuncture procedure and blood samples were spiked with various standard glucose concentrations before analysis. We investigated the electrocatalytic activity of CuS modified SPE towards detection of glucose in blood using cyclic voltammetry (CV). The oxidation potentials and the comparative current response are shown in table 1. The modified SPE's were further used in electroanalysis of glucose in blood samples using Chronoamperometry and interference studies were also conducted.

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Nanostructured Materials with Boosting Efficiency for Hydrogen Evolution

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Water electrolysis is a promising approach for large-scale and sustainable high-purity hydrogen production. While, its reaction kinetics is slow and requires precious metal electrocatalysts to boosting the catalytic efficiency. Both the design and synthesis of low-cost and high-performance electrocatalysts for hydrogen evolution reaction (HER) remain challenging.

In recent two years, we focus on developing novel nanostructure electrocatalysts for HER, such as carbon-encapsulated WO_x hybrids (WO_x@C), N-doped porous molybdenum carbide nanobelts, S and P co-doped Cu nanowire arrays, CoNi (oxy) hydroxide nanosheets, flower-like P-doped CNTs encapsulated nickel hybrids, boron-doped RhFe alloys, worm-like S-doped RhNi alloys, 3D-graphene anchoring FeP nanoparticles and so on. The synthesized materials displayed excellent catalytic activity for hydrogen evolution, and some also can be used as bifunctional electrocatalysts for full water splitting.

The improved activity and active origin of the as-prepared electrocatalysts are clarified through experimental analysis and DFT calculation. These works provide a facile approach to design cost-effective electrocatalysts with high efficiency and excellent stability for electrochemical applications.

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Influence of Benzyl Alcohol Addition on the Photocurrent of TiO_2-CNT Thin Film Electrode Prepared by Sol-Gel Dip Coating

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1, Introduction

Titanium dioxide (TiO_2) is a widely used as a photocatalysis in many different areas including surface self-cleaning, air/water purification, and solar-to-hydrogen energy conversion systems. A large-scale application of these systems requires a TiO_2 film production process of simple, reliable and low cost. And, increase of active area for photocalatysis is significant for increasing the photo-catalytic efficiency. To develop these properties, we have so far investigated on preparation of carbon nanotube (CNT)–TiO_2 thin films electrodes by several methods using sol–gel reaction. However, the low affinity of hydrophobic surface of bare CNT with hydrophilic TiO_2 sol limit the photo-catalytic efficiency [1]. Then, in our laboratory, utilization of additives including benzyl alcohol, which is able to interact both TiO_2 and CNT surfaces[2] have been investigated. In this preparation, we discuss on the effect of benzyl alcohol on the catalytic activity of TiO_2-CNT thin film electrodes, prepared by the sol-gel dip coating method, for hydrogen production.

2, Experimental

The coating solutions were prepared with 3 mL of titanium butoxide, 15 mL of 2-propanol, carbon nanotube (CNT) and benzyl alcohol (BA). Here, the concentration of CNT used in the coating solution ranged from 1 to 4 wt%, and the amount of BA was 0 mL to 3.27 mL. The Indium-tin oxides glass substrates were washed with 2-propanol, distilled water and ethanol in an ultrasonic bath, and dried by blowing nitrogen. The substrates were dipped in the coating solution, and withdrawn vertically to the surface of the solution at a speed of 10 mm/s. The film was dried for 30 min in air at room temperature, and finally the films were annealed at 450℃. The surface morphology of the thin films was analyzed by scanning electron microscopy. Photoresponse of the films electrodes were investigated in 1 M Na_2SO_4 with illuminating the samples with a 100 mW/cm^2 xenon lamp of AM 1.5.

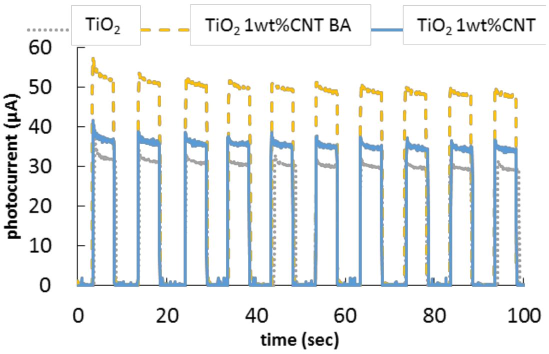

Fig. 1 Photoresponse of TiO_2-CNT electrode with BA, TiO_2-CNT electrode without BA, and TiO_2 thin film electrodes. Potential: 0.245 V vs. Ag/AgCl, electrolyte: 1 M Na_2SO_4. Conter electrode: Pt.

3, Results and discussion

As a result, the TiO_2 film is observed to coat wholly on CNT surface with coating solution at the best composition, and the largest photocurrent is observed. Fig. 1 shows the photoresponse of the film electrodes. From the figure, the electrode prepared with BA and CNT show photocurrent 1.5 times higher than that without BA and that without both BA and CNT. This is considered to be because BA adsorbs at the CNTs' surface via π–π interactions with its benzene ring, while at the same time providing hydrophilic hydroxyl groups for the hydrolysis of the titanium precursor[1]. In the presentation, the effect of the concentration of BA on the photocurrent will be also discussed in detail.

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Evaluation of the potential of MAX phases as alternative supports to carbon black in PEMFC's

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Power generation in the world is currently dominated by the use of non-renewable sources of energy such as coal, crude oil and other fossil fuels. The use of these fossil fuels as primary sources has resulted in climate change. It has become imperative to explore more environmentally friendly power-generation technologies that use renewable sources of energy and one such technology is the fuel cell. Proton exchange membrane fuel cells (PEMFC) in particular produce clean energy, with no greenhouse gases released to the atmosphere.

Platinum and platinum alloys have been found to be the catalysts of choice for use in fuel cells while carbon black is the most vastly used electro-catalyst support (Sharma & Pollet, 2012). The challenge with the Pt/C catalyst is that the carbon is prone to oxidation under the operating conditions of the fuel cell, which depletes the functionality of the fuel cell (Sharma & Pollet, 2012). This deems the Pt/C catalyst unfavourable for large scale use to meet energy demands. Alternative electro-catalyst support materials need to be explored, and one promising material is MAX phases. MAX phases are made up of a transition metal (M) carbide or nitride (X) with group 13-16 metals (A) interleaved in the MX layers (Barsoum & Radovic, 2011). MAX phases combine the best properties of metals and ceramics, with the most relevant to PEMFC's being high electrical conductivity, high oxidation resistance and a large surface area (Barsoum & Radovic, 2011) .

The aim of this study is to evaluate the potential of MAX phases as alternative supports to carbon black using the most researched MAX phases; Ti_2AlC, Ti_3AlC_2, and Ti_3SiC_2. These were synthesised by pressureless sintering of commercial elemental powders using an induction furnace. The MAX phases were characterised using X-ray diffraction (XRD) and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS). It was found that pressureless sintering produces MAX phases with impurities mostly composed of titanium carbide and Ti-Al intermetallic. The intermetallic may aid conductivity, while the titanium carbide may decrease it. Platinum catalyst nanoparticles were deposited onto the prepared MAX phases using an in-house developed thermal decomposition method (Jackson, Conrad & Levecque, 2017). The electrocatalytic properties of the Pt/MAX phase catalyst were evaluated using the thin film rotating disc electrode (RDE) technique. Cyclic voltammetry was used to determine the electrochemical active surface area (ECSA) and linear sweep voltammetry under RDE conditions was used to determine the ORR activity. Furthermore, accelerated durability tests simulating load cycling and start-stop conditions were performed to investigate the stability of the catalyst.

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CuAg bimetallic nanoparticles for the electrochemical reduction of carbon dioxide

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Fuels and chemicals that drive the global economy can potentially be produced via the electrochemical reduction of carbon dioxide at room temperature and atmospheric pressure, rather than from depleting fossil resources. As this process requires energy input, intermittent renewable energy such as solar and wind can be coupled to this process, allowing for renewable energy storage via chemical bonds. However, current catalysts that activate the reduction of carbon dioxide are highly unselective and require operation at high overpotentials to produce significant amounts of products [1]. Copper has been the only catalyst that has been identified to produce significant amounts of hydrocarbons and oxygenates [2]. However, for this catalyst, operation at low overpotentials is dominated by the undesired hydrogen evolution reaction [3]. Over a wide range of potentials, it has been shown that the production of H_2 is in competition with CO on Cu electrocatalysts [3]. Transition metals such as Au, Ag, and Zn are stated to reduce CO_2 to a CO-rich stream because of their weak CO adsorption energy [4]. To inhibit the hydrogen evolution reaction at low overpotentials, this study aims to investigate the performance of CuAg bimetallic nanoparticles in the electrochemical reduction of carbon dioxide, and study the effect of Cu/Ag ratio on the product distribution. It is proposed that increasing the Ag content of the CuAg catalyst, would increase the coverage of CO and thus limit the reduction of H^+ ions to undesired H_2.

Cu, Ag, $Cu_{50}Ag_{50}$, $Cu_{20}Ag_{80}$, and $Cu_{80}Ag_{20}$ nanoparticles prepared under ice-cold and inert conditions are characterised using Transmission Electron Microscopy (TEM) and X-ray Diffraction (XRD). The electrocatalytic performance of these nanoparticles supported on a gas diffusion electrode is studied at various potentials, with the gas and liquid phase analysed. The effect of increasing the Ag content in the CuAg catalyst on the product distribution is presented and discussed.

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Anodizing treatments of AZ31 alloys to control corrosion rate

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Metallic materials are widely used for biomedical applications, as repair or replacement materials of the diseased or damaged bone tissue. Compared with traditionally employed stainless steels, titanium alloys and Cr-Co based alloys, magnesium and its alloys show special properties, such as a low density (1.74 – 2.0 g cm^{-3}), an elastic modulus between 41 and 45 GPa, very well matching with that of natural bone. And last but not least, once implanted in vivo the ions and/or particles released as a consequence of corrosion as well as wear processes are not harmful to the body [1]. Therefore, magnesium and its alloys are candidate materials for biodegradable implants for orthopedic applications and vascular stents [2, 3].

However, due to the very low reduction potential and to the poor corrosion resistance in chloride containing environments (as human body fluids or blood plasma), the degradation rate of magnesium and its alloys is so high that the mechanical integrity before the diseased or damaged bone tissue healed is not always maintained. Moreover, since water reduction is the common cathodic process during corrosion of Mg and its alloys, the high corrosion rate implies a high H_2 evolution rate, with consequent detrimental gas pockets formation around the implant, and alkalization occurring in the vicinity of the corroding surface discussed as possibly being deleterious for the surrounding biological environment [4].

The simplest way to slow down corrosion is to form a coating on the magnesium substrate to provide a barrier toward the contact between the substrate and the environments. There are many coating technologies which can be used to coat the magnesium substrate, such as electrochemical plating, chemical conversion coating, physical vapour deposition, laser surface treatment and anodic oxidation. Among these technologies the latter is one of the most effective and popular methods, even if the growth of protective anodic layers on Mg and Mg alloys is difficult due to the unfavourable Pilling-Bedworth ratio for MgO.

In the present work, we studied the anodizing of AZ31 alloys in different conditions going from soft sparking regime to plasma electrolytic oxidation. Scanning Electron Microscopy, Energy Dispersive X-ray Spectroscopy and X-ray diffraction (XRD) were employed in order to assess the effect of electrical parameters (d.c or a.c. current, final formation voltage, waveform, etc.), bath composition and temperature on the structure and composition of the resultant films. In the attempt to seal the pores of the anodic layers and to improve their biocompatibility, the growth oh Hydroxyapatite (HAP) on the samples surface was induced by a deep coating procedure. The successful formation of HAP was confirmed by SEM observation, EDS and Raman analysis.

The corrosion resistance of the resulting composite coatings was characterized in Simulated Body Fluid at 37°C by Open Circuit Potential (OCP) measurements, Electrochemical Impedance Spectroscopy (EIS) and by recording polarization curves. All the experiments proved a small shift of the corrosion potential toward more anodic values, a strong increase of the polarization resistance and a reduction of the corrosion current density, i.e. of the hydrogen evolution rate.

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Scanning electrochemical microscopy: in-situ studies of photocatalytic processes at modified carbon nanomembranes

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The development of new and alternative ways for renewable energies, among those the splitting of water into hydrogen and oxygen by solar energy, is of high research interest. Besides semiconductor materials, e.g., titanium dioxide, molybdenum disulfide (MoS_2) etc. as abundant and cheap alternatives to Pt for hydrogen evolution reaction (HER), light-driven molecular catalysts inspired by nature have attracted significant interest for water splitting. However, there are still problems, such as long-term stability, reversibility and integration in suitable materials that need to be addressed. Spatially resolved information on catalysts using electrochemical scanning probe techniques such as scanning electrochemical microscopy and scanning electrochemical cell microscopy have been recently demonstrated[1, 2]. For example, SECM has been used to measure the hydrogen evolution reaction at $BiVo_4$ based photo catalyst arrays, and MoS_2/GO nanocomposite materials and also at Ni[3, 4, 5].

Within this contribution, we present an adapted SECM setup to study photocatalytic processes at the sub-microscopic scale. Local illumination of the sample by means of a blue LED coupled via glass fiber is implemented into the SECM setup. Carbon nanomembrane (CNM)[6] modified with $[Ru(bpy)_3{}^{2+}]$[7] as photosensitizer (PS) will be investigated in respect to hydrogen evolution under illumination. CNM are 2D materials, which are a highly suitable material for integration of molecular photo catalysts[6]. Combined with a HER catalyst, like cobalt-catalyst the production of hydrogen should be advanced by the illumination with blue LED, which can be directly determined with the UME positioned in close proximity to the membrane surface. In addition, SECM is highly suitable to determine electron transfer characteristics at such membranes in dependence of the layer numbers. First SECM investigations for studying such catalytic systems will be presented.

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Highly Sensitive Electrochemical Glucose Sensing Using a Mesoporous Platinum Electrode in Alkaline Solutions

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1. Introduction

Nonenzymatic glucose sensors are attracting attention from the viewpoint of easy to handle and life as compared with enzyme glucose sensors. In our previous study, a mesoporous platinum, which has a lot of high index surface, shows high sensitivity for electrochemical glucose sensing (1). However, there are problems such as the improvement in sensing sensitivity and the influence of interfering species.

Various solutions such as NaOH, H_2SO_4, Phosphate Buffer, etc. can be used as an electrolyte of nonenzymatic glucose sensing. In this work, we examined the sensing sensitivity in glucose sensing using mesoporous platinum electrode in alkaline solution in comparison with acidic solution.

2. Experiment

To make the mesoporous platinum electrode, a potential of -0.1 V was applied to the platinum electrode (diameter: 1.6 mm) in a solution of 20 mM potassium tetrachloroplatinate (II) (K_2PtCl_4) containing 1 wt% Brij 58 ($C_{16}EO_{20}$). In order to regulate the amount of platinum, platinum ion was electrodeposited with a charge amount of -1.98 mC. After the deposition, it was immersed in ethanol for 18 hours, and the surfactant was removed to give a mesoporous structure. Charge transfer resistance (R_{ct}) was measured by electrochemical impedance spectroscopy (EIS). Electrochemical measurements were carried out in three electrode cell using an Ag/AgCl electrode for the reference electrode, a Pt wire for the counter electrode and a mesoporous platinum electrode for the working electrode.

3. Result and discussion

Table 1. 5 mM glucose peak current density and charge transfer resistance R_{ct} comparison between NaOH and H_2SO_4. Electrolyte concentration: 50 mM.

Electrolyte	Substance	Peak current density (mA/cm²)	R_{ct} (Ω・cm²)
NaOH	Glucose	4.85	12000
H_2SO_4	Glucose	0.12	32000

The sensitivity of glucose sensing improves in alkaline solution compared with acidic solution (Table 1.). For this reason, highly reactive mutarotation abundance ratio for glucose oxidation is larger in alkaline solution than acidic solution (2). It is known that mutarotation of glucose has α and β anomers. The hydrogen atom at C-1 of β anomer is easily activated. In alkaline solution, abundance ratio of β anomers is larger than acidic solution. Also, charge transfer resistance (R_{ct}) was decreased. Therefore, glucose sensing performance was improved in alkaline solution.

The mutarotation of glucose is a slow process. This process is distinguished in alkaline and acidic solutions. Fig.1. shows that the time effect of glucose sensing sensitivity in alkaline solution. From this result, it can be seen that anomers having a high reactivity exists in alkaline solution for a long time.

In this way, it is possible to try to improve the sensing performance by the electrolyte in addition to the electrochemically active surface area (ECSA).

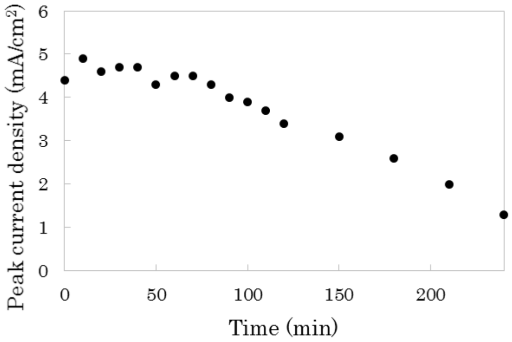

Fig.1. Time effect of peak current density of glucose oxidation in alkaline solution.

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Development of three - electrode type lactic acid sensor with flow path for continuous monitoring of perspiration

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It is desirable to develop a novel method to remove old sweat from surface and constantly supply a new sweat on the electrode surface in order to detect changes in lactate concentration in sweat in real time using a wearable electrochemical biosensor [1], [2]. In this study, we aimed to prepare and evaluate a printed type three-electrode type lactic acid biosensors with flow channel for continuous monitoring of lactic acid concentration in sweat.

A screen-printed three-electrodes were fabricated on a PET film by screen printing. 1, 2-naphthoquinone and lactate oxidase was immobilized on the working electrode surface with a chitosan nanofiber to form the lactic acid biosensor. A non-woven cloth was used as a flow channel. Fig.1 shows structure of the newly fabricated lactate biosensor The nonwoven fabric and the water repellent tape are stacked on the printing type electrode. The artificial sweat containing lactate reaches the working electrode via the nonwoven fabric, and the solution diffuses to the counter electrode by the capillary phenomenon of the nonwoven fabric. The sweat gradually passes through and then flows out of the nonwoven fabric by its own weight.

A pulse chronoamperometry was performed while supplying the measurement solution to each electrode. In the measurement, the potential was stepped to 0.5 V at which the catalytic oxidation reaction occurres sufficiently from - 0.1 V at which the oxidation reaction of lactic acid does not proceed. After that, it was held at 0.5 V for 30 s and returned to -0.1 V. While repeating the pulse chloroamperometry, artificial sweat containing different lactic acid concentrations were continuously dropped onto the sensor.

Fig. 2 shows the chronoamperogram when the lactic acid concentration supplied on the electrode was changed to 1, 3, 5, 3 and 1 mmol dm^{-3}. As you can see, the current values corresponding to the lactate concentration were clearly measured repeatedly. By using this technique, a current value due to the lactic acid concentration could be clearly detected since the baseline is clarified by applying the electric potential in a pulse form. This method allows not to leave a history of lactate and it is possible to monitor the concentration of lactic acid high reproducibly and high precisely.

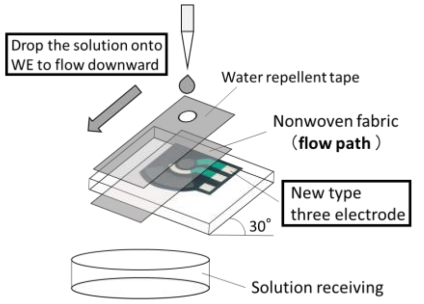

Fig.1 Structure and experimental setup of the lactate biosensor

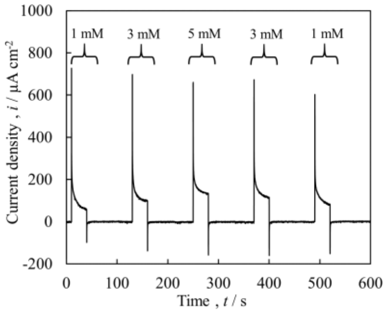

Fig. 2 Continuous measurement with varying concentration of lactate

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Fabricated a Screen-printed Paper-based Glucose Biofuel Cell Array for Self-Powered Diaper Sensor

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We have reported a paper-based glucose biofuel cells in which porous carbon materials were printed by screen printing technique [1,2]. The biofuel cell is expected to be applied to self-powered urine sugar biosensor for inspecting diabetes. In this study, for power source of a self-powered diaper sensor, we fabricated a new disk-shaped paper-based biofuel cell array on a diaper. A glucose oxidase (GOD) and glucose dehydrogenase (GDH) were used as enzymes for glucose oxidation catalysts with several mediators. In this abstract, we introduce the typical results of GOD/Tetrathiafulvalene (TTF)-based biofuel cell.

The paper-based biofuel cell anode and cathode were fabricated by screen-printing. The MgO-templated porous carbon ink was printed for bioanode and biocathode. TTF and GOD were modified on the bioanode surface. The biocathode was prepared by modifying bilirubin oxidase (BOD). A single biofuel cell was prepared by stacking the bioanode and biocathode. In addition, a new 6-series biofuel cell array was fabricated by printing the lead layer, resist layer and porous carbon layer in order by screen printing and modifying the mediator and enzyme on all electrodes.

Figure 1 shows the relation between power density and operating cell voltage with different concentration of glucose at 37 °C in the single biofuel cell. It was confirmed that the output power density increased along with increase of the glucose concentration. Finally, the disk-type biofuel cell array showed an open circuit voltage of 3.4 V and a maximum output power of 552 µW in the presence of 100 mM glucose as shown in Fig.2. In addition, it succeeded to directly drive buzzer and LED without any booster circuit.

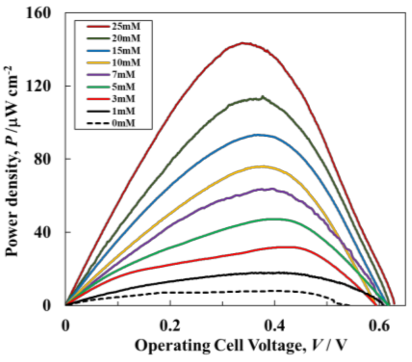

Fig.1 Output power density curve of the biofuel cell for various glucose concentrations (0-25 mM)

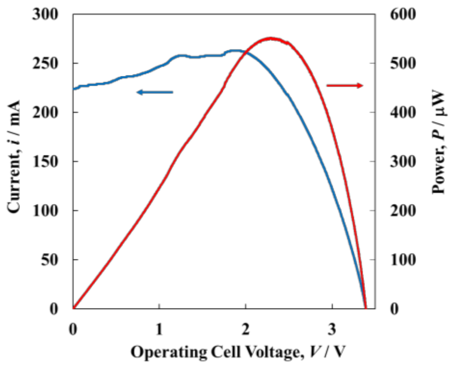

Fig.2 Current-potential and power potential curve of the biofuel cell arrey

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Wearable dial ion sensor in sweat based on heat transfer printing

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A wearable ion sensor for real time monitoring of biomarkers in sweat has attracted attention. For example, wearable ion sensors in sweat based on tattoo paper has been reported [1, 2]. On the other hand, we have reported a new heat-transfer-type printable wearable sodium ion and ammonium ion sensors fabricated on a non-woven cloth substrate that could monitor the sodium or ammonium ion concentration in sweat [3, 4]. In this research, we newly fabricated a dual sensor to perform simultaneous quantitative monitoring of the two ions.

A schematic diagram of the dual sensor is shown in Fig. 1. The electrodes of the sensor were fabricated by screen printing. An ammonium ion selective film containing nonactin was formed on the carbon working electrode 1 (WE 1). In working electrode 2 (WE 2), a sodium ion selective membrane containing sodium ionophore X was formed [3]. For the reference electrode, a solid reference electrode film containing potassium chloride formed on an Ag / AgCl electrode was used. A sensor was formed on a non-woven cloth surface using a heat transfer machine. Responses of the sensor was performed by measuring the open circuit potential (EMF) measurements with changing in the concentration of ammonium chloride and sodium chloride.

Figure 2 shows the EMF of the sensor for ammonium and sodium ion concentrations. The EMF of the sensor for sodium ion concentration was changed in 57.2 mV/log C_{Na^+}. The EMF change of the ammonium ion sensor was 56.7 mV/log $C_{NH_4^+}$. These results indicated that the Nernst response was obtained (90% confidence interval, n = 3). Since the concentration of ammonium ion in human perspiration is 0.1 to 1 mM and the sodium ion concentration is 30 to 100 mM in general, it was suggested that the sensor could be used for the determination of ammonium ion and sodium ion in perspiration.

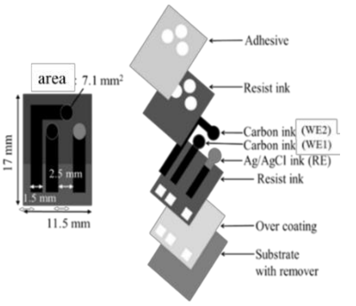

Fig. 1 Schematic diagram of dual ion sensor (left) and Structure schematic diagram of electrode (right)

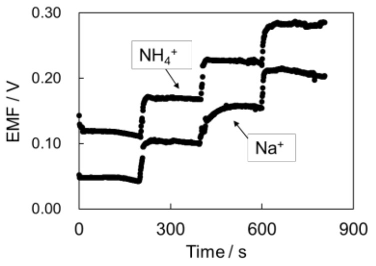

Fig. 2 Dependence of membrane potential on ammonium and sodium concentrations

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High-potential cathodes for sodium-ion batteries: synthesis, study of the intercalation process and improvement of the electrode interface

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Sodium-ion batteries (SIBs) are considered a key technology to implement the wide-scale diffusion of electrochemical energy storage systems thanks to the high abundance and the low-cost of sodium, and its environmentally friendly nature. The electrochemical potential of Na, only 330 mV above that of lithium, makes SIBs a suitable technology for high energy density batteries. However, actual SIBs are characterized by a low specific energy and power, short cycle life, and insufficient specific power, owing to the heavier mass and larger radius of sodium vs. lithium ion. The cathode materials are key components to address such issues and to foster the SIBs mass-marketing production [1-8]. In this work cathodes based on $NaLi_{0,2}Ni_{0,25}Mn_{0,75}O_{\delta}$ (NLNMO) and $Na_2Fe\,[Fe(CN)_6]$ (NFCN) were synthesized from the respective acetates. The syntheses of NLNMO and NFCN are here presented and discussed along with the chemical-physical and electrochemical characterization of NLNMO and NFCN-based electrodes. The sodium deintercalation/intercalation processes were analyzed in $NaLi_{0,2}Ni_{0,25}Mn_{0,75}O_{\delta}$ by X-ray diffraction, highlighting the reduction of the inter-plane distance between the planes occupied by Mn during the sodium ions intercalation. In order to improve the electrode/electrolyte interface, four different electrolytes were tested, consisting of mixtures of ethylene carbonate (EC), propylene carbonate (PC), 1-fluoroethylenecarbonate (FEC) and dimethylcarbonate (DMC) as solvents and $NaPF_6$ as sodium salt. The PC:FEC (95:5) electrolyte mixture has shown, for both the electrodes, an improvement of the electrode/electrolyte interphase properties. The electrochemical impedance spectroscopy was also carried out to evaluate the electrode/electrolyte interface of the NLNMO-based electrodes, after a thin polymer film was electro-deposited on the cathode surface.

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Comprehensive study of the performance of alkaline organic redox flow batteries as large-scale energy storage systems

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Alkaline-based organic redox flow batteries (AORFBs) attract significant interest because they can retain the advantages of vanadium redox flow batteries (VRFBs) while their cost is low because expensive vanadium is replaced with easily synthesizable metal-free organic compounds and earth-abundant raw materials. A comprehensive experimental study on the performance of alkaline-based ORFBs using alloxazine 7/8-carboxylic acid (ACA) and ferrocyanide was conducted to investigate their feasibility as large-scale energy storage systems. Various operating conditions, such as different electrolyte concentrations, flow rates, and temperatures, were tested in this study. The results show that the alkaline-based ORFBs (AORFBs) achieve an energy efficiency above 71% at 80 mA cm^{-2}, which is lower than that of VRFBs (80% energy efficiency) under the same operating conditions. However, AORFBs have a very good thermal stability (≥ 50 ºC) and capacity retention compared to those of VRFBs. Additionally, a large-scale AORFB was constructed and tested to confirm the effectiveness of AORFBs.

Keywords: organic redox flow battery; alkaline; alloxazine 7/8-carboxylic acid; ferrocyanide; energy storage system

Noble Metal Free Materials as Efficient Catalysts for Water Splitting

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Water electrolysis is a promising approach for large-scale and sustainable hydrogen production. However, its kinetics is slow and requires precious metal catalysts to efficiently operate. Therefore, great efforts are being undertaken to design and prepare low-cost and highly efficient catalysts to boost the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Currently, we developed different noble metal free materials as efficient catalysts for HER, OER, and full water splitting.

For HER, the catalysts with novel nanostructures were prepared, such as carbon-encapsulated WO_x (WO_x@C), N-doped porous MoN nanobelts, nitrogen and fluorine dual-doped porous graphene-nanosheets, $K_{0.4}TaO_{2.4}F_{0.6}$ nanocubes, Ni_3S_2 nanowires, TiN nanowires, nanoflower-like MoO_2, *et al.* For OER catalysts, the Mo- and Fe-modified $Ni(OH)_2$/NiOOH nanosheets, nitrogen-decorated iron-nickel sulfide nanosheets, Mo-doped NiOOH nanosheets, tantalum dioxyfluoride, pristine carbon nanotubes, graphene supported MnO_2 nanowires were studied. For full water splitting, the porous WO_2 hexahedral networks, heteroatoms dual doped porous graphene nanosheets, three-dimensional porous $MoNi_4$ networks, porous MoO_2 nanosheets, dye functionalized carbon nanotubes were studied. The synthesized materials displayed excellent catalytic activity for hydrogen evolution, oxygen evolution, and full water splitting, and can be applied as low cost and highly active multifunctional catalysts with excellent ORR and OER performance.

The improved activity and active origin of aforementioned catalysts are clarified through experimental analysis and DFT calculation. These studies pave the way for the design and development of cheaper, highly efficiently and more durable catalysts for wider applications.

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Fabrication of PAN/Fe_3O_4 nanofibers: photocatalysis and characterization antimicrobial properties

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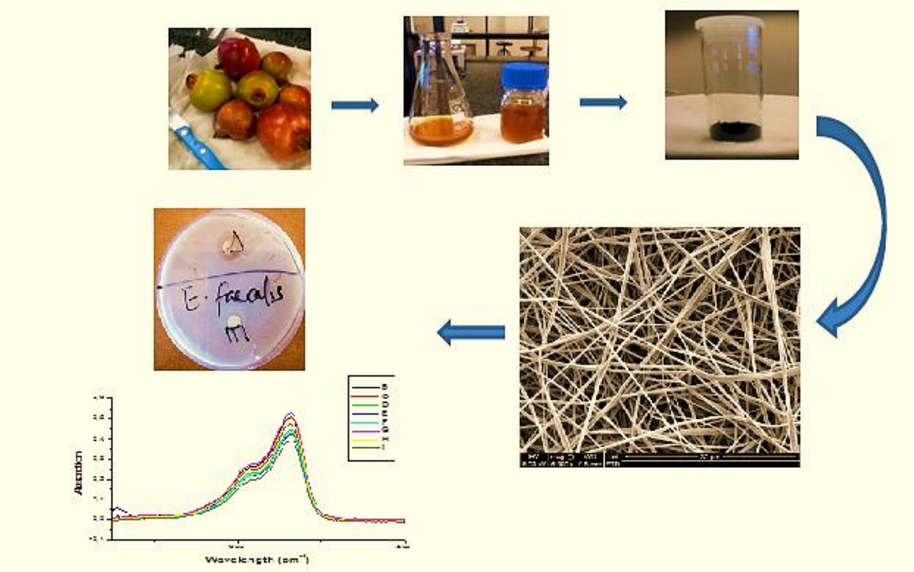

The present study aimed at green mediated synthesized iron oxides nanoparticles from peel extracts from pomegranate peel extract which is of immense medical and biological and environmental value. The synthesized nanoparticles were characterized by using FT-IR, UV-Visible spectroscopy, SEM and TEM. FTIR revealed characteristics peaks for Fe_3O_4 nanoparticles at 3271 cm^{-1} and 1600 cm^{-1} synthesized from peel extract. SEM showed the morphology of Fe_3O_4 NPs to be round in shape. Photocatalytic process exhibited that PAN/ Fe_3O_4 nanofibers composites and Fe_3O_4 nanoparticles increased efficiently towards the degradation of methylene-blue dye, which shown their potential application on waste water treatment. Green mediated Fe_3O_4 NPs exhibited an excellent antimicrobial activity against some selected pathogens conducted by disc diffusion method.

Low-Cost Electrochemical Micro Sensors for Technical Applications and Environmental Monitoring

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Abstract:

Metalloporphyrins and other related N_4-macrocyclic complexes are used as electrocatalysts for the oxidation and reduction of a wide range of molecules and compounds in electrochemistry. Examples of electrocatalytic reactions catalyzed by metalloporphyrins include electrooxidation of, nitric oxide, carbon monoxide, hydrazine, mercaptoethanol, oxalic acid among others, and the electroreduction of oxygen, carbon dioxide, nitrate ions, and cystine among others. Some of the molecules mentioned above are hazardous and their existence in the environment requires routine monitoring. However, wide commercialization of well known functional devices incorporating metalloporphyrins, such as sensors, still awaits the development and design of very active, robust and reliable devices. The mechanism of reactions eletrocatalyzed by metalloporphyrins involves an inner-sphere electron transfer step which precedes, succeeds or occurs simultaneously with an adsorption or desorption step of the electrocatalyzed substrate, its intermediates or the product(s). The strengths of the adsorption or desorption processes clearly influence the kinetics and mechanism of the overall reaction. However, the strengths of the adsorption or desorption processes depend on the nature of the central metal for a given N_4-macrocyclic ligand. Additionally, the strengths of the adsorption and desorption processes can also be varied by redesigning the ligand, for which a variety of strategies are feasible. In this presentation, the effect of variation of the central metal atom on the response of metalloporphyrin electrocatalyzed reactions will be discussed and demonstrated using the electrocatalytic reduction of oxygen, and the electrocatalytic oxidation of Nitric oxide. The dependency of the activity of these reactions on the central metal, for the first raw transition metals, will be graphically shown to yield a volcano shaped plot, whose description is in accordance with the Sabatier principle of heterogonous catalysis, which requires that, neither reactants, their intermediates nor the products should bind either too strongly or too weakly on a catalyst surface for optimal catalysis. This observation is satisfactorily explained using intermolecular

hardness, based on the electrophilicity of the N_4-macrocyclic complex and corroborated by the frontier molecular orbital theory. Systematic criteria will be presented for the selection and design of microsensors for oxygen and nitric oxide as examples to illustrate the broad applicability of these principles.

An anode electrode for high performance water splitting system using copper cobaltite grown on Ni foam

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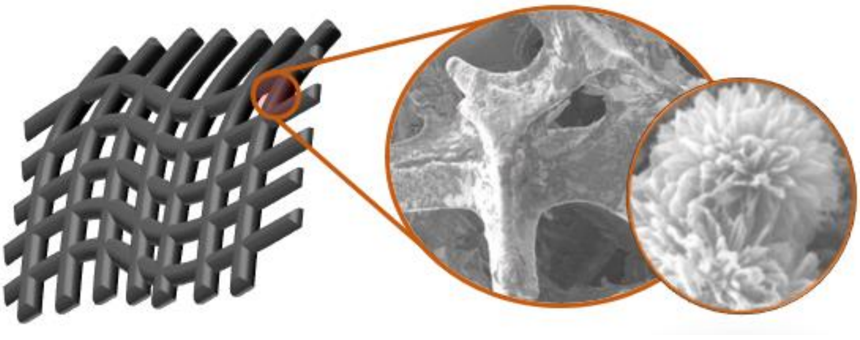
The oxygen evolution reaction (OER) is a fundamental process that is critical for water splitting. Despite the importance of OER, the high overpotential of OER at conventional water-splitting anodes yield slow reaction kinetics and decreased water-splitting reaction efficiency. Generally, precious metal-based catalysts, such as Ir and Ru-group metals, are considered ideal for OER. They allow very low overpotentials with fast kinetics in both basic and acidic conditions. However, although these precious metals are the most effective OER catalysts, their high cost and scarcity are serious problems. Therefore, replacement of precious metal catalysts with abundant and non-precious materials is highly desirable.

Uniquely nanostructured $CuCo_2O_4$ (CCO) is presented as electrocatalysts for OER. To be specific, by directly growing CCO on a Ni-based substrate (Ni foam), chestnut-burr-like shape CCO (CCO* where * = chestnut-burr) with high loading was synthesized by simple hydrothermal method. Chestnut-burrs in 4 µm in average had thorns consisting of less than five threads. Each thread was made of a consecutive array of nano-beads less than 10 nm. Nano-voids or nanopores were found between nano-beads. The chestnut-burr structure of CCO* allowed RuO_2-overwhelming OER activity. By using the hierarchically nanostructured electrocatalyst directly grown on current collectors without binders and conducting agents, high performances of water splitting stack system was demonstrated. We have improved the performance of water splitting system by using directly grown CCO. Three merits of the electrode architecture were emphasized. First, mass transfer pathways for reactants and products were secured in a microscale between thorns and in a nanoscale between nano-beads. Second, more active sites were exposed to electrolyte in the hierarchical structure. Third, direct growth of active materials on conductive substrates improved adhesion and electrical conduction. Using the advantages of capacitive current and direct growth, enhanced performance was obtained. This can be explained by the facts that CCO on Ni foam is a capacitive material and high loading system which is an advantage of direct growth. In order to overcome the limitation of existing high loading system, we used direct growth method. Here we successfully constructed the ion and electron pathways using a burr-like structure of CCO. This also helped to obtain high power density in the water splitting system.



Investigating reactive sputtered $Ir_xNi_yO_z$ electrocatalysts for the oxygen evolution reaction in alkaline media

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Alkaline water electrolysis is currently catalysed by expensive metals such as Ru and Ir [1], thus rendering this process for H_2 production cost-ineffective and not commercially favourable. In an effort to reduce the cost of alkaline water electrolysis, studies of inexpensive metal catalysts show that nickel (Ni) and especially Ni oxides exhibit reasonable activity and corrosion resistance in an alkaline environment [2]. As the supporting structure is directly related to the morphology of the active surface area, it is an important factor to consider. In an attempt to increase the activity of alternative electrocatalysts, Vulcan Carbon (VC) with Nafion (Naf) binder is used as catalyst support on glassy carbon (GC) to investigate the electrocatalytic activity of sputtered $Ir_xNi_yO_z$ electrocatalysts for the oxygen evolution reaction (OER) in alkaline media [3]. Single electrode linear sweep voltammetry (LSV) and chronopotentiometry (CP) were employed to compare the catalytic activity and stability of the selected $Ir_{100}O_z$, $Ni_{100}O_z$ and $Ir_{73}Ni_{27}O_z$ thin films (40nm). Results indicated that the$Ir_{73}Ni_{27}O_z$ on VC support exhibited (i) good activity at a benchmark current density of 10 mA.cm^{-2} (Fig 1a,b), and (ii) similar overpotential before CP and showing the least amount of change in overpotential after CP compared to $Ir_{100}O_x$ and $Ni_{100}O_x$ (Table 1). This suggests improved catalyst utilisation and that a sputtered $Ir_{73}Ni_{27}O_z$ combination is a possible alternative electrocatalyst for catalysing the OER in alkaline media.

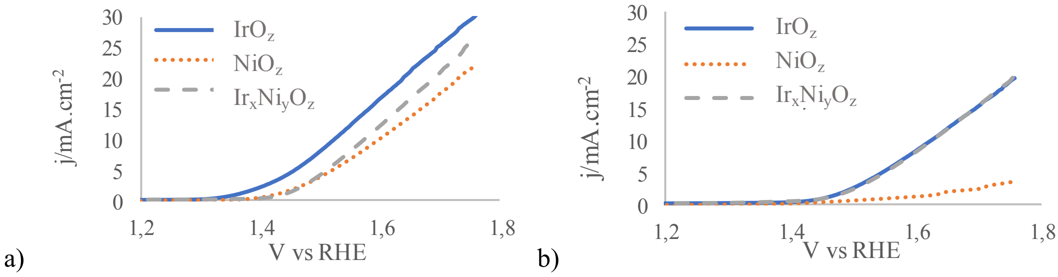

Figure 1: a) LSV of IrO_x, NiO_x and $Ir_{73}Ni_{27}O_z$ before and b) after CP (6 hours) testing.

Table 1: Summary of elemental composition (EDX), overpotential before and after CP, and Tafel slope

Sample	**Composition**		**Overpotential before CP (10mA.cm^{-2})**	**Overpotential after CP (10mA.cm^{-2})**	**Tafel Slope (mV.dec^{-1})**
	%Ir	**%Ni**			
IrO_z	100	0	0.29 ± 0.06	0.40 ± 0.01	70 ± 0.5
NiO_{zx}	0	100	0.37 ± 0.01	-	102 ± 9.0
$Ir_xNi_yO_z$	73	27	0.35 ± 0.01	0.39 ± 0.02	75 ± 7.3

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Electrochemical detection of methyl nicotinate biomarker produced by mycobacterium tuberculosis

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Abstract

Yearly tuberculosis (TB) continues to claim millions of lives, this occurring most in middle income and low income countries. The normal diagnostic regimes for TB include molecular biology technologies, such as "GeneXpert[1]. However the current method rely on the use of blood and sputum and they also suffer from severe drawbacks which include but not limited to prolonged availability of results and they are not point of care friendly (POC). As a result there is an overarching need to look at other viable options for the diagnosis of TB, for its management and control. This work seeks to look at other methods for early detection of TB. Exhaled human breath promises to revolutionize TB detection due to its attractiveness as an analyte for fast, non-invasiness. TB has been reported to produce volatile organic biomarkers (VOBs) namely methyl nicotinate which can be used to diagnose or identify this disease in its early stages[2,3]. Gas chromatography integrated with mass spectroscopy has been the principal method used for the identification of these biomarkers; however it also suffers from limitations. On the other hand electrochemical methods offer many advantages such as easy of miniaturization, POC, easy of handling etc. Co_3O_4 nanoparticles were used as a catalyst of interest in this work. These were synthesized through hydrothermal[4] method and were characterized with transmission electron microscopy (TEM), X-ray diffraction (XRD) and the electrochemical studies of methyl nicotinate were determined using cyclic voltammetry (CV) and chronoamperometry (CA).

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Synthesis and Cyclic voltammetry characterization of PANI-Au Modified Screen-Printed Carbon Electrode for electrocatalysis of Aflatoxins

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Abstract

Nanotechnology is playing an increasingly important role in the development of nanosensors**.** The present study present the synthesis of polyaniline (PANI) from aniline and functionalization with gold (Au) nanoparticles to result in a Polyaniline/Gold nanocomposite (PANI-Au). The synthesized nanoparticles were characterized by using FTIR, Ultraviolet-visible spectroscopy, EDS, SEM, TEM and XRD. FTIR spectra show successful incorporation of Au into the conductivity polymer PANI. Uv-visible showed maximum absorbance for Au, PANI and PANI-Au. EDS analysis revealed percentage composition for carbon, Nitrogen, gold and oxygen in the PANI-Au nanocomposite. Cyclic voltammetry (CV) was done using dropsens screen-printed carbon electrode. The CV peak results showed that the modified electrode SPC/PANI-Au has a higher current which is about 3 times greater than the bare SPC electrode as shown in Figure 1.

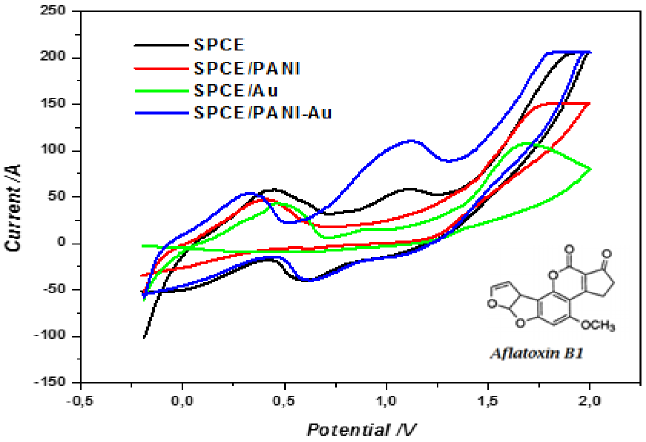

Figure 1: Comparative CV study for bare, PANI, Au and PANI-Au electrodes

The nanocomposite is also anticipated to show good electrocatalytic properties towards the detection of Aflatoxins. Conclusion and the significance of the study produced an observation that the sensitivity and performance of nanoparticles based sensors are improved.

Understanding and Improving Strategies of lithium-salt on Capacity Degradation for 4 V-Class Rechargeable All-Solid-State Lithium-metal Polymer Battery

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Rechargeable all-solid-state Lithium-metal polymer battery (ASSLPB) with organic-inorganic composite solid-state electrolyte (CSSE) has been recognized as one of the most promising next-generation battery system, because of high safety and considerable energy density. However, 4 V or above-class ASSLPB still suffered capacity degradation seriously resulting from the complex and various interfaces between the electrode (or active/ inactive materials) and electrolytes. Inhere, 4 V-class cathode material $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811) has been applied in ASSLPB with LiTFSI-PEO-LAGP CSSE. Furthermore, capacity degradation mechanisms of 4 V class ASSLPB are comprehensively investigated by electrochemical tests and physical characterization. The oxidation of anion from LiTFSI and the interaction between PEO and the oxidation product of $TFSI^-$ are the important reasons, which result in the damage of the interface between electrode and electrolyte and corrosion phenomenon of Al foil current collector. Therefore, the retention of capacity of ASSLPBs is reduced upon cycles. At last, two strategies about lithium salts, decreasing the content of LiTFSI in the interface of cathode and electrolyte coupling with LiBOB instead of LiTFSI in NCM811 composite cathode, were proved to be effective to improve the cycling stability of ASSLPBs. After that, the ASSLPB show a high reversible discharge capacity of 127.4 mAh g^{-1} at 30 mA/g, and the retention of capacity of ASSLPBs is up to 81% (3.0-4.2 V) and 72% (3.0-4.3 V) after 180 cycles at 35 °C with the charge/discharge current density of 30 mA/g.

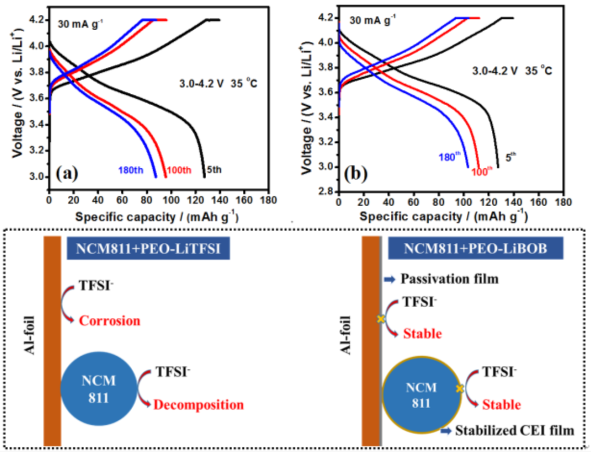

Fig.1 The charge/discharge curves of NCM811+PEO-LiTFSI/CSSE@20/Li (a) and NCM811+PEO-LiBOB/CSSE@20/Li (b) batteries from 3.0 to 4.3 V at 35 °C; (c) Schematic diagram of cycle performance enhancement mechanism of solid-state battery with NCM811+PEO-LiBOB/CSSE@20/Li configuration.

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Towards Antibiotic Susceptibility Testing with Scanning Ion Conductance Microscopy (SICM)

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Due to the emergence of anti-microbial resistance (AMR), mortality rate from bacterial infections is estimated to hit 10 million annually by 2050.[1] Physicians commonly administer a broad-spectrum antibiotic based on experience because current antibiotic susceptibility tests (ASTs) are based on slow bacterial culturing, that may take up to 2 days depending on growth rate. [2] This results in diminished success rate as bacterial strains are continually evolving in resistance to initial treatment, and further complicates the challenge of AMR. Hence there is urgent need for faster and effective means of predicting the *in vivo* success or failure of antibiotic therapy in order to inform more efficient drug dispensation.[2-3] Drug action has been speculatively attributed to surface charge, membrane potential and morphology, but the underpinning mechanism is largely unclear.

Scanning ion conductance microscopy (SICM), is a powerful tool yet to be engaged in bacterial biophysics. It presents a highly promising, facile and non-culture means to rapidly profile the resistance or susceptibility of bacteria strains based on important cell surface properties common to all bacteria strains. Compared with other scanning probe microscopy (SPM) techniques, SICM is compatible to study living cells, allowing analysis in biological media, with utilizing a simple probe design and low cost tip fabrication process and non-invasive scanning mode.[4] SICM is capable of topographical, surface charge, and potential imaging with nanometer spatial resolution and can be used for single bacterium multi-parametric study to also capture intra-population variability (Figure 1).[4-5] Herein, we report the first SICM studies on *Bacillus subtilis* NCIB3610 strains with static and dynamic probe protocols. This reveals the alterations in cell morphology, surface charge and potential of *B. subtilis* with useful correlation with drug action for possible AST application. Finally, this work further shows the strength of SICM for bacterial biophysics and opens up opportunities to provide more comprehensive understanding of bacterial metabolism, sporulation, communication, and ABR mechanism.

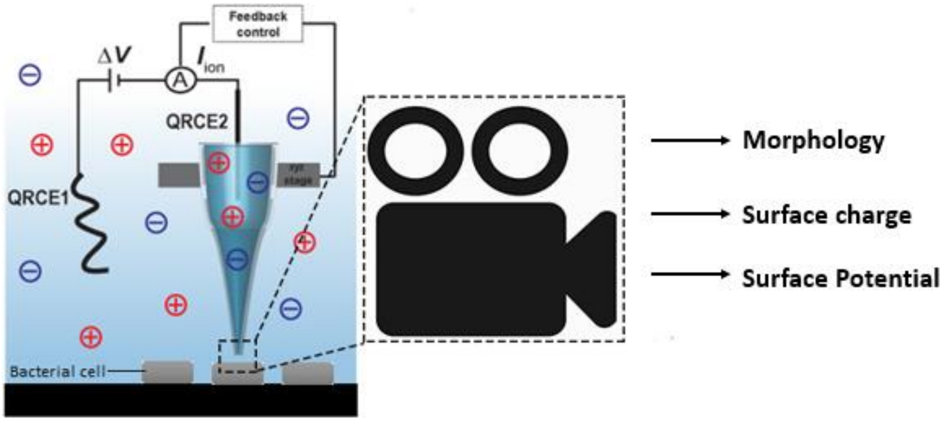

Figure 1: Typical scheme for SICM setup consisting nanopipette mounted on xyz stage to scan bacterial cells (before and after antibiotic treatment) affixed to glass in bath of electrolyte. Bias is applied between quasi reference electrodes in nanopipette and in bulk solution while feedback control is achieved by monitoring % change in ion current as nanopipette approaches substrate with pixel level self-referencing. Time-lapse scans revealing dynamics changes surface charge, potential and morphology are thus acquired.

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Computational approaches for durable electro-catalyst in ORR and OER with experimental studies

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Development of highly active electrocatalysts that are cost competitive takes the center stage in research fields for next-generation electrochemical energy conversion and storage systems like fuel cell and metal-air battery. Regarding the systems for commercialization, there are various challengeable issues, which should overcome sluggish kinetics and stability on the electro-catalyst for the aimed reactions such as oxygen reduction reaction (ORR) or oxygen evolution reaction (OER) occurred in the high over-potential and harsh condition. Although there was huge technological advancement as minimizing a usage of noble metal or developing non-precious owing to many attempts to reach the purpose in the past decade, it still needs further improvement in order to gain acceptance in a market. To find new material or optimize, the efficient way would be initializes from the knowledge of the underlying physical and chemical mechanisms in a material system. For the reason, therefore, fundamental studies using quantum mechanics (QM) along with experimental confirmation have been commonly conducted to explain the activity and stability of oxygen reactions. These approaches are very successful and provide a fundamental insight to scientist and researcher. Nevertheless, calculative simulations are still the restrictions to obtain trustable data and to predict correct consequences. For instant, QM simulation, which is well known as the most accurate computational prediction method, is slow and limited below 1,000 atoms, whereas molecular dynamics (MD) method is fast and can calculate over the million atoms but not exact, because classical MD is not able to simulate the chemical reaction. This talk will present recent our efforts for accurate modeling with experimental data. We predicted and validated the ORR and OER activity and stability on various materials like carbon-based materials (e.g., N-fullerene, N-graphene etc.), metal oxides and metals in density functional theory (DFT) design, applying to energy conversion and storage devices such as fuel cells, metal-air batteries systems. The force field, which is efficient way of describing the dynamics with large-scale simulations, was developed to simulate large sale models. This synergetic approach using both computational models and experiments with physicochemical analyses would accelerate to find new materials and to optimize catalyst performance.

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Computational approaches for improving catalytic activity and stability as electrocatalyst support for ORR in PEMFC

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The electrocatalyst support used in the fuel cell should satisfy an electrical conductivity and thermodynamic electrochemical stability. Currently, the most commonly used carbon black in Pt/C has the limitation caused by being oxidized at high potential over the 1.0 V vs RHE, thus alternative supports has been investigated for further developments.[1] In this study, we have tried to improve the durability and activity of the fuel cell catalyst by improving the problems existed by carbon black through doping dopants like N, Ti, Si, S, and P into graphene structure. By using Density Functional Theory (DFT) as a first-principle calculation, we have investigated the favored energies with Nafion calculating charge densities on doping graphene, as well as found preferred dopants having high stability in graphene. For the purpose, we calculated the formation energy of each structure generated from 0 to 100 at% of the doping material by employing the cluster expansion theory. We found a thermodynamically stable structure by drawing Convex Hull. *Ab-initio* MD was conducted that not only what Nafion structure is favored on co-doped graphene surface with Pt nanoparticles but also unveil mechanism regarding improved stability by the structure. Consequently, the dissolution potential of Pt itself was calculated to determine thermodynamic durability in fuel cell operating condition.

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Photocurrent increase by Perylene Derivative as Light-Harvesting Antenna on TiO_2 in Photosystem I-based Bio-Photovoltaic Device

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Photosynthetic pigment-protein-based bio-photovoltaic devices are attracting interest as environmentally friendly energy sources. Photosystem I (PSI), a photosynthetic pigment-protein, is a proven bio-photovoltaic material because of its abundance and high charge separation quantum efficiency. However, the photocurrent of these bio-photovoltaic devices is not high because of their low spectral response. In nature, to compensate for the low spectral response of the reaction centers of photosynthetic protein-pigments, förster resonance energy transfer (FRET) is used by the light-harvesting (LH) antennas. In this work, we have integrated an artificial LH antenna into a PSI-based bio-photovoltaic device in the form of a fluorescent dye, perylene di-imide derivative (PTCDI) to expand the spectral response.

The bio-photovoltaic devices were fabricated in the same way as dye-sensitized solar cells (DSSCs); assembling a PTCDI/PSI-TiO_2 photoanode and Pt counter electrode with surlyn film. The electrolyte was used an iodide/tri-iodide redox-based ionic liquid. The incident photon-to-current conversion efficiency (IPCE) spectra and the photocurrent-density–voltage (J–V) curve under AM 1.5 G (100 mW cm^{-2}) were measured. Remarkably, in photovoltaic cells formed from the PTCDI/PSI-assembled TiO_2 electrode, the magnitude of the IPCE spectrum is significantly enhanced in the range of 450–750 nm. This range matches the absorption range of the PTCDI/PSI-assembled electrode; thus, the high-intensity part of the solar spectrum can be used to generate electric power. Consequently, the short-circuit current density (J_{SC}) of the PTCDI/PSI photovoltaic device reaches 0.47 mA/cm^2 and the PCE improves to 0.13 %.

According to the IPCE spectrum, the PTCDI appears to minimally increase the power of the PTCDI/PSI solar cells. From the J–V data, low J_{SC} and V_{OC} are also observed under AM 1.5. However, in the PTCDI/PSI integrated photovoltaic, enhancement of the performance was observed. The observations that the PTCDI did not increase the power of the solar cell while PTCDI/PSI integration did imply that energy transfer occurs as seen in previous studies on DSSCs that applied artificial LH antenna [1]; that is, the photons absorbed by PTCDI might transfer to PSI via FRET in the PTCDI absorption range. According to the fluorescence spectrum of the PTCDI/PSI-assembled ZrO_2 electrode, a decrease in PTCDI fluorescent intensity at around 670 nm and a redshift of the peak maximum were observed. These results may be caused by quenching of the PTCDI excimer and the increase of fluorescence intensity at around 720 nm derived from PSI. Moreover, in methanol solution, PTCDI was previously reported to be quenched in proportion to the concentration of PSI, following the Stern–Volmer equation [2]. These results can be interpreted as evidence that the photons absorbed at PTCDI were transferred to PSI via FRET.

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Bio-Hybrid Solar Cells: Putting Photosystem I to Work

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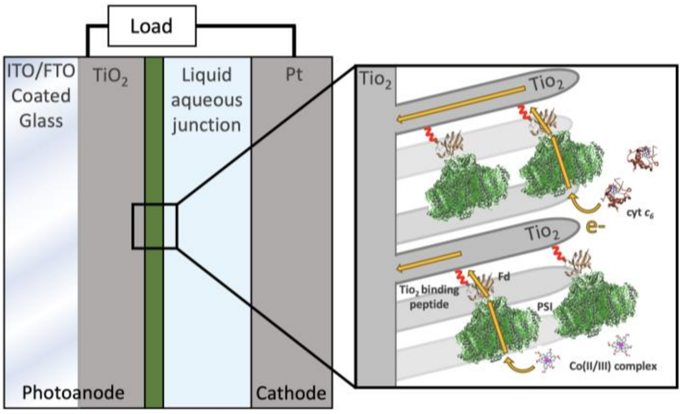
Future energy resources on Earth must be renewable, carbon-free, and sustainable. Most energy analysts recognize photovoltaics (PV) as a major contributor to help meet this need. However, many PV materials are difficult to fabricate and are often resource-limited, such as indium or other rare metals[1]. However, naturally occurring photosynthetic organisms utilize earth-abundant metals to harness and convert solar energy into a work-available form. These photosynthetic organisms harness solar energy via direct conversion to electronic energy using protein-pigment complexes, known as photosynthetic reaction centers (RC), with a quantum efficiency approaching unity. The field of applied photosynthesis aims to integrate RCs into novel, biohybrid solar cells[2-4]. Our lab has worked to integrate Photosystem I (PSI) from the thermophilic cyanobacterium *T. elongatus* into TiO_2 based solar cells[5]. The device is built around the direct attachment of PSI to the TiO_2 via a TiO_2 binding peptide attached to the PSI electron acceptor protein, ferredoxin (Fd)[6,7]. Currently we are using computational tools to bioengineer the affinity of Fd to the surface of PSI[8] to enable a tight and properly-oriented attachment of Fd-PSI to TiO_2 nanoparticles. This design places PSI on the TiO_2 surface with the lumenal surface exposed permitting reduction of photo-oxidized PSI by a water-soluble donor. However, one of the major limitations of these biohybrid devices is the slow reduction rate of *T. elongatus* PSI which leads to a loss of photocurrent. Therefore, we are also working to enhance the rate of electron donation to PSI using native, non-native, and synthetic donors. The first approach involves bioengineering of the native *T. elongatus* PSI electron donor protein, cyt. c_6. The second method comprises characterization of non-native algal/cyanobacterial cyt. c_6 interactions with PSI to identify features that promote the ~1000-fold increase in e$^-$ transfer rate seen over evolutionary time. The third approach takes a different approach, namely the development and characterization of synthetic organometallic complexes utilizing the abundant transition metal, cobalt in a manner that is compatible with biological PSI. Collectively, this research aims develop methods of enhancing the electrochemical activity of PSI in a sustainable, non-toxic manner to facilitate bioenergy and device applications.



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Electrodeposition of 3D hydrogels using 3D electrode arrays in applications of cell culture

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Hydrogels are widely used for bioapplications in tissue engineering and organs-on-a-chip. These applications require a method that can fabricate shape-designed hydrogels. Several methods have been proposed to prepare them. Recently, electrochemical methods have been proposed [1-8]. For examples, electrochemical acidification due to water electrolysis produces Ca^{2+} from $CaCO_3$ particles in a solution with alginate, resulting in formation calcium alginate hydrogels [1-6].

By using a wire electrode, tube hydrogels were fabricated around the wire [1]. Thus, by using shape-designed electrodes hydrogels, shape-designed hydrogels are fabricated. Recently, an electrode array device was applied for fabrication of three-dimensional (3D) hydrogels [7]. Four hundred electrodes were incorporated into the device, and each electrode worked independently. By applying a proper potential at each electrode, 2D hydrogels were rapidly fabricated on the device. In addition, by controlling the applied time, the height of the hydrogels was controlled, resulting in formation of 3D hydrogels. However, the height of the hydrogels was less than 1 mm due to the limitation of the diffusion layers.

To solve the problem, we fabricated 3D electrode array device [8]. In the device, many pin electrodes were arranged. The pin electrodes were independently slid, resulting in fabrication of a 3D relief of the pin electrodes. At the 3D relief, hydrogels were electrodeposited, resulting in a large size of 3D hydrogels. Since the length of the pin electrodes is easily controlled, the hydrogel size can be controlled.

In addition, mammalian cells were cultured inside the cells. The cells were successfully cultured, indicating that the toxicity of the method was low.

Thus, we developed a novel method using the 3D electrode array for fabricating 3D hydrogels. In the future, by culturing liver cells inside electrodeposited 3D hydrogels, liver tissues will be fabricated. Also, the fabrication system will be used for biosensors, not only cell culture platforms.

Acknowledgements
We would like to thank Prof. Tomokazu Matsue in Tohoku University for device fabrication, electrochemical detection and cell culture.

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Development of a Nanostructured Carbon-MnO_2 Hybrid Framework by Spray Coating and Electrodeposition as High Performance Electrode Material for Supercapacitor

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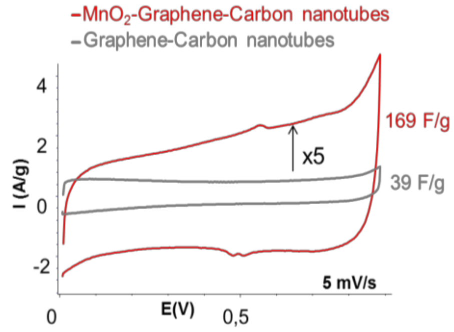
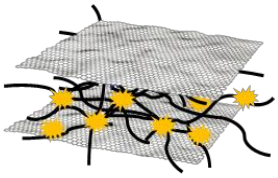
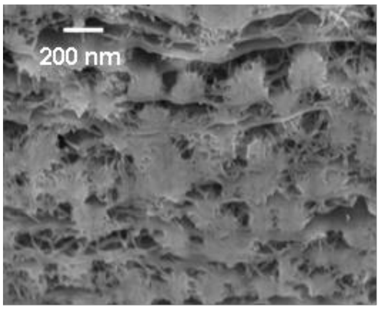
Nano-engineering of electrode through a versatile spray coating and subsequent electrochemical controlled modifications with metal oxide have been explorated toward a specific design of electroactive material targeting an increased energy density in supercapacitors while maintaining a high power density. Exploiting pseudocapacitance and nanostructuration by combining transition metal oxides and nanostructured carbon materials in one electrode is considered as one of the best ways to achieve these performances.

In this study, carbon nanotubes/graphene/manganese dioxide nanostructured films were designed as supercapacitors electrodes. MnO_2 is a well-known pseudocapacitive material used to increase the energy density. The selected carbon nanomaterials generate high conductivity and their association is an efficient way to insure large surface area to maintain a high power density. The challenge is to assemble these materials into a nanostructured electrode with controlled homogeneity, morphology, and composition. Our approach consists in synthesizing MnO_2 by anodic electrodeposition directly onto the conductive nanostructured carbon framework. The association of carbon nanotubes and graphene in a specific multi-layered organization by dynamic spray gun deposition aim at creating a controlled porous network in the electrodes with a highly accessible and electroactive surface.

The carbon nanomaterials were deposited onto a current collector by dynamic automated spray gun deposition, an easily scalable, reproducible and industrially suitable method used for nanostructuration of thin films. Materials were characterized by SEM, XPS, microporosity analysis and electrochemistry. Results demonstrate that the capacitance can reach up to 190 F/g (110 F/cm^3) for binder free electrodes thanks to a control of the MnO_2 morphology, particle size and mass loading.







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Cost-effective gold nanoparticles functionalized with *Musa paradisiaca* and *Vitis vinifera* extracts as sensing platforms for the detection of *E.coli O157:H7*

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Abstract

Modification of electrodes using metal nanoparticles is fast attracting intense interest because of the widespread applications of these electrodes as sensors in electroanalysis. Herein, we demonstrate the novel synthesis of cost-effective and environmentally friendly gold nanoparticles functionalized with a combination of *Musa paradisiaca and Vitis vinifera* extracts to enhance the stability, reactivity and biocompatibility of the nanoparticles. The reaction mixture of aqueous gold chloride and *Musa paradisiaca* and *Vitis vinifera* extracts revealed a purple colour after 1 hr an indication of the presence of gold nanoparticles which were also confirmed by an absorption band at 535 nm using Ultraviolet spectroscopy (UV-vis). The polydispersity nature of the nanoparticles was revealed using Small angle x-ray (SAX) and High-resolution transmission electron microscopy (HRTEM); techniques which also confirmed the average size of the nanoparticles to being 16 nm. X-ray diffraction (XRD) studies confirmed the spherical structure of the nanoparticles while Fourier transform infrared spectroscopy (FTIR) studies revealed the structure of these nanoparticles which included carbonyl groups, primary amine groups, OH groups and other stabilizing functional groups characteristic of the properties of *Musa paradisiaca* and *Vitis vinifera* extracts. Cyclic (CV) and square wave (SWV) voltammetric studies on glassy carbon electrodes further revealed the electrochemical properties of these nanoparticles necessary for the fabrication of *E. coli O157:H7* sensors.

Oxide Supported Electrocatalysts for Energy Conversion Devices: From Concept to Reality

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Metal oxides have gained considerable interest in electrocatalysis for their use as alternatives to high surface area carbon supports, and for the reduction of platinum-group metals content in both polymer electrolyte fuel cell (PEFC) and water electrolyser (PEWE) applications [1]. On the one hand, these materials offer unique thermodynamic stability for improved corrosion resistance at high electrode potentials, and, on the other hand, intrinsic catalytic properties of the supported catalyst nanoparticles can be influenced by interactions between catalyst and metal oxide support, akin to the metal–support interactions (MSI) observed in conventional heterogenous catalysis.

In electrocatalysis, the additional requirement of sufficient electronic conductivity of the support is often not provided for by metal oxides, as most of these materials are intrinsically isolating. A wide range of semiconducting properties can however be explored by generating defects, i.e. by introducing dopant atoms or creating oxygen vacancies in the oxide lattice, enabling their use as electrocatalytic support materials.

In this talk, I will discuss our recent findings on an electrochemical potential-dependent conductivity switching mechanism, observed in the semiconducting Sb-doped SnO_2 (ATO) supported Pt system [2]. Several drawbacks associated with the use of ATO as a support material for Pt catalysts for the ORR will further be described [3]. Finally, I will showcase our current work combining computational density functional theory, a novel catalyst synthesis approach, and a range of electrochemical and advanced physical characterisation techniques for the development of metal oxide-supported electrocatalysts for the oxygen evolution reaction used in PEWE applications.

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Electrochemical sensing of acetaminophen using nanocomposites comprised of cobalt phthalocyanines and multiwalled carbon nanotubes

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A recent study conducted on water samples acquired from the Msunduzi river in KwaZulu-Natal, illustrated that widespread contamination of pharmaceuticals has occurred [**1**]. Among these pharmaceuticals include Acetaminophen, {N-acetyl-p-aminophenol}, APAP which is an over-the-counter drug commonly used for analgesic and antipyretic therapy. Due to its non-prescriptive access, concentrations of APAP in domestic and medical wastes are high and its contamination in urban surface water resources has become an emerging water contaminant problem globally [**2**]. Furthermore, increased concentration levels of APAP in water directly affect the eco-balance and -sustainability of the affected aquatic ecosystems while portable water systems heavily contaminated with APAP can lead to organ failure [**3**].

Chemically modified electrodes (CMEs) have been widely used as electrocatalytic detectors of APAP as the electron mediating thin films addresses the poor recognition capabilities of the analyte in complex matrixes as well as minimizes passivation by oxidation by-products. In this research study, we report the efficient electrocatalysis of APAP using glassy carbon electrodes (GCEs) modified with nanoconjugates comprised of carboxylic acid functionalized multiwalled carbon nanotubes (*f*-MWCNTs) and cobalt phthalocyanines (CoPcs) tetrasubstituted flavone (flav) or benzoxazole (bo) moieties [**4**]. In addition, CoPcs are well known for their molecular recognition capabilities which are promoted by their metal- and ligand based redox properties while the latter can be readily influenced by the stereo-electronic properties of the substituents.

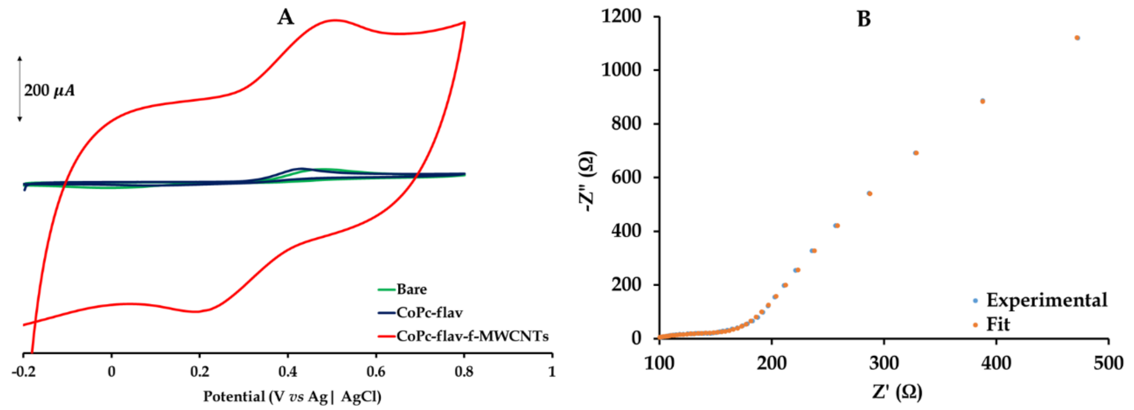

Fig. 1: (**A**) *Overlay CVs conducted in 1 mM of acetaminophen (APAP) in the PBS buffer using the CoPc-flav-f-MWCNTs, CoPc-flav and bare GCEs.* (**B**): *Nyquist plot attained in a solution of 5 mM* $[Fe^{III}(CN)_6]$ *prepared in PBS buffer using the CoPc-flav-f-MWCNTs GCE.*

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Paper based electrochemical sensor for environmental analysis

Paper is a well-known material that is made up of cellulose fibre, it can be found everywhere and is mostly used for writing, printing, drawing and packaging. The potential of using paper beyond these simple and traditional means rises from its physical properties. The main constituent of paper is cellulose fibre which acts as a solid substrate is highly attractive for certain applications as it allows liquids to move within its hydrophilic fibre matrix without assistance from an active pump or external source as paper usually exhibits wicking effects [1]. Due to the different properties such as grades, sizes, flow rate, thickness and pore size that different materials of paper substrates have, depending on the target analytes the requirement of the paper substrate will differ. Choosing the right paper material is important in order to fully make use of the characteristics of the paper substrate of choice to enhance the sensitivity of analysis and the choice is also important based on the fabrication steps required in the development of the device [2].In cases where wicking of the paper is not important in the application, paper such as office paper, glossy paper and paper towels can be used as a flexible support substrate for electrodes [3]. Electrodes can be printed onto paper using a number of different techniques, among those techniques screen printing and inkjet printing are the methods that are mostly used for constructing of electrodes. Screen printing is used frequently for fabrication of paper based electrochemical sensors. This technique uses ink, mesh pore stencil and a squeegee. Screen printing technique provides an inexpensive way to print electrodes by transferring the carbon ink or other printable inks onto paper substrate surface [4]. In this work a conductive screen printable polyamic acid-carbon ink was developed by mixing commercial carbon ink with synthesised polyamic acid. The ink was screen printed onto photo paper to fabricate the electrodes. The electrodes were further characterised by scanning electron microscopy to study the surface morphology of the electrodes and the electrochemical behaviour of the electrodes were studied by cyclic voltammetry.

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Effect of Residual Stress on Corrosion Behaviour of Hot and Cold Rolled Duplex Stainless Steel in Chloride Media

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Abstract

The use of duplex stainless steel in the petrochemical and nuclear industries is fast replacing carbon steel and other convectional stainless steel due to the mechanical strength and excellent corrosion resistance offered by it. The effect of residual stress on corrosion behaviour of hot and cold rolled duplex stainless steel to chloride media is investigated. As received hot and cold rolled duplex stainless-steel samples were characterized using optical microscope and scanning electron microscope for microstructural analysis. Residual stresses of varying percentage (20, 40 and 60%) were applied to stainless steel samples machined to micro tensile dimension. Residual stress analysis of the necked region was analysed using Bruker D8 Advance X-ray diffractometer, while potentiodynamic polarization and chronopotentiometry tests were carried out in 3.5 wt.% NaCl to access the corrosion integrity of the necked region. The center and average principal stress analysis (S11 and S22) of hot and cold rolled stainless steel in the necked region showed the deformation of austenite and ferrite phases due to tensile pulling with more tensile stress in the austenite phase. Micrographs from Scanning Electron Microscope (SEM) for corrosion substrates revealed the dominance of corrosion in the austenite phase in the necked region of hot rolled samples.

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Influence of the Potential Scan Rate and Temperature Variation on the Behavior of Rhodium Spherical Single Crystal Electrodes in Aqueous Acidic Media

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Rhodium is known for its high catalytic activity towards many electrocatalytic reactions including the hydrogen oxidation and oxygen reduction reactions, high corrosion resistance and ability to act as an effective alloying agent with other platinum group metals. While polycrystalline Rh has been studied in detail, very little work has been conducted on monocrystalline surfaces. This is important because polycrystalline materials whether they be in the form of wires, rods, sheets or foils have grain boundaries and mechanical stress that is introduced as an unavoidable consequence of their fabrication processes. Their impact on fundamental processes involving adsorption/desorption phenomena and interactions with ions in aqueous acidic environments on polycrystalline Rh electrode surfaces is unknown and difficult to study. As preliminary work, experiments were conducted on Rh spherical single crystal electrodes (Rh(hkl)) in aqueous sulfuric acid solution to better understand the adsorption/desorption behavior of hydrogen and anions on various Rh electrode surfaces. This allows for the study of multiple surface structures simultaneously and working with an electrode surface that is free of mechanical stress and grain boundaries that are present when using polycrystalline materials as electrodes. Rh(hkl) were grown in-house using a single crystal growth apparatus developed in our laboratory [1]. The electrochemical measurements were performed using methods that are described in earlier publications [2]. Temperature dependent measurements where conducted in the hydrogen underpotential deposition (H_{UPD}) region at the potential range of $0.05 \leq E \leq 0.40$ V with respect to RHE, in 0.50 M aqueous H_2SO_4 electrolyte. The effect of changing potential scan rate was also studied, using a wide range of potential scan rate range of $0.50 \leq s \leq 500$ mV s^{-1}. The cyclic voltammetry profile (CV) reveals two distinct H_{UPD} peaks (E_{peak-1} = 0.106 V and E_{peak-2} = 0.150 V at 298 K with a scan rate of 10.0 mV s^{-1}) characteristic of Rh(hkl). Capacitance plots reveal that the peak potentials shift considerably with changes in scan rate. The two peaks separate at low scan rates, reaching an equilibrium potential at 1.0 mV s^{-1} and overlap at high scan rates higher than 50.0 mV s^{-1}. The equilibrium potential remains true throughout the entire temperature range. This implies that cyclic voltammetry experiments that are conducted on Rh monocrystalline and polycrystalline surfaces, should be conducted at 1.00 mV s^{-1} or less, to achieve the best resolution of peak potentials for hydrogen adsorption on Rh in aqueous sulfuric acid. This work is a crucial first step in understanding the thermodynamics and kinetics of adsorption on monocrystalline Rh.

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Investigation of doped carbon as a catalyst support for electrochemical energy conversion devices

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The oxygen reduction and evolution reactions (ORR and OER) are key reactions in electrochemical energy conversion devices such as polymer electrolyte fuel cells (PEFCs) and electrolysers (PEWEs), respectively. For these reactions, it has been shown that supporting the platinum group metal-based catalyst nanoparticles can improve catalytic activity and noble metal utilisation, while prolonging catalyst lifetime in the harsh electrochemical environments where these reactions take place [1].

Carbon materials has been used extensively as support materials in electrocatalysis for their specific properties; stability in electrolyte, ability to tune textural and surface properties, and possibility of precious metal recovery by further oxidation of the carbon support. Although elemental carbon is not suitable for application in PEM electrolysis, as it undergoes rapid degradation at the high anodic potentials, it has been shown that doping carbon with heteroatoms such as boron, nitrogen, oxygen and sulphur can readily tune intrinsic properties such as the electronic structure, surface and local chemical features. The electronic structural modification of carbon by the insertion of dopants can stabilise the carbon support at high anodic potentials; enabling the usage of carbon as a support for OER and ORR applications [1-3].

In this work, the production of nitrogen-doped carbon using a renewable biopolymer is explored for its application as a catalyst support. Biopolymers chitin and chitosan have been utilised for the production of doped "green carbon" by thermal decomposition. The advantage associated with the use of chitosan as a carbon source is related to the wide availability of this biopolymer, particularly from food waste, where a high carbon yield is obtained after pyrolysis (~50%) and the presence of an amine in the structure leads to nitrogen self-doping of the derived carbon materials [4,5].

Chitosan and derivatives thereof were utilised for the synthesis of nitrogen-doped carbon. The derivatives contain additional nitrogen moieties which affect the doping level of the carbons obtained after pyrolysis, a novel aspect of this study. These carbons were loaded with iridium/platinum nanoparticles *via* an in-house developed chemical deposition technique. Physical characterisation techniques such as transition electron microscopy, thermogravimetric analysis and elemental analysis were used to understand the structural characteristics of the catalysts. Electrochemical performance was evaluated by cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy, using the thin-film rotating disk electrode technique.

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A cobalt(II) phthalocyanine with indole substituents: Formation, Characterization and Electrocatalytic studies

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Metallophthalocyanines have been recognized for their astounding electrochemical properties which are well suited for the development of the next-generation sensitive, selective and reproducible electrochemical sensors. In particular, CoPcs are the most widely studied since their metal-based redox couples typically electrocatalyses bio-analytes [**1**, **2**]. Furthermore, the nature and position of their substituents as well as *axial* ligand coordination can influence their electrocatalytic activities [**3**]. Moreover, the use of MPcs in conjunction with multi-walled carbon nanotubes (MWCNTs) has attracted attention in sensor development since their advantageous properties like high surface areas, high thermal conductivity, excellent chemical and thermal stability are inherited by the MPc-MWCNT conjugates [**4**, **5**].

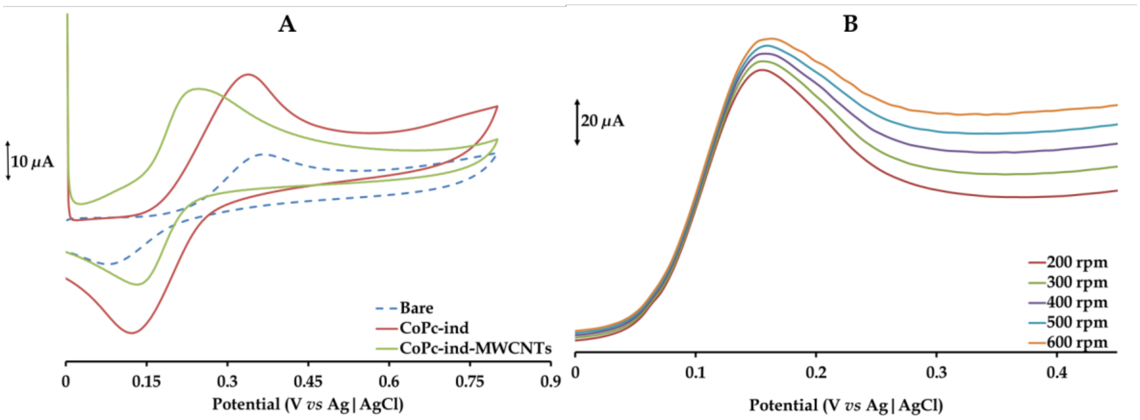

Figure 1 (**A**): *Overlay CVs conducted in 1 mM Dopamine prepared in pH 4 buffer using the bare, CoPc-ind and CoPc-ind-MWCNTs Pt electrodes.* (**B**): *Comparative RDE voltammograms for a dopamine analyte solution acquired using the CoPc-ind-MWCNTs Pt electrode at different rotational speeds*.

Abnormal levels of dopamine in the body can lead to diverse behavioral and neurodegenerative disorders that include schizophrenia, autism, Parkinson's, Alzheimer's and Huntington's diseases [**6**]. Hence, the development of efficient and rapid methods that can selectively and reliably detect dopamine is crucial for accurate diagnosis. In this research study, a cobalt phthalocyanine (CoPc) bearing peripherally tetrasubstituted indole (ind) moieties was synthesized and characterized. Electronic spectroelectrochemical experiments confirmed the metal- and Pc-based redox processes made during voltammetry analysis. The metallocyclic compound, CoPc-ind was electrodeposited onto respective Pt working electrodes and then multi-walled carbon nanotubes (MWCNTs) were adsorbed onto the surface of the modified working electrode. During dopamine electrocatalysis, the modified electrode showed faster electron transfer kinetics than the bare Pt electrode, see **Figure 1**. Furthermore, structural similarities between the N_4-macrocyclic core of the CoPc and one of the bio-interferents, L-tryptophan proved to be an influential factor during the selectivity studies.

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Differences in the Electrochemical Deposition of Zinc from the Ionic Liquid [MPPI][TFSI] on Au(111) and Au(100) Model Electrodes

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In this contribution we show the differences between the electrochemical deposition and dissolution of zinc on Au(111) and Au(100) model electrodes from the ionic liquid (IL) *N*-methyl-*N*-propyl-piperidinium (MPPI) bis(trifluoromethanesulfonyl)imide (TFSI). To fully understand the fundamental processes which take place during the deposition and dissolution of zinc from this ionic liquid, first characterisation of the pure IL has been conducted on Au(111) and Au(100) model electrodes via cyclic voltammetry (CV), *in-situ* scanning tunneling microscopy (STM) and Auger electron spectroscopy (AES). Here a very similar electrochemical behaviour on both surfaces was found. Also, *in-situ* STM measurements did not reveal any etching processes as long as the IL was held in between its electrochemical stability window.

Afterwards, measurements with a 20 mM $Zn(TFSI)_2$ solution have been performed. The rather different initial stages of electro-crystallization on both electrode surfaces reveal the strong influence of the electrode surface structure on the initial stages of metal deposition (Figure 1). Nevertheless, on both electrodes a very well-defined decomposition potential of [MPPI][TFSI] on the deposited Zn was found. Consequently, staying within the stability regime of the IL on the deposited Zn layers resulted in a highly reversible deposition and stripping process on Au(111).

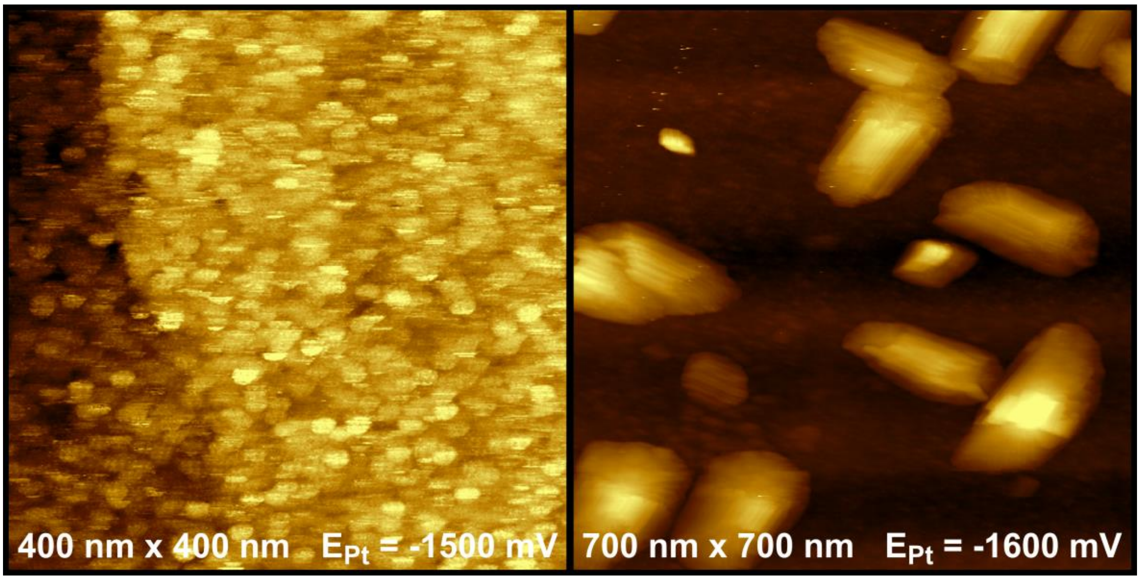

Figure 1: STM images of the early stages of the zinc deposition on Au(111) (left) and Au(100) (right).

Although *in-situ* STM as well as AES indicated alloy formation at negative potentials, still a complete plating of the electrode upon continued potential cycling was found. Furthermore, all processes on the Au(111) electrode were highly reversible and no dendrite formation of the deposited zinc could be observed on both electrodes.

A cobalt(II) phthalocyanine with indole substituents: Formation, Characterization and Electrocatalytic studies

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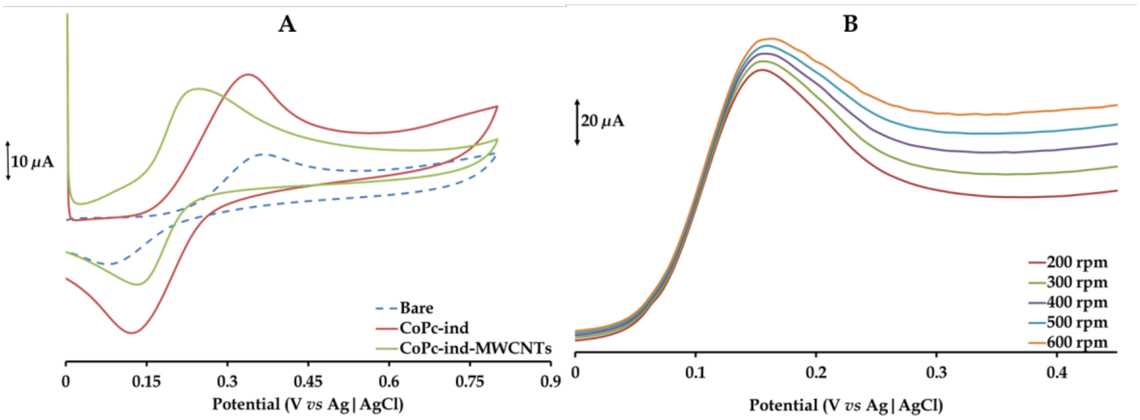

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Electronic and structural properties of caffeine mediated indium nanoparticles for the electrochemical detection of lamivudine

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South Africa is reported to have the biggest and most high-profile HIV epidemic in the world, with an estimated 7 million people living with HIV in 2015. In the same year, there were 380,000 new infections while 180,000 South Africans died from AIDS-related illnesses. Currently, South Africa has the largest antiretroviral treatment (ART) programme globally financed from its own domestic resources estimated at $1.5 billion annually. It has however been reported that a great number of these patients die to antiretroviral (ARV) drug treatment related complications, in particular those who are slow metabolisers of these drugs. Consequently, this study reports a single pot procedure for the synthesis of caffeine capped indium nanoparticles for the spectro-electrochemical detection of the antiretroviral drug lamivudine. Ultra-visible spectroscopic (UV-vis) studies revealed an absorption spectrum in the ultraviolet region of 273 nm an indication of the successful development of the prepared nanoparticles where an optical energy band gap of 3.7 eV was determined using a Tauc plot. Additionally, X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) was used to interrogate the reducing and stabilising properties of caffeine as well as the structural properties of the synthesised indium nanoparticles. Small-angle X-ray scattering (SAXS) was used to determine the size of nanoparticles where an average size of 11 nm was determined and confirmed with High Resolution Transmission Electron Microscopy (HRTEM) techniques which also revealed the spherical nature of the nanoparticles. The electrochemical properties of the synthesised indium nanoparticles were studied on glassy carbon electrodes where redox peaks were observed using cyclic voltammetry (CV) which were seen to shift and reduce in the presence of lamivudine. These findings confirmed their potential use of indium nanoparticles in the development of sensors for antiretroviral drugs.

Surface Modification of Al-7075 Alloy by Electrografting of 4-Nitrobenzenediazonium Salts

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Several benefits can be obtained from the electrografting of aryldiazonium salts films on the surfaces of alloys, such as increase of adhesion between materials, modification of surface wettabilities, corrosion protection and biocompatibility [1]. Recent works have reported the electrografting of these aryldiazonium salts on metal [2, 3] and metal alloy surfaces [1], finding an improvement in terms of the corrosion properties of the studied substrates. Particularly, aluminum nanoparticles [3] and aluminum alloys [4] have been modified with aryldiazonium salts, showing high adhesion on these surfaces which suggest them as good candidates for promising applications.

In this work, the electrografting of Al-7075 aluminum alloy substrates with 4-nitrobenzenediazonium salt (4-NBD) films has been performed, in order to evaluate them as corrosion protector films. Before applying the electrografting, the substrates were submitted at different cleaning treatments (solvent cleaning, mirror polish and chemical/ion polishing) to determine the influence of the natural oxide layer growth on the surface in their corrosion properties and the adhesion of the 4-NBD films. The films were formed by chronoamperometry at different times and their resistance toward corrosion was assessed by Tafel polarisation and electrochemical impedance spectroscopy in a borate buffer containing 50 mM NaCl. Additionally, the bare and modified substrates were characterized by surface techniques (SEM, EDX, Raman spectroscopy, XPS and PM-IRRAS) to determine the changes in the morphology and the oxidation states of the elements conforming the studied alloy.

The previous results demonstrated an improved deposition of 4-NBD on the chemical/ion polished substrate, as a consequence of the decrease in the thickness of the oxide layer naturally growth during the surface oxidation of the alloy. Moreover, a decrease in the corrosion current values was observed (see Figure 1), which was proportional to the increase in the time employed to deposit the films. The shift of the corrosion potentials toward negative values suggests a corrosion protection by inhibition of the cathodic reaction (oxygen reduction reaction). Moreover, the presence of chlorides in the electrolyte induce a change in the roughness of the substrates as a consequence of the corrosion process.

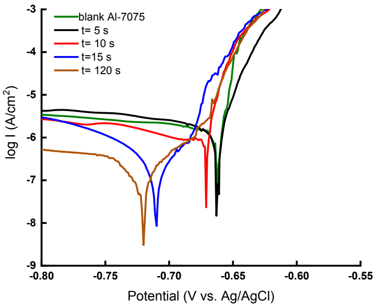

Figure 1. Tafel polarisation plots for 4-NBD-modified Al-7075 alloy substrates in borate buffer containing 50 mM NaCl.

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Simple impedance analysis of porous electrodes for the rational development of metal-sulfur batteries

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Sulfur is cheap, abundant and environmentally friendly, and combined with lithium or aluminum, it forms rechargeable batteries with high theoretical energy density. The reactions in metal-sulfur batteries involve the reduction of solid S_8 to a variety of soluble polysulfide species, which can then be further reduced to form sulfide (Li_2S or Al_2S_3). Due to the low conductivity of S_8, batteries are made by incorporating conductive carbon in the positive electrode. A delicate balance between high electronic conductivity, with minimum amount of carbon in the electrode (to produce a light battery), and high porosity and low tortuosity (to enable fast ion transport to facilitate the electrochemical reactions) is required to develop high performance batteries. We have recently demonstrated the use of a simple impedance analysis of porous electrodes, using a transmission line model with only two fitting parameters, to quantify the rate of ion transport within the porous electrode, which we have shown is a key property determining the electrode performance [1]. Figure 1 illustrates the physical meaning of the model, with electrons travelling through the carbon conductive additive (in **black**) and ions (e.g. Li^+) travelling through the electrolyte filling the pores (in **blue**). The associated impedance response is a single element, known as open-Warburg or De Levi element, from which the rate of ion transport through the electrolyte-wetted electrode can be quantified. The rate of ion transport is also affected by ion-ion interactions, which are concentration dependent [2] and, therefore, optimization of performance has to be done by balancing and exploiting the synergies between electrode structure development and electrolyte formulation development.

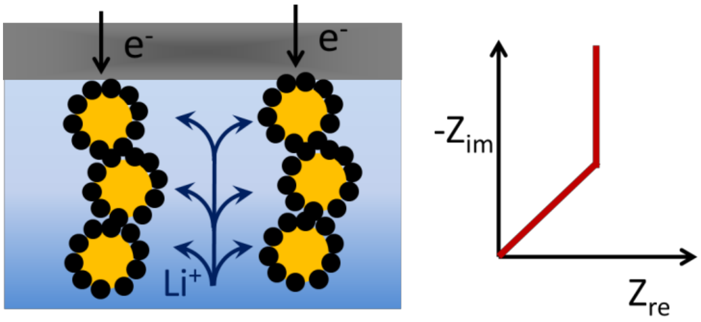

Figure 1. Illustration of the meaning of the transmission line model used to characterize sulfur-carbon composites for Li-S battery applications [1].

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Optimisation of Catalyst Coated Membrane Fabrication Protocol

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Hydrogen Economy represents a progressive way of future power management of renewable energy sources. Hydrogen, as an energy vector, can be utilised effectively and ecologically for electric energy production in fuel cells. Specifically, fuel cell with proton-exchange membrane operating at ambient conditions is among the fuel cell types ideal for mobile and small stationary applications.

Low temperature fuel cell with proton-exchange membrane consists of two gas diffusion layers with Pt-based catalytic layer, separated by perfluorinated sulfonated polymer membrane. This arrangement, i.e. membrane-electrode assembly, is arguably the most important part in relation to fuel cell performance. Choice of materials, especially for gas diffusion layer, and membrane-electrode assembly preparation procedure are major factors influencing performance of fuel cell. Therefore, development of reproducible and scalable membrane-electrode assembly fabrication method would significantly further effort towards fuel cell serial production.

Two, principally different methods can be utilised for catalytic layer deposition during membrane-electrode assembly fabrication. First approach consists of deposition of catalytic layer onto the gas diffusion support, forming gas diffusion electrodes (CCE) in process. Subsequently, prepared electrodes are pressed to membrane at elevated temperature. Second approach utilises deposition of catalytic layer directly onto the membrane (CCM), with subsequent pressing of gas diffusion media to catalytic layers on the both sides of membrane. Deposition method, together with intended fuel cell operating temperature, influences also choice of gas diffusion layer in terms of hydrophobicity and morphology. It is not decided yet, whether CCE or CCM approach is more suitable, since there are pros and cons for the both methods.

Preparation of CCE is relatively simple, rigorous process. Due to negligible weight change of gas diffusion layer during the preparation and good mechanical stability of CCE, loading of catalyst is relatively well defined. However, three-phase contact between the Pt, proton-exchange media and gas on electrode-membrane interface is an issue. To certain degree, hot pressing techniques can reduce this problem. On the other hand, hot pressing can lead to deformation of membrane and gas diffusion layer, not to mention problematic humidification of membrane after hot pressing.

In case of CCM, problems related to three-phase contact are significantly reduced. On the other hand, membrane undergoes drying and, consequently, its weight changes during catalytic layer deposition. This leads to less defined catalyst loading. Also, long-term heating of membrane up to 130 °C can lead to structural changes and reactivation might be complicated. Finally yet importantly, low membrane thickness can present an issue during catalytic layer deposition due to wrinkling and tearing.

Aim of presented work was to optimise preparation of CCM for various catalyst and membrane types. Ink composition, heating temperature and level of vacuum on workbench are among the studied catalytic layer deposition parameters. Using in-house prepared CCMs, we fabricated membrane-electrode assemblies and tested them in single fuel cell arrangement at various temperatures. A relation between the CCM preparation procedure and fuel cell performance was determined and optimised CCM preparation protocol formulated. This scientific effort of CCM preparation optimising will contribute to eventual process of automatic membrane-electrode assembly fabrication and provide data for procedure standardisation.

The work was supported from European Regional Development Fund-Project "Fuel Cells with Low Platinum Content" (No. CZ.02.1.01/0.0/0.0/16_025/0007414).

Grand Canonical Monte Carlo simulations for the co-adsorption of two electroactive species

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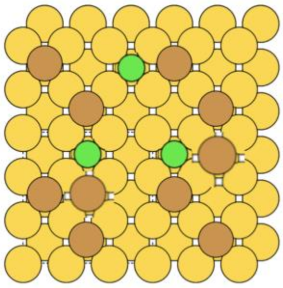
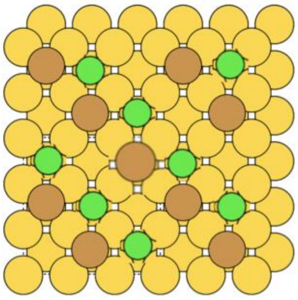
The under potential deposition (UPD) of metals in solution can be affected by the presence of other adsorbing species. For example, it has been shown that the presence of halide anions splits the Cu UPD onto Pt(111) into a two-stage process whereby formation of a full Cu monolayer is preceded by an incommensurate Cu-halide bilayer [1]. Studies of Cu UPD onto Au(111) in sulfuric acid where a $\left(\sqrt{3}x\sqrt{3}\right)R30°$ adlayer was originally assigned to 1/3 of a monolayer of Cu atoms [2] but more recently was shown to consist of 2/3 of a monolayer of Cu and 1/3 of a monolayer of (bi) sulfate anions [3]. Such inconsistencies also highlight the problems of accurately determining surface coverages in an electrochemical environment. Theoretical simulations such as Grand Canonical Monte Carlo (GCMC) are suitable for the interpretation of experimental measurements of complicated processes of electrodeposition.

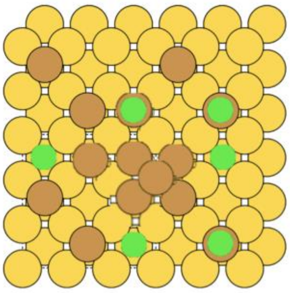
Our model applies Monte Carlo (MC) simulations in the grand canonical ensemble to study the co-adsorption of two electroactive species A and B on a substrate S. We consider first neighbor interactions (A-A, B-B, A-B, A-S, B-S), and the possibility of the formation of a second overlayer.

In order to compare our results with experimental data, we have estimated interactions parameters for several systems of interest, such as for the deposition of copper on Au(100) in the presence of chloride, by DFT calculations. The adsorption thermodynamics is analyzed through the total and partial isotherms (coverage versus electrochemical potential). Also the formation of ordered phases and the transition between phases with different configurations has been investigated for several initial conditions.

According to the interactions parameters several distribution of the two species on both overlayers are possible. Some examples:







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Voltammetric determination of metformin and its analogues using Cu modified polymer electrodes

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Metformin is a widely approved antidiabetic drug that is used to treat type II diabetes mellitus particularly in obese patients [1]. Metformin lowers blood glucose level by reducing hepatic glucose production and enhancing hepatic glucose uptake. However metformin have a shortcoming of low oral bioavailability ranging between 40-60% in intestinal environment, which can lead to large accumulation on the enterocytes; that indicate poor permeability [2]. Thus it was of interest to synthesis metformin analogues following an organic route where the side chains at the CH3 site were replace through allylation or amination chemistry for example. The synthesised analogues were detected by electro-analytical methods such as CV and SWV since they are highly sensitive and simple. A sensor was designed by modifying polymer electrode with copper nanoparticles due to the fact that copper have high binding affinity with metformin. The designed sensor was used to detect metformin and metformin analogues in synthetic urine samples [3].

Keywords: Diabetes, Type II diabetes mellitus, metformin analogues

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Atomistic insights on the electrode material CuDEPP: Combining the advantages of batteries and super capacitors

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Devices for electrical energy storage need to provide high energy yields as well as output power while at the same time guaranteeing safety, low costs and long operation times. The porphyrin CuDEPP [5,15-bis(ethynyl)-10,20-diphenylporphinato]copper(II) is a promising electrode material for various battery systems both as anode or cathode. In contrast to the slow discharge/charge processes in traditional lithium-ion batteries, the CuDEPP electrode features a fast redox conversion in which up to four electrons are transferred. CuDEPP combines the positive properties of lithium ion batteries (high energy density) with those of a supercapacitor (fast electron release and absorption). While its functionality has been demonstrated experimentally,[1] there had been no atomistic information as to why CuDEPP expresses these interesting properties or how the incorporation of ions affects its structure.

To answer these questions, we have investigated CuDEPP using density functional theory (DFT). Starting with the smallest possible unit (*i.e.* a single molecule) we successively increased the spatial dimensionality of the structure by studying: a) di- and trimers, b) molecular stacking in a 1D chain, c) extending these chains to planar CuDEPP sheets and finally c) a three-dimensional extended polymer structure. Combining the individual results of the molecule, the chain, the plane and the extended polymer lead to a comprehensive and consecutive understanding of the CuDEPP system.

Having thoroughly investigated the isolated properties of the CuDEPP material itself, afterwards the insertion (or intercalation) of different ions (including Li, Mg and Na) has been studied, in order to understand the energetics, diffusion barriers and structural changes (*e.g.* volume expansion) within the CuDEPP host material. Based on the optimal ion intercalation structure, discharge voltage curves have been calculated. The thus-obtained cell voltages can be directly compared to experimental measurements.

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Redox behaviour of Substituted Tris(1,10-phenanthroline)cobalt(II) Complexes

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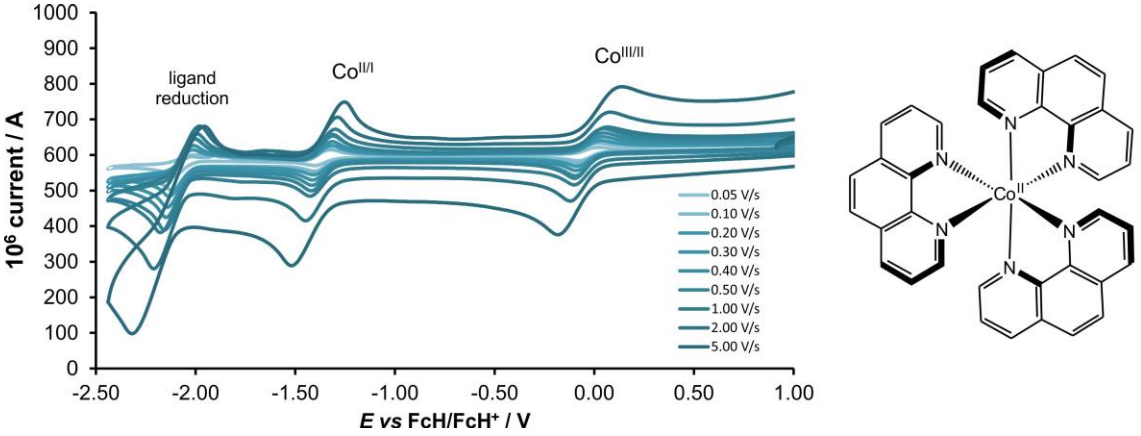
The redox chemistry of cobalt complexes tris(1,10-phenanthroline)cobalt(II), tris(bipyridine)cobalt(II) and bis(terpyridine)cobalt(II), plays an important role in various processes. For example, the Co(III/II) redox couples of $[Co(bipyridine)_3]^{2+}$ and $[Co(phenanthroline)_3]^{2+}$ were shown to act as electron mediators for Z-scheme photocatalyst systems, for the splitting of water molecules into H_2 and O_2, upon irradiation with visible light.[1] Complex $[Co(terpyridine)_2]^{2+}$ can be used for the electrochemical reduction of protons (H^+) to molecular hydrogen (H_2), thereby allowing the storage of energy through formation of an H-H chemical bond.[2] $[Co(terpyridine)_2]^{3+}$ can also be used as redox catalyst for carbon dioxide (CO_2) reduction to carbon monoxide (CO). The reduction of CO_2 is a promising strategy for the storage of renewable energy in various fuels.[3] The Co(III/II) redox couples of different Co(II) and Co(III) complexes with polypyridine ligands (phenanthroline, bipyridine or terpyridine), demonstrated promising properties as potential mediators for photo-electrochemical solar cells.[4]

For all these applications, a detailed knowledge is vital of the exact redox potential of the involved redox processes. The redox potential can be influenced by substituting different groups on the polypyridine ligands, leading to a broad variation in their potentials. In this contribution it is shown that the experimental redox potential of differently substituted phenanthroline-Co(II) complexes,[5] is directly related to the density functional theory calculated energies, such as the HOMO energies, LUMO energies, electron affinity, ionization potential, electrochemical potential, electrophilicity index[6], and the Mulliken electronegativity.[7] All these relationships are important in the design of novel substituted polypyridine-Co(II) complexes, with specific customized redox properties, as required for a specific application.



Cyclic voltammograms of 0.001 M $[Co(phenanthroline)_3]^{2+}$ at nine different scan rates, measured in 0.100 mol dm^{-3} $[NBu_4][PF_6]/CH_3CN$, on a glassy carbon working electrode at 25 °C.

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Cadmium selenide nanoparticles under methylene blue performance: Investigation of bio-optoelectronic application

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XRD showed a strong peak associated with (111) plane of hexagonal CdSe suggesting formation of highly orientated nanorods. The longitudinal optical phonon shifted slightly due to strain whereas strong low-energy shoulder shift can be explained within a model for surface optical phonons. XPS spectra showed spin-orbit splitting resolved peaks related to Cd $3d_{5/2}$ (404.41 eV) and Cd $3d_{3/2}$ (411.88 eV) of CdSe agree well the values of Cd 4d (54.32 eV), Se 3d (63.26 eV), Cd $3d_{5/2}$ (404.41 eV) and Cd $3d_{3/2}$ (411.88 eV) as reported for CdSe nanoparticles. The prepared QDs (CdSe) showed two redox couples at oxidation peak potentials ($E_{p,a}$) of 1.33 V and reduction peak potential ($E_{p,c}$) = 1.28 V, respectively. Photocatalytic activity of CdSe nanorods were investigated by exploiting photocatalytic degradation of methylene blue (MB). The typical UV-vis absorption spectra of methylene blue solution at different time intervals it can be clearly seen that the relative intensity of the absorption peak corresponding to MB, with the catalyst for different concentration time intervals (0 mM, 2 mM, 5 mM & 10 mM) of the prepared CdSe nanorods. After completion of 5 mM % the dye was completely degraded and the absorption spectra act as a photocatalyst.

Sulfur Spillover on Carbon Materials and Possible Impacts on Metal–Sulfur Batteries

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There is currently intense research on sulfur/carbon composite materials as positive electrodes for rechargeable batteries. Such composites are commonly prepared by ball milling or (melt/solution) impregnation to achieve intimate contact between both elements with the hope to improve battery performance. Herein, we report that sulfur shows an unexpected "spillover effect" when in contact with porous carbon materials under ambient conditions. When sulfur and porous carbon are gently mixed in a 1:1 mass ratio, complete surface coverage takes place within just a few days along with the loss of the sulfur bulk properties (crystallinity, melting point, Raman signals). Regarding the preparation of C/S nanocomposites, this phenomenon can also be interpreted as a self-infiltration process that may supersede many of the commonly used approaches to prepare C/S nanocomposites for metal–sulfur batteries. Although the origin and mechanism of the sulfur spillover remain largely unknown thus far, this phenomenon adds another important aspect to metal–sulfur batteries, and we suggest that its understanding will be of significant relevance to further improving this type of batteries. Consequences of this phenomenon are discussed using a sodium–sulfur cell with a solid electrolyte membrane as example.

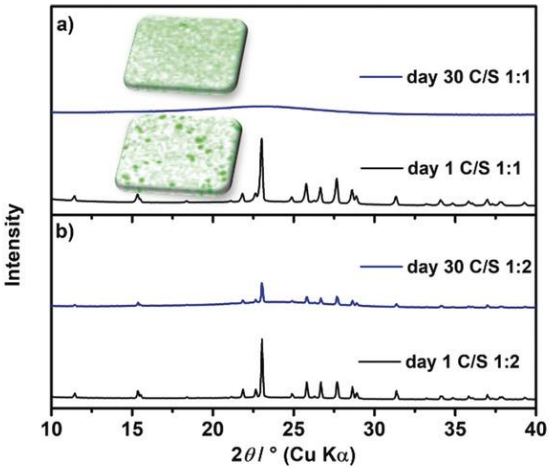

Figure 1 XRD diffraction patterns of carbon-sulfur mixtures in 1:1 and 1:2 ratio. Both mixtures were simply prepared by mixing them in a mortar at room temperature. While directly after mixing, sulfur is still crystalline, no signals are detected after 30 days of rest at room temperature. Even for a mixture of 66wt% sulfur, only a small fraction remains crystalline. In line this apparent loss in crystallinity, sulfur also loses other bulk properties such as Raman vibrations and melting point. The underlying phenomenon is called *sulfur spillover* and likely has major consequences for the electrodes of metal-sulfur batteries that rely on carbon/sulfur composites materials as positive electrode.

Related publications:

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Amino acid based new zwitterionic polymers for inhibition of mild steel corrosion in 1 M HCl

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Abstract:

1-Bromo-3-(diethylphosphonato) propane was prepared from triethyl phosphate and 1,3-dibromopropane, which was then reacted with diallylamine, followed by the treatment of NaOH then purified by distillation to obtain ethyl 3- (*N, N*-diallylammonio) propanephosphonate [1]. *N, N*-diallyl methionine ethyl ester was formed by the reaction between ethyl ester hydrochloride of essential amino acid methionine and allyl bromide, which was treated with NaOH followed by an acidification by HCl to form zwitterionic *N, N*-diallyl-l- methionine hydrochloride [2]. The homo and copolymer of *N, N*-diallyl-l-methionine hydrichloride and *N, N*-diallylamino propanephosphonate were prepared using Butler's cyclopolymerization protocol [3]. Under the influence of pH, the polyelectrolyte-zwitterions could then be converted into cationic, zwitterionic and zwitterionic/anionic polymers with tremendous scientific and technological interest. The polyelectrolytes were characterized by various spectroscopic techniques such as Fourier transform infrared spectroscopy (FT-IR), Nuclear magnetic resonance spectroscopy (NMR) and thermal gravimetric analysis (TGA). The solution properties of these polymers were studied in detail. The performance of these synthesized compounds on mild steel was investigated by gravimetric method, Tafel extrapolation, Linear polarization method, and electrochemical impedance spectroscopy in acid media. Different adsorption isotherms were also explored to find the best fit, and the surface morphology of mild steel corrosion was evaluated in absence or presence of polymers by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDX), and X-ray Photoelectron Spectroscopy (XPS). The X-ray photoelectron spectroscopy (XPS) confirms that the inhibitor molecules form a film at the metal surface. The surface coverage data demonstrated that the inhibitor molecules undergo adsorption onto the metal surface. The synthesized corrosion inhibitors showed high inhibition efficiency and found to be thermally stable. The plethora of pH-responsive polymers containing essential amino acid residues of methionine demonstrated superb corrosion inhibition behavior in arresting corrosion in aqueous acidic media.

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Integrated approach towards quantitative prediction of electrochemical infrared and Raman spectra from single-crystal electrode/liquid interfaces

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In situ electrochemical (EC) infrared (IR) and Raman spectroscopies play an important role in characterizing the potential-dependent interfacial structures at solid/liquid electrochemical interfaces. However, in many cases the spectra are too complicated to be exactly interpreted, due to the complexity of EC interfaces even at model single-crystal/liquid interfaces. This has puzzled spectroelectrochemists for many years. Here, we present a methodology by integrating the surface charged method, the implicit solvation model, and the finite difference method to precisely reproduce the measured potential-dependent IR and Raman spectra with not only frequencies but also intensities. As shown in Figure 1, both of the calculated vibrational frequencies and the EC-IR and -Raman intensities of the adstructure Pt(111)(2×2)-3CO α_1 agree well with the experimental spectra of the well-known ordered adstructure of Pt(111)-CO in a CO-saturated 0.1 M $HClO_4$ aqueous solution. The inclusion of solvation model is essential for precise prediction of the vibrational frequencies and the Stark tuning slopes. The Stark tuning slopes of CO stretching modes and PtC stretching modes are opposite-sign, which indicates that the electrons decrease in CO $2\pi^*$ orbitals and increase in PtC σ orbitals as the potential increases. Moreover, precision criteria of the convergence in the self-consistent field (SCF) should be as high as 1×10^{-9} eV for reasonable prediction of the relative intensities. Finally, we predict the EC-IR and -Raman spectra of two meta-stable CO/Pt(111) adstructures which might be in tiny areas at 0.36 — 0.45 V. The as-developed method could pave a way to well reveal the mechanisms in many interfacial EC systems including electrocatalytic reactions.

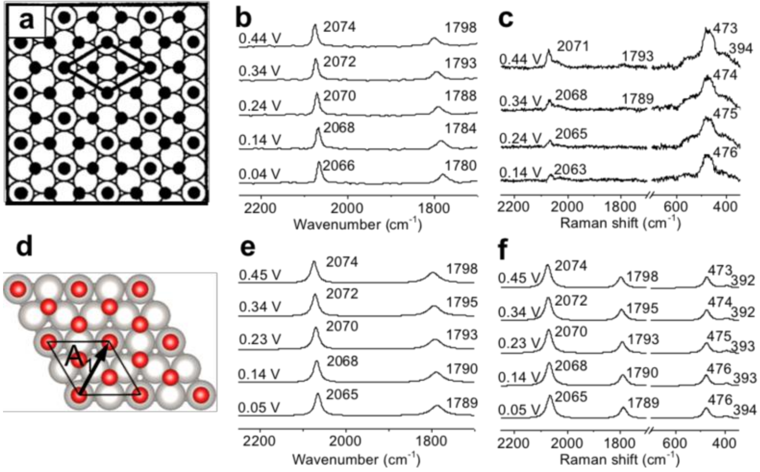

Figure 1. The Pt(111)(2×2)-3CO α_1 adstructure at 0.04 — 0.44 V vs SHE in a CO-saturated 0.1 M $HClO_4$ aqueous solution. (a) and (d) the possible adstructure proposed by Villegas *et al*. and the optimized structure by first-principles calculation.[1] (b) and (e) the measured and calculated EC-IR spectra.[2] (c) and (f) the measured EC-Raman spectra by SHINERS technical and the calculated EC-Raman spectra. Image (a) adapted from ref. 1 with permission, copyright (1994) American Institute of Physics; Image (b) adapted from ref. 2 with permission, copyright (2000) American Chemical Society.

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Electrochemistry of, and ~~electroanalysis~~ Electroanalysis in, ~~chiral~~ Chiral and ~~inherently~~ Inherently ~~chiral~~ Chiral ~~ionic~~ Ionic ~~liquid~~ Liquid ~~media~~Media

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Ionic liquids ILs are attractive media for electrochemistry and electroanalysis, since, in addition to other useful properties, they provide both solvent and supporting electrolyte; moreover, they feature an extremely well defined structure at the interphase with a charged electrode, resembling somehow a ~~semisolid crystal or a~~ bulk liquid crystal, extending for many layers, also standing in the presence of water traces, and possibly tunable by *in-situ* present additives. [1-3] For this reason *chiral* ionic liquids (CILs), of which a rich palette is already available, are surprisingly still nearly unexplored by electrochemists, in spite of appearing quite attractive, since they could transmit chiral information more effectively than chiral organic solvents or chiral supporting electrolytes. [1]

In this context, we have recently started a detailed investigation of (a) bio-based chiral ionic liquids and (b) *inherently chiral* ionic liquids (ICILs), investigating both their physico-chemical and electrochemical features and their performance as media for chiral electroanalysis experiments. Our bio-based CILs feature cations with a building block of natural origin, including one or more localized stereocentres, from which their chirality arises (as in most so far available CILs) [4]. Instead, in our ICILs chirality is intrinsic of the whole biheteroaromatic cation, which features a ~~high torsional angle~~stereogenic axis related to a torsion between two equal heteroaromatic moieties, with a related energy barrier too high to be overcome at room temperature, so that the ICIL can be obtained in two stable enantiopure antipodes. In inherently chiral molecules and materials both chirality and functional properties originate from the same structural element, which can coincide with the main molecular backbone; thus their chirality manifestations can be very powerful, as recently evidenced by some of us in electroanalytical, chiroptical and magneto-electrochemistry experiments with electrodes modified by inherently chiral oligomer thin films.

Actually, while interesting but (at least so far) small are the chirality effects observed~~,~~ working in our bio-based CILs with localized stereocentres [4], large peak potential differences have been observed for the enantiomers of very different chiral probes in CV experiments in an enantiopure bulk ICIL. Very conveniently, impressive enantiodiscrimination is observed even using ICILs (or other related inherently chiral molecular salts, solid at room *T*, but of easier synthesis) as low-concentration chiral additives in common achiral ionic liquids (ILs) [5,6]. Furthermore, similar impressive performances have also been observed dissolving in an achiral IL a thiahelicene-based additive, ~~also~~ an inherently chiral oligothiophene, but uncharged and based on a different stereogenic element, *i.e.* a *helical* scaffold. Among possible explanations we are considering the possibility of a chiral reorganization effect by the inherently chiral additives in the locally highly ordered IL structure at the interphase with the charged electrode, similarly to the well-known transitions from ~~mesomeric~~ nematic to cholesteric order induced by chiral additives in bulk liquid crystals.

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Electrocatalytic Reduction of Heteroaromatic Halides on Gold and Silver Electrodes: Synergy in Electrocatalysis

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The electrocatalytic reductive cleavage of carbon–halogen C–X bonds on electrode surfaces with high halide affinity like Ag and Au is of potential great interest in analytical, synthetic and environmental contexts, resulting in many cases in impressive positive shifts of the halide reduction potentials, often with significant changes in mechanism and products, too. [1] The process has also been thoroughly studied as an excellent model for dissociative electron transfer (DET) in electrocatalytic conditions, modulated by many factors, including molecular structure (halide leaving group and aliphatic/benzylic/aromatic residue), working medium (our parallel presentation), as well as electrode surface.[1]

In particular, comparing Ag and Au as catalytic electrode materials for the reductive activation of many organic halides, we have observed that Au, in spite of its higher intrinsic affinity for halide ions, generally results in much lower catalytic effects than Ag (in terms of positive peak potential shifts *vs* glassy carbon GC as non-catalytic reference), which we justified considering that, compared to Ag, Au should have a much more positive pzc in our working media, resulting in higher negative surface charge in the working potential range, and therefore in higher repulsive effects towards halide anions.

However, the presence of S or N heteroatoms on the halide organic residue can have a remarkable impact on this situation, as we have recently observed comparing the behaviour of aromatic halides with a rich palette of *hetero*aromatic ones, like halo- and polyhalo- thiophenes [2], bithiophenes and benzodithiophenes, as well as halo- and polyhalo cyclic triimidazoles. The S or N atoms included in such conjugated systems not only make the aromatic ring(s) asymmetric from the perspective of the electron density, but, importantly, can themselves have specific interactions with the electrode surface, in addition to the interactions of the C–X group undergoing DET; therefore heteroatoms can act as “adsorption auxiliary groups” on the catalytic surface.

Thus, as we will show, the presence of heteroatom anchoring groups can promote the electrocatalytic cleavage of C-X bonds on Au and Ag, enhancing the "intrinsic" catalytic effects of the electrode surface. However, such enhancement is much more impressive in the case of the less catalytic Au surface, which appears to recover most of its intrinsically high catalytic activity, overcoming the repulsive effect of the surface charge in the working potential range, thanks to the presence of the heteroatom "anchor(s)". Several cases are particularly impressive, with the Au performance appearing to approach or even overcome the Ag one.

Interestingly, such impressive enhancement of the Au catalytic activity can be modulated by the relative position(s) of the heteroatom(s) with respect to the halide leaving group(s) in the molecule undergoing DET. For example, a higher catalytic shift is observed for the reduction of 2-Br-thiophene, having the leaving Br group adjacent to the S atom, as compared to 3-Br-thiophene; instead in the Ag case the leaving group position is less determining, possibly on account of prevailing silver-halide interactions.

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Interactions of Ions Inside and Outside Carbon Nanotubes

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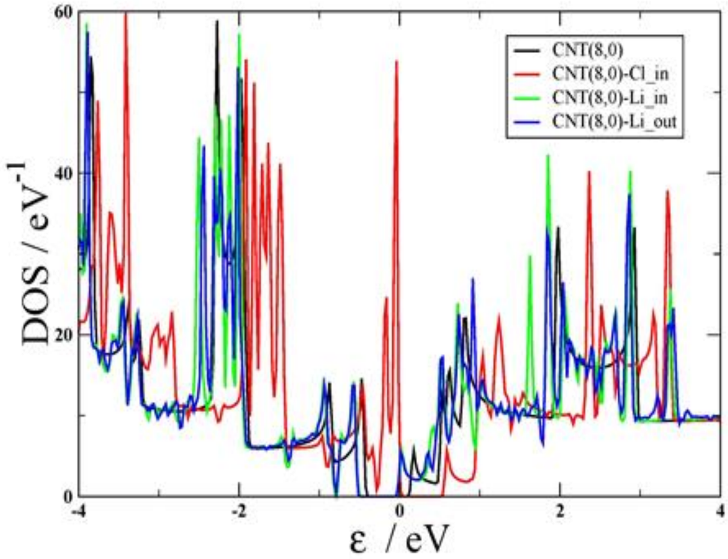
Carbon nanotubes (CNTs) interact strongly with ions in the vicinity. To study this effect in detail, we have performed DFT calculations for a variety of ions both inside and outside the tube, considering both a semiconducting (8,0) and a conducting (5,5) CNT. We have focused on the question, how the presence of the tube modifies the interaction between ions.

In the simplest case a polarization or image charge forms on the surface of the tube, which strongly affects the electrostatic interaction between ions [1]. If both ions are inside our outside the tube, the interaction is significantly reduced by the image forces. In effect, the Coulomb interaction between charges is replaced by dipole-dipole interactions. The effect is even stronger when one ion is inside the tube and the other one outside; in this case the direct Coulomb interaction is totally screened by the tube. The electronic density of states (DOS) of the tube is not directly affected, but the Fermi level is shifted so that locally the extra charge can be accommodated. In the semiconducting (8,0) tube this shift is larger than in the conducting (5,5) tube. In the case of two Li$^+$ ions, one inside and one outside the tube, this can lead to an effective attraction between the ions [2], which again is stronger for the semiconducting tube.

Halide ions such as Cl$^-$ tend to form adsorption bonds with the carbon tubes, which complicates the interactions. In this case the density of states of the CNT is significantly modified, and not just shifted (see figure). Nevertheless, a Li$^+$ ion inside the tube affects the adsorption energy of a Cl$^-$ outside. Even though there is no direct electrostatic interaction, the adsorption of the Cl$^-$ outside is enhanced.



DOS for a pristine (8,0)CNT, and for the same tube with 1 Li outside, and for 1 Li inside and 1 Li outside, 1 Cl inside and 1 Li outside. The Fermi level has been set to zero.

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Electrochemistry of gamma-substituted complexes of bis(β- diketonato)copper(II)

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The development of unique liquid crystalline compounds with exciting technological applications (LCD, spatial light modulators, molecular sensors, optical switches, etc.) is one of the main research goals in the area of molecular-based materials.[1] In particular, the synthesis of metal complexes of organic ligands (metallomesogens) has grown quite significantly. Metallomesogens combine the variety and wide-range of metal-based coordination chemistry with the special physical properties demonstrated by liquid crystals.[2] Bis(β-diketonato) metal complexes containing side-chain substituents at the γ-position of the ligands, are among the best known disc-shaped coordination compounds exhibiting liquid crystal properties[3] In this study, bis(β-diketonato)copper(II) containing γ-substituted β-diketones (with $[Cu(L3)_2]$ as an example, as shown in Figure 1), was synthesised. Cyclic voltammetry of the studied γ-substituted β-diketones and their corresponding copper(II) complexes, showed irreversible electrochemical and chemical behaviour in their reduction.

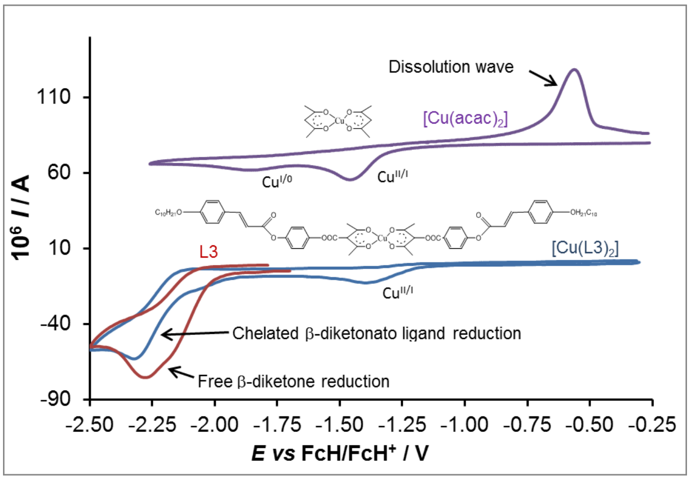

Figure 1. Cyclic voltammograms of 0.001 M solutions of $[Cu(acac)_2]$ in purple, free ligand [L3] in red, and complex $[Cu(L3)_2]$ in blue, given in V *vs* FcH/FcH$^+$. Measured in 0.100 mol dm^{-3} $[NBu_4][PF_6]/CH_3CN$, on a glassy carbon working electrode at 25 °C.

For complex $[Cu(acac)_2]$ (where Hacac = acetylacetone, with γ-substitutent = H), the following peaks were observed: the $Cu^{II} \rightarrow Cu^{I}$ reduction peak (at −1.45 V *vs* FcH/FcH$^+$), the $Cu^{I} \rightarrow Cu^{0}$ reduction peak (at −1.90 V *vs* FcH/FcH$^+$), as well as the sharp anodic dissolution wave of deposited copper (*) at *ca.* −0.55 V *vs* FcH/FcH$^+$.[4] For the $[Cu(L3)_2]$ gamma-substituted complex (with γ-substitutent = $(CH_3COC(C_{10}H_{21}OC_6H_4C_2H_2COOC_6H_4COO)COCH_3)$), the following peaks were observed: the $Cu^{II} \rightarrow Cu^{I}$ reduction peak at a slightly higher potential than the first reduction of $[Cu(acac)_2]$ (namely −1.38 V *vs* FcH/FcH$^+$), and the second reduction peak much lower (at −2.30 V *vs* FcH/FcH$^+$), while no sharp anodic dissolution wave was obtained. This suggests that no Cu^0 was formed or deposited on the electrode, as has been observed for $[Cu(acac)_2]$. The second reduction of complex $[Cu(L3)_2]$ was much lower than the second reduction of $[Cu(acac)_2]$ and in the same region as reduction of the free uncoordinated ligand L3 (see Figure 1), suggesting that the second reduction might be ligand based instead. This also suggests that the long chain at the γ-position of the conjugated ligand (L3) added stability to the $[Cu(L3)_2]$ metallomesogen system, resulting in the copper remaining attached to the metal complex.

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Zinc-Based Spinel-Oxide Materials Showing Reversible Spinel–Rocksalt Transition for High-Energy-Density Magnesium Rechargeable Batteries

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Development of ecologically friendly "multivalent metal-anode rechargeable batteries" using such as Mg, Zn, Al, etc. is an attractive issue for future sustainable society. Especially, Mg rechargeable battery (MRB) has been a promising candidate for next-generation batteries used for electric vehicles and smart-grid systems. In MRBs, since Mg can be deposited without dendritic formation unlike Li metal, Mg metal itself [with high specific capacity (2205 mAh g^{-1}) and low electrode potential (-2.4 V vs. SHE)] can be used as the anode material. In addition, MRBs are suitable for large-scale applications in terms of their safety and abundant resources. Despite their obvious advantages, the development has been plagued by the lack of high-performance cathode materials. Several years ago, our group pioneeringly show that several Mg-based spinel oxides (e.g., $MgCo_2O_4$) allow Mg insertion via spinel-to-rocksalt transition upon discharge at elevated temperatures around 150°C [1]. However, their poor cyclabilities have been a significant problem; this is probably because the resulting rocksalt phase is fairly stubborn and the inverse "rocksalt-to-spinel" transition is sluggish to occur.

In this work, we show that utilizing Zn that prefers tetrahedral environment in oxides is a key to facilitate the inverse rocksalt-to-spinel transition, which allows "reversible" spinel–rocksalt transition with Mg insertion/extraction. In view of the mechanism we have proposed for the spinel-to-rocksalt transition [1], where the cations at the tetrahedral (8a, #227) site in the spinel structure migrate to the vacant octahedral (16c, #227) sites accompanied with Mg insertion, eventually leading to rocksalt structure, we predict that applying the cation such as Zn that prefers tetrahedral environment would facilitate the inverse rocksalt-to-spinel transition. In fact, by means of ab initio calculations, we substantiate that Zn strongly prefers the tetrahedral 8a site owing to a covalency of Zn–O. Furthermore, we experimentally demonstrate that Zn-based spinel oxides (i.e., $ZnCo_2O_4$ and $ZnFe_2O_4$) show significantly improved cyclability compared to Ni-based ones (e.g., $NiCo_2O_4$), where Ni is a well-known element to favor octahedral environment in oxides unlike Zn. Especially for $ZnFe_2O_4$, the volume change in discharge/charge is significantly small compared to that for $ZnCo_2O_4$, which can provide a nearly zero-strain cathode material with superior cyclability (Fig. 1). In this presentation, we will discuss fundamental strategies for designing spinel oxides in terms of cation distribution, structural stability, coherent strain, etc. for achieving high-performance cathode materials.

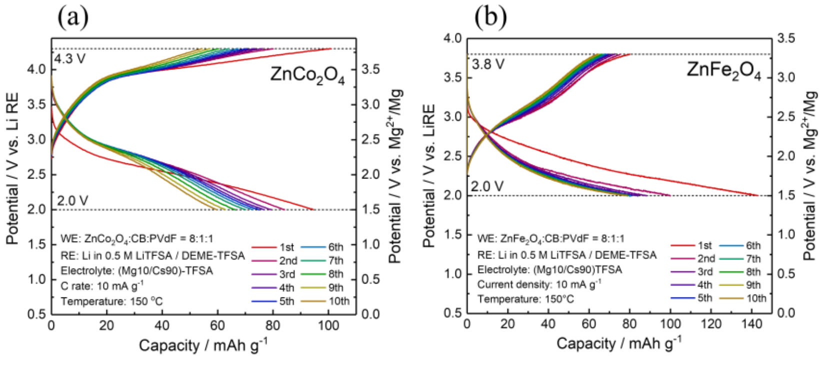

Fig. 1 Cathode performance of (a) $ZnCo_2O_4$ and (b) $ZnFe_2O_4$ at 150°C

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Novel Preparation of Hollow-Heterostructure $Co_3O_4@SiO_2$ Nanoparticles for Optimized Li-Ion Storage

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Abstract:

Mechanical and chemical degradations during the lithiation/delithiation process still limiting the long-life transition-metal oxide (TMO) and silicon anodes for future lithium-ion batteries. Here, A novel design of hollow structured $Co_3O_4@SiO_2$ nanocomposites was obtained, which not only demonstrates the fast Li-ion transport achieved by designing nanofluidic channels of surface holes and massive inner channels as an anode of LIBs, but also prevents aggregation of Co_3O_4 and fabricates stable solid electrolyte interphase during long-term cycling.

Especially, the stable hollow-heterostructure based on $Co_3O_4@SiO_2$, exhibits excellent rate performance (463 and 205 mAh g^{-1} at 10 and 20 A g^{-1}, respectively) and high specific capacity (1140, 680 and 276 mAh g^{-1} at 0.1, 1 and 5 A g^{-1}, respectively) with a Coulombic efficiency of more than 95%. The present work promises a way for rational design of the advanced electrodes as the next-generation high specific capacity energy device.

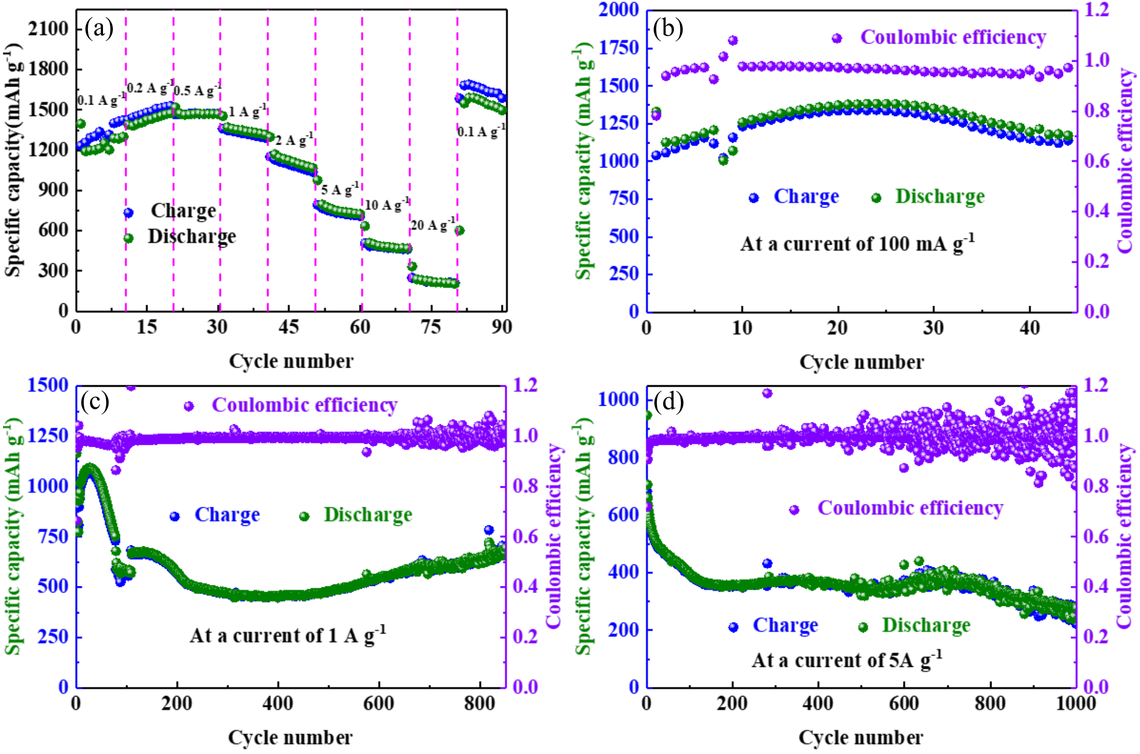

Figure 1. (a) Specific capacity of $Co_3O_4@SiO_2$ at various charge and discharge rates. (b, c, d) Specific capacity of $Co_3O_4@SiO_2$ at the current of 0.1, 1 and 5 A g^{-1}.

Synthesis and Electrochemical Study of Graphene Based Nanomaterials and Nanocomposites

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Graphene-based nanomaterials have been demonstrated in advanced energy and environmental applications [1-4]. However, their wide utilization in practical applications is strongly hindered due to the lack of simple, cost effective, and environmentally compatible synthetic methods for the mass production of graphene. To date, mechanical, solution, and chemical based approaches have been extensively explored in the synthesis of graphene; but each approach has its limitations, particularly in terms of scalability and the characteristics of the resulting graphene. In addition, as for pristine graphene, inherent restacking issues have hampered the use of these nanomaterials in electrochemical applications. Novel properties may be achieved through the introduction of various functional groups and dopants into the graphene, or via the meticulous design of three-dimensional (3D) superstructures. Graphene oxide is a promising intermediate for the preparation of graphene-based nanomaterials in bulk. In this presentation, we report on the synthesis of interconnected reduced graphene oxide (IC-rGO), fluorinated graphene oxide (F-GO) and cobalt/graphene nanocomposite quantum dots (QDs) and their promising energy and environmental applications.

Unique 3D IC-rGO was synthesized using a facile one-pot synthesis process that we refer to as Streamlined Hummers Method. The 3D hierarchical structure was advantageous in overcoming restacking issues while improving the heterogeneous electron transfer kinetics of the 2D materials. Unlike the conventional procedure that involved cross-linkers and multiple steps to produce 3D graphene structures, the interconnections were enabled though the inherent oxygen functional groups of the graphene oxide. These functionalities were confirmed using infrared and X-ray photoelectron spectroscopy. The structure of the synthesized 3D IC-rGO was also characterized using X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. The fabricated 3D IC-rGO was further tested as an electrode material for supercapacitor applications. The IC-rGO showed high cyclic stability and an enhanced specific capacitance over conventional thermally reduced graphene oxide. The formed F-GO exhibited improved double-layer capacitance in contrast to its non-doped counterpart and showed high activity for the sensitive detection of heavy metal pollutants, such as Cd, Pb, and Hg ions.

Hydrogen production via electrochemical water splitting is limited thermodynamically by the sluggish oxygen evolution reaction (OER) at the anode. The use of noble metal-based catalysts leads to an economic bottleneck due to the high cost associated with such materials. The fabricated cobalt/graphene nanocomposite QDs exhibited much higher current density and much lower overpotential for the OER compared with cobalt nanoparticles and the state-of-the-art Pt/C commercial catalyst. The design of different graphene-based nanomaterials and nanocomposites for clean energy and environmental applications is highlighted.

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Influence of Organic Binders to the Properties of Lithium-Sulfur Batteries

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Advanced energy storage systems and electric vehicles play an increasingly important role nowadays and their role will be crucial for limitation of CO_2 emissions in the future. These applications require higher energy density to cover future requirements such as longer range or more renewable energy stored for longer periods of time. Lithium-sulfur (Li-S) batteries can cover these requirements thanks to their several advantages such as high theoretical energy density (about 3000 Wh/kg), low cost of raw material and low environmental impact 1. However, Li-S batteries have also many drawbacks such as solubility of polysulfides in the electrolyte during discharging which leads to a decrease of capacity. Another obstacle is about 80% volume expansion of sulfur during cycling. This expansion leads to capacity decrease due to damage to the internal structure of the electrode. Another problem is the insulating nature of sulphur 2. There are several ways how these problems can be fixed. For example, preparation of sulfur-carbone composites, sulfur-graphene composites, sulfur-polymer composites, sulfur-metal oxide composites, porous 3D collectors or modified separators and interlayers 3 4 5 6. In this work, the optimization of the Li-S electrode stability by means of three types of organic binders is presented. The electrochemical performance of a standard electrode with poly(vinylidenefluoride) binder was compared with the organic binders. It was found that these binders improve the stability of electrode during cycling thanks to improved structural stability of the electrode. They have better binding properties which decrease the amount of binder needed and increase the amount of sulfur in the electrode. Stable capacity of about 1100 mAh/g was achieved during cycling at 0.2 C and it was over 500 mAh/g during cycling at 2 C with sulfur loading of the electrode over 2 mg/cm^2.

Acknowledgements:

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Is all ·OH calculated correctly?

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For the first time, Kapalka [1] gave an insight into form and magnitude of hydroxyl radical distribution at Boron Doped Diamond (BDD) anodes, which may produce highly reactive species such as ·OH. For this, the following second-order differential equation was solved:

$$D_{\bullet OH}\ d^2C_{\bullet OH} / dx^2 - 4k_{\bullet OH}\ C^2_{\bullet OH} = 0 \qquad (1)$$

The stoichiometric coefficient 4 in Eq. 1 is based on the limiting assumption that all hydroxyl radicals are converted into oxygen. However, it can be found in experiments that other species (ozone, hydrogen peroxide etc.) may be formed. In addition, the boundary condition (Eq. 2) seems to be a contradiction in terms.

$$D_{\bullet OH}\ dC_{\bullet OH} / dx = -j/(n\,F) \qquad \text{(for } x=0) \qquad (2)$$

This paper is is targeted on formulae improvement by taking into account additional chemical reactions. In a first step, another limiting case was considered – the total conversion of hydroxyl radicals into hydrogen peroxide (k = 5.5 E+06 $m^3/(mol\ s)$, firstly discussed in [2]):

$$2\ \bullet OH \rightarrow H_2O_2 \qquad (3)$$

The model is approximately justified for relatively low current densities j and special electrode structuring. To solve the system, the stoichiometric coefficient 4 in Eq. 1 has to be changed into 2. Consequently, the surface concentration for hydroxyl radicals is obtained higher – compared to the Kapalka model.

Eq. 4 represents the second differential equation necessary for finding a solution with respect to H_2O_2 concentration distribution.

$$D_{H2O2}\ d^2C_{H2O2} / dx^2 + k_{\bullet OH}\ C^2_{\bullet OH} = 0 \qquad (4)$$

It can be easily shown that for boundary conditions as applied by Kapalka with "zero-concentration" of peroxide at the anode surface the hydrogen peroxide concentration curve must have a maximum. The second boundary conditions is defined by the complete reactor model for continuous operation.
Eq. 4 was solved analytically and by using a second mathematical approach for better applicability in further calculations.

In a second step, the boundary condition according to Eq. 2 was partially replaced by defined peroxide occupation at x=0 at the anode surface. In this case, the surface concentration is drastically reduced compared to the very first model [1].

Conclusions and application consequences are discussed.

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Effect of nanoparticle incorporation in silane-polymer composite coating on corrosion protection of Mg-Zn-Al alloy in aggressive corrosive media

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In acidic, sulfuric acid containing 3.5% NaCl aqueous electrolytes, the electrochemical behavior of magnesium-aluminum-zinc alloy with composition alloy Mg (93) Zn (1) Al (6) is studied. To characterize the behavior of the alloy in these electrolytes, electrochemical techniques such as D.C polarization and electrochemical impedance (EIS) measurements are used. The data indicated the alloy's direct dissolution as evidenced by ICP measurements and surface examination following the exposure to the corrosive medium.

The alloy was treated with a silane-polymer coating that proved effective in protecting the surface against corrosion. In order to improve its corrosion protection and film quality, the silane - polymer coating is further treated with metallic nanoparticles. The protecting film is composed of 1,2-bis(triethoxysilyl)ethanepoly (vinyl alcohol) hybrid (TESEPVA).

The hybrid film was applied to the alloy surface either by sequential spin-coating or layer-by-layer spin-coating. Before and after exposure to the corroding electrolytes, surface examination of the alloy or film - coated alloy was carried out. The techniques used are field-emission scanning electron microscopy (FE-SEM) with energy dispersive X-ray analysis, X-ray photoelectron spectroscopy (XPS) and surface enhanced Raman spectroscopy (SERS).

The film thickness and surface wettability were also determined with the film displaying relative increase in the hydrophobic character.

Determination of electrochemical, spectral and computational properties of substituted [Ru(phen)$_3$]$^{2+}$ and [Ru(bpy)$_3$]$^{2+}$ complexes

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The investigation of metal-to-ligand charge transfer complexes already started as early as 1966 [1]. In 2000 the Millennium Technology Prize was awarded to Michael Grätzel for his research in the application of ruthenium bipyridyl complexes in dye sensitized solar cell (DSSC) technology [2,3]. In the research and application of dye sensitized solar cells and photo-catalytic H_2O and CO_2 reduction, properties such as metal-to-ligand charge transfer in nitrogen-based ruthenium complexes form part of the central component. Alterations of ligands and substituents cause spectral and electronic tuning. In this study an electronically altered phenanthroline and bipyridine ruthenium complex series was synthesized and characterized using UV-visible spectra and cyclic voltammograms, see Figure 1. The electrochemical redox potentials obtained ($\Delta E^{0'} > 1.0$ V for Ru$^{II/III}$), amongst others, were correlated with DFT calculated ionization potentials and HOMO energies. A computational tool that predicts redox potentials is hereby provided, based on the linear relationship of $R^2 > 0.98$ in the DFT correlation of the phenanthroline series. Spectral properties of both phenanthroline and bipyridine ruthenium complex series were simulated, where λ_{max} values varies from 450 to 520 nm. The most stable complex in the present series is the diamine-substituted bipyridine complex, based on the fact that it has the smallest DFT calculated HOMO-LUMO energy gap [4].

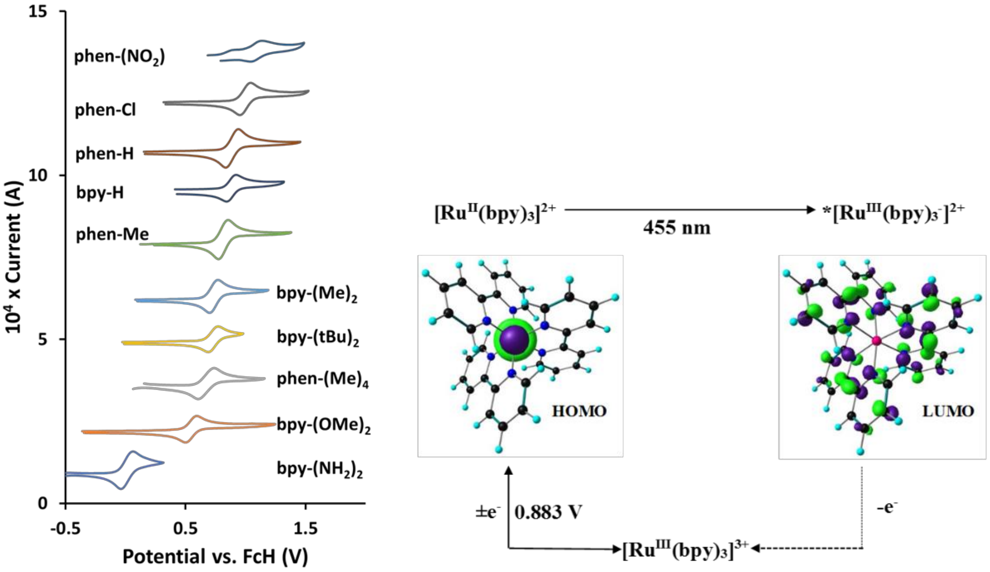

Figure 1. Left: cyclic voltammograms of the Ru$^{II/III}$ redox couple of a series of Ru-phenanthroline (phen) and Ru-bipyridine (bpy) complexes. Right: Illustration of the frontier molecular orbitals (MOs) involved in the redox and UV-excitation processes of these complexes.

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Manganese Oxide-Modified Carbon Nanofibres as Bifunctional Electrocatalysts for Oxygen Reduction and Oxygen Evolution Reactions

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The widespread application of renewable energy technologies such as unitized regenerative fuel cells (URFC) and metal-air batteries (examplezn-air, A-air)suffers from drawbacks such as the fabrication of bifunctionaloxygen electrodes that are both low cost and highly active. The ability to achieve both high performance and reversibility of the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) has proven to be a major challenge because the reactions are known to be kinetically very slow. Although transition metal heteroatom-doped carbon materials (example Fe-N-C and Co-N-C) has been extensively studied, with promising results in oxygen reduction reactions in alkaline media. While in oxygen evolution reactions, transition metal compound based electrocatalysts are known to be highly efficient in alkaline medium. The major drawback in the utility of these catalysts is their low electrical conductivity. Therefore the challenge is to create highly effective bifunctional oxygen electrodes capable of reversibly catalysing both reactions over a long time during cycling in URFCs.

In this work, manganese oxide (MnO_x) integrated with carbon nanofibre(CNF) suppor tis being investigated as a bifunctional electrocatalysts for ORR and OER. Electrospinning technique is employed to first fabricate the polymer nanofibre from polyacrilonitrile (PAN) which is then carbonised at controlled temperatures to obtain the CNF. Two different sources of manganese salts are used to introduce the MnOx into the CNFs. The electrode materials are characterized using scanning electron microscopy and high resolution transmission electron microscopy (HRTEM). The particle size, size distribution and morphology of the functionalized MnO_x/CNF electrocatalysts will be determined using transmission electron microscopy (TEM), X-ray diffraction (XRD) analysis. The surface composition of the catalysts will be determined using high resolution X-ray photoelectron spectroscopy (XPS). The bifunctional eletrocatalyic activity and stability of the prepared MnOx/CNF towards OER and ORR are being investigated using linear sweep voltammetry (LSV), and will be presented as a poster at the conference.

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Interrogating the Effects of Ion-Implantation-Induced Defects on the Energy Storage Properties of Bulk Crystalline and Powder Molybdenum Disulphide

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A number of studies on enhancing MoS_2 as an electrode material have been reported. Some of the approaches include incorporation with graphene, [1-3] carbon nanospheres,[4] onion-like carbons[5] polyaniline (PANI) and polypyrrole (PPy).[6] Defects are known to affect transport and electronic properties of materials.[7-9]

In this study Mo and W ions were irradiated onto the surface of the bulk crystalline MoS_2 at a constant acceleration voltage of 10 keV induces defects at the near-surface (from the surface to ≈ 15 nm depth). The induced defects significantly had impact on the general electrochemical and energy storage properties of the bulk crystalline MoS_2, (in terms of capacity, cycling stability, coulombic efficiency, and electron transfer kinetics) compared to the pristine MoS_2 samples. Ion implantation with W at fluence of 10^{12} ions/cm^2 gave an enhanced electrochemistry compared to the Mo counterpart.

However, after successfully synthesizing flower-like powder MoS_2 (proven be Raman, XRD, EDS, SEM and TEM), ion implantation of Mo and W ions was done on electrodes made from it. The ion irradiation was aimed at implanting the ions near-surface. Same implantation energy as used in bulk (10 keV) was used on these too. These electrodes showed that the ion implantation suppresses the general electrochemical and energy storage properties of the flower-like MoS_2 electrodes, contrary to what was observed in the case of bulk. The reduction in the performance of these electrodes after ion implantation has been attributed to the reduction of the pore sizes revealed by Brunauer-Emmett-Teller (BET). Also shown is the difference in the electrochemical processes of flower-like MoS_2 and those of bulk MoS_2. The sample annealed at 450 degrees reported the most enhanced electrochemistry before ion implantation compared to the as-synthesized counterpart.

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Sodium Metal Fluorophosphate (Na_2MPO_4F) Family of Insertion Materials for Sodium-ion and Sodium-air Batteries

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Sodium-ion batteries have emerged as a viable alternative to Li-ion batteries due to their high abundance, low cost and operational similarity. Owing to versatile nature in terms of anion substitution coupled with high thermal and structural stability, polyanionic materials are now widely studied as cathode materials for secondary batteries. Major advantage in using polyanions as cathode is the enhanced voltage due to high electronegativity of the central metal atom. Fluorine being the most electronegative element in the periodic table can be combined with other anions resulting in further increase of the cell voltage. $Na_2Fe(II)PO_4F$ is one such example where F-ion is combined with PO_4-group making it a 3-V cathode material. The present work involves an economic solution combustion synthesis starting from Fe(III) precursor yielding phase-pure carbon-coated material in one-minute. The material was studied as cathode for both Li-ion and Na-ion batteries. Different (dis)charge profiles were observed in both configuration. While the operating mechanism of the material in Li-configuration has been well explained by some groups, the redox mechanism of (de)intercalation is still under debate for Na-configuration. An effort was made to study the mechanism by the help of *in-operando* XRD combined with some theory calculations. The structural, electrochemical and mechanistic analysis will be presented in detail.

On another note, metal-air batteries based on O_2-H_2O chemistry have garnered a lot of interest due to their high-energy density (~5200 Wh kg^{-1}). With high safety, low cost and enhanced ionic conductivity, the performance of air-battery is still largely affected due to the formation of insoluble discharge products. Therefore, hybrid aqueous air batteries stand out in this case as the discharge product is soluble. Air batteries function on two processes namely oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), kinetics of which are too slow. Hence, a catalyst is required to increase the rate of reaction. Existing catalysts are costly and lacks bifunctionality. Motivated by recent reports of various phosphate based materials having bifunctional activity, we hereby report the electrocatalytic activity of Na_2MPO_4F (M: Fe, Mn, Co) fluorophosphate family. Carbon coated grains were obtained for all materials using combustion method. Presence of carbon not only helps in enhancing the electrical conductivity of the materials but also improves their catalytic properties. Catalytic performance of all three materials were studied and Na_2CoPO_4F was found to give the best results. The onset potential of Na_2CoPO_4F was found to be 0.854 V vs. RHE for ORR process, which is comparable to 20% Pt/C while an onset potential of 1.591 V vs. RHE was recorded for OER process. A hybrid Na-air battery was fabricated using Na_2CoPO_4F as an air-cathode and a roundtrip efficiency of 88% was recorded for over 30 cycles. The catalytic properties of all three materials were also investigated by means of density functional theory (DFT) analysis. A detailed structural and catalytic analysis of this fluorophosphate family will be presented [1-5].

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Physico-chemical properties of catalyst-free carbon nano-onions grown by the flame pyrolysis method for possible application in supercapacitors

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Carbon nano-onions (CNOs) are a relatively new member of the carbon nanomaterials family with spherical concentric fullerene-like shells resembling that of an onion. CNOs are the choice of material as an electrode for industrial applications and energy storage devices due to its excellent properties such as natural abundance, non-toxicity, low cost, higher specific area (1 to > 2000 m^2/g), high chemical stability and excellent electrical conductivity [1]. The synthesis of CNOs is normally achieved by use arc-dis-charge between two electrodes submerged in water, ion implantation and Chemical vapour Deposition (use of metal catalysts) [2]. However, most of the methods above-mentioned require high energy input, acid treatments and CNOs are sometimes of low yield or just as a by-product. To counter this problem, we report on the facile synthesis of CNOs through a capillary action using grapeseed oil via a flame pyrolysis method [3]. The capillary method was not only reported to be a cheap alternative, but it provides pure materials with high product yield. Properties of the as-prepared carbon nano materials were investigated using powder X-ray diffractometer (PXRD), transmission electron microscopy (TEM), Thermal gravimetric analysis and Raman spectroscopy. TEM analysis revealed that microstructural features of the as-prepared CNOs from flame pyrolysis were made of particles having quasi-spherical shapes that are agglomerated in an interconnected network as shown in Fig.1. XRD shows that the CNOs have two main peaks corresponding to sp^2 graphitic layers at 2θ values of 25° (002 plane) and around 43° (100 plane). Raman analyses shows that the materials become graphitic upon annealing at different temperatures and time. TGA shows that the materials were made entirely of carbon since they decompose up to completion at around 780 ºC. Preliminary electrochemical screening of the materials using Cyclic Voltammetry (CV) shows that CNOs annealed at 750 ºC (2h) and 850 ºC (2h) exhibit better supercapacitive properties in lithium sulphate electrolyte than other materials obtained under similar conditions.

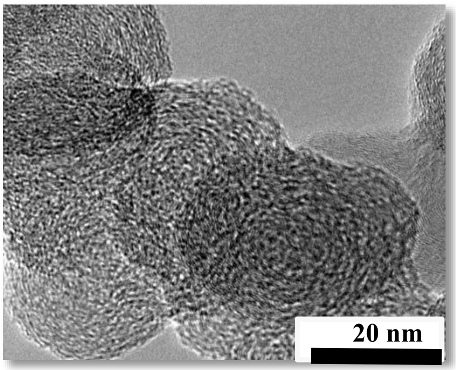

Figure 1: TEM image of the pristine CNOs taken at high magnification.

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Surface-Selective Solution Deposition of Anisotropic Metal Nanostructures: Electroless Plating Meets Shape-Controlled Nanoparticle Synthesis

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Electroless plating traditionally is employed to provide work pieces with protective or electrically conducting coatings, and produces smooth, compact metal films. While the method is becoming increasingly popular for nanofabrication, typical applications of metal nanomaterials demand high roughness, porosity, and specific nanostructure. While the excellent conformity of electroless plating allows producing intricate architectures by template replication,[1] such routes necessitate additional processing steps, and typically result in materials without precisely defined crystallinity.

In this contribution, we summarize our recent efforts in overcoming these limitations with a new electroless plating strategy, in which the bath chemistry is tuned to yield anisotropic deposits such as nanowires,[2] nanoplates[3,4] or nanospikes[5,6] (Figure 1). Likewise to the mechanistically related synthesis of nanoparticles by reducing metal complex solutions, our approach realizes specific product shapes by adjusting the underlying nucleation and growth processes, not by spatially directing metal deposition with templates. This hybrid technique combines the substrate flexibility and surface selectivity of electroless plating with the intrinsic morphological control of colloidal nanoparticle syntheses, while maintaining the scalability and simplicity of its solution deposition origins. Due to its favorable characteristics, shape-controlled electroless plating represents a promising tool for directly growing functional nanostructures on work pieces and for designing sensors and (electro)catalysts,[2-5] including miniaturized and multi-length-scale variants such as microreactors[3] and hierarchically structured nano-networks.[6]

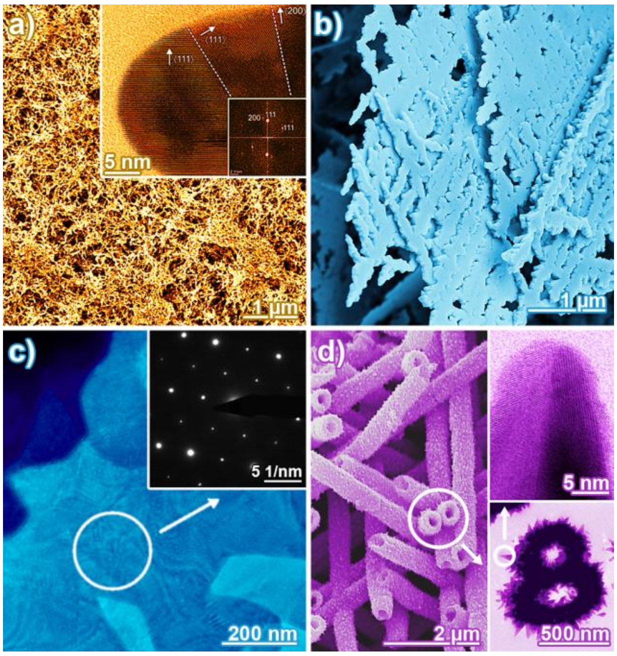

Figure 1. Electron micrographs of electrolessly plated a) Au nanowires, b, c) disrupted Ag nanoplates, and d) Ni nanospike covered nanotube networks.

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Improving Electronic Conductivity of SnO_2 and TiO_2 via Doping: A Hybrid-Functional DFT study

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One of the biggest challenges in electrocatalysis is the discovery of materials—as both catalysts and supports—that are stable in the electrolyte environment and, at the same time, electronically conductive. State-of-the-art anode electrodes for water electrolysis consist of unsupported iridium oxide catalysing the oxygen evolution reaction (OER) [1]. Due to the scarcity and high cost of iridium, there is a strong need to maximise iridium utilisation efficiency. This can be achieved by exploiting the catalytically active surface area of iridium oxide nanoparticles when supported on durable and electrically conductive supports, thus highlighting the need for suitable support materials. Despite their high electrochemical stability, metal oxides, e.g. SnO_2 and TiO_2, are unsuitable as OER catalyst support materials due to poor electronic conductivity [2]. However, doping these host oxides with foreign metals can dramatically improve their conductivity. Using accurate hybrid functionals within density functional theory (DFT) as implemented in the Vienna ab-initio simulation package (VASP) [3,4], we investigated the electronic properties of cation-doped SnO_2 and TiO_2 bulk materials. We report on the dopant stability, conductivity, and the suitability of metal doped oxides for application as OER catalyst supports. Figure 1 shows the effect of oxygen vacancy and metal dopant on the band structure of bulk SnO_2.

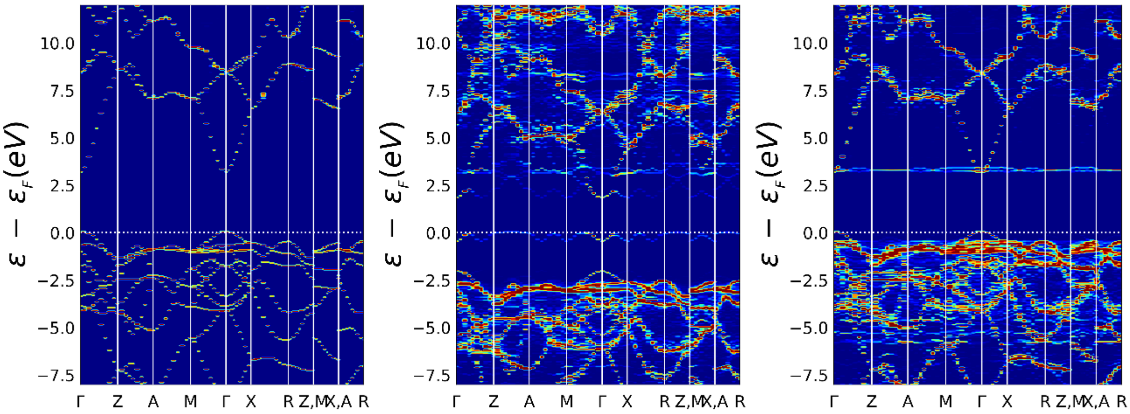

Fig. 1: Band structures of (a) pure SnO_2, (b) SnO_2 with oxygen vacancy, and (c) doped SnO_2.

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High performance nanostructured Pt-W/CeO_2-graphene composite Electrocatalysts for Application in Direct Methanol Fuel cell

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Fuel cells are promising alternative sources of energy that directly convert chemical energy of fuels into electrical energy via a chemical reaction with near zero emissions. Some of the major problems hindering commercialization of direct methanol fuel cells (DMFC) are high cost of platinum electrocatalyst and poisoning of single metallic platinum electrocatalyst by carbon monoxide intermediate generated during methanol electro-oxidation reaction. This problem triggers development of various composite electrocatalysts. However, in theory there is infinite number of ways of preparing composite electrocatalysts. Researchers seldom optimize the compositions of composite electrocatalysts using multivariate approach for optimum performance of fuel cells. The proposed work is aimed at developing Pt-W/CeO_2-graphene composite electrocatalysts for methanol electrooxidation reaction at the anode of DMFC. The work involves design and optimization of the composition of Pt-W/CeO_2-graphene composite electrocatalysts with the aid of statistical mixture design, synthesis of Pt-W/CeO_2-graphene composites and their characterization using BET, FTIR, XRD, SEM, EDX, TEM and electrochemistry in order to investigate their electrocatalytic activity. The proposed work also features modelling and optimization of the operational process variables (temperature, methanol concentration, methanol flow rate and oxygen flow rate) of DMFC using the response surface methodology. This presentation will describe the electrocatalytic performance of the optimized Pt-W/CeO_2-graphene electrocatalyst for DMFC. The mechanism of the electrocatalytic activity of the Pt-W/CeO_2-graphene electrocatalyst will be eluicidated. A mathematical model and optimum conditions for the application of the optimized electrocatalyst in DMFC will be discussed.

The Synthesis and Characterization of S-Doped Complex Support ORR Catalyst

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N-doped non-precious metal catalysts (M-N/C) act as the most promising substitutes of high-cost limited-storage commercial precious metal ORR catalysts have attracted lots of researchers due to their low cost, high activity and perfect stability [1]. In this research, we develop a facile low-cost and simple method to synthesize S-doped complex support non-precious metal catalyst (S-doped p-Fe-g-C_3N_4@KB/rGO) and meanwhile, focus on improving its activity and stability in acid medium and find out the role of 3D structure in the improvement of stability. Fig.1a compares the cyclic voltammograms of S-doped p-Fe-g-C_3N_4@KB/rGO, p-Fe-g-C_3N_4@KB/rGO and commercial Pt/C catalysts in O_2 saturated 1 mol L^{-1} $HClO_4$ solution at room temperature. The result shows that S-doped p-Fe-g-C_3N_4@KB/rGO has a satisfactory activity in acid medium and S-doping significantly improves the ORR activity. And Fig.1b shows that the catalyst has higher stability than commercial Pt/C in acid solution. These results reveal that S-doping complex carbon support is very helpful in the improvement of ORR activity and stability.

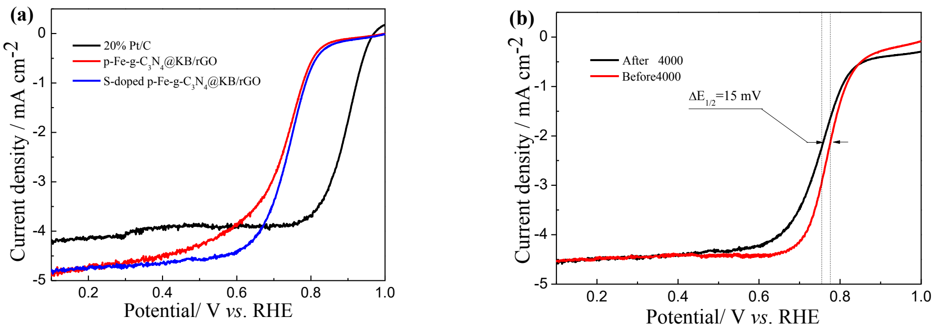

Fig.1 (a) ORR activity of S-doped p-Fe-g-C_3N_4@KB/rGO, p-Fe-g-C_3N_4@KB/rGO and commercial Pt black catalysts at room temperature in O_2-saturated 0.1 mol L^{-1} $HClO_4$ solution; (b) ADT test comparison of S-doped p-Fe-g-C_3N_4@KB/rGO in room temperature at a scan rate of 50 mV s^{-1} between 0.6 to 1.1 V before and after 4000 cycles.

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Mycolic Acid Based Immunosensor for Active Tuberculosis

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Tuberculosis (TB) is an infectious disease mostly caused by *Mycobacterium tuberculosis* (MTB), and very rarely caused by *Mycobacterium bovis* and *Mycobacterium africanum.* TB is one of the top 10 causes of death worldwide (1). It is a major health problem affecting one-third of the world population, of which approximately 8 to 9 million people develop it and approximately 2 million people are killed annually as reported by the World Health Organization (WHO) (2,3) making it the leading cause of death from a single infectious agent (4). Over 95% of TB deaths occur in low- and middle-income countries, and it is among the top three causes of mortality for women aged 15–44 years.

Mycolic acids (MA) have been shown with enzyme-linked immunosorbent assay (5), optical biosensor (6) and Electrochemical Impedance spectroscopy (7) to be promising mycobacterial antigens in serodiagnosis of active pulmonary TB in HIV infected populations. However, these methods are still in need of optimization to improve accuracy and reliability before they can be tried for any clinical application.

A strategy proposed in this study was to use electrochemical techniques, Electrochemical Impedance Spectroscopy as reported before (7) and Square Wave for the biosensor surface characterization, but now using a low-cost glassy carbon electrode as the working electrode. We modified the glassy carbon electrode with MA as the active antigens for the recognition of anti-mycolic acid antibodies present in TB-positive human serum co-infected with human immunodeficiency virus (HIV).

Electrochemical characterization of the new immunosensor surface showed that the mycolic acid was recognized by the anti-mycolic acid antibodies in the sera. This newly designed immunosensor surface has a strong potential to improve TB sero-diagnosis, because the mycolic motif, which has been shown to be important for antibody recognition, is not tampered with.

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Iron phthalocyanine modified carbon microfiber hybrids as high-performance supercapacitor

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Metallophthalocyanines (M-PCs) are the most researched macrocyclic organometallic functional materials, in particular, supercapacitor applications.[1] Supercapacitors are in need of alternative electrode materials to optimize performance parameters such as energy density and cycling stability.[2] M-PCs hold promise considering their efficient electron transfer abilities.[3] The major issues to be addressed concerning the M-PCs based electrodes include the very poor cycle life, poor rate capability and high solubility in liquid electrolytes. Recent efforts focus on employing M-PCs compound encapsulated by a protective electron conducting material in Lithium-ion battery application.[4] This work aims to produce electrically conductive polyacrylonitrile (PAN) fibers embedded with multiple primary particles of a FePC compound via electrospinning method to form FePC/PAN fibers which were subsequently heat treated in a protective atmosphere to Fe-N_4/CMF, see figure 1. The supercapacitive behaviour of the composites was investigated using cyclic voltammetry galvanostatic charge-discharge and electrochemical impedance spectroscopy. A maximum specific capacitance of 107 F/g with a measured power density of 5500 W/kg at an energy density of 8 Wh/kg in an aqueous electrolyte solution was obtained. Meanwhile, the supercapacitor devices exhibit excellent long cycle life along with ∼100% specific capacitance retained after 2000 cycle tests. These remarkable results demonstrate the exciting commercial potential for high performance, environmentally friendly and low-cost electrical energy storage devices based on this new Fe-N_4/CMF material.

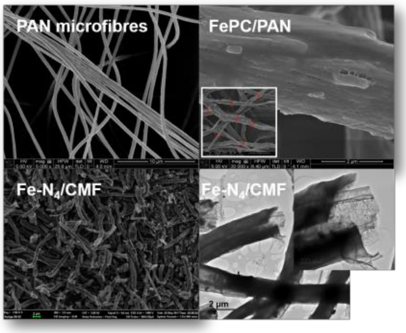

Figure 1. TEM/SEM images of porous **Fe-N_4/CMF**

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Hierarchical material of carbon nanotubes grown on carbon nanofibers as electrode material for supercapacitors

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Supercapacitors are an emerging technology that promises to play an advance role in new generation of electronic devices and systems. Carbon based electrodes (activated carbon, graphene, carbon nanofibers and carbon nanotube) have attracted tremendous attention for their potential application in supercapacitors due to their excellent mechanical strength, good electrical conductivity, high electron mobilities, various morphological structures, and large specific surface area [1]. The practical application of the carbon based electrodes has been hindered because of the lack of proper graphitization of the material. In order to accomplish performance beyond the limitations of each material, especially energy density and durability, composite materials have been studied [2]. The literature reports showed that most composites are carbon-based materials and metal nanoparticles supported on carbon [3, 4, 5]. In this work, carbon nanotubes (CNTs) were grown on top of carbon nanofibers (CNFs) using two facile techniques-electrospinning and chemical vapour deposition (CVD) to form a CNFs/CNTs composite. The structure of CNFs/CNTs composite has been precisely controlled by adjusting the reaction time and catalyst deposition on the surface of CNFs. The microstructures and electrochemical properties of the materials were investigated by PXRD spectroscopy, Raman spectroscopy, SEM, TEM and electrochemical measurements. The results revealed that the composite CNFs/CNTs has an improved specific capacitance of 167 F/g, at the current density of 0.25 A/g as compared with the pristine CNFs which has 78 F/g at current density of 0.25 A/g. The better performance of the composite can be attributed to the hierarchical structure of CNFs/CNTs which provides sufficient accessible sites for charge storage and the CNTs skeleton which offer channels for charge transport.

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Platinum nanoparticles supported on titanium dioxide nanoparticles for ethanol electro-oxidation.

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Fuel cell technology has attracted tremendous interest due to its potential to substitute the currently used fossil fuels for energy supply. This technology is both environmentally friendly and sustainable.[1,2]Amongst the known fuel cells, direct ethanol fuel cells (DEFC) is of significant growing interest due to the non – toxic, natural abundance and high power density of ethanol.[3] Commercialization of these devices comprise of high platinum loading which raises concerns in terms of their cost and scarce platinum reserves. Of the most significant components for feasible development of this device is the design of reduced – cost, efficient and effective electrocatalysts for the ethanol oxidation reaction (EOR).[4,5] Carbon is widely used as support platinum nanoparticles. However, it is susceptible to corrosion in acidic medium thus compromising the efficiency and stability of the electrocatalysts.Transition metal carbides or oxides have proved to exhibit excellent corrosion resistant properties, with strong synergistic effect with Pt nanoparticles, enhancing its electro – catalytic properties.[6]

In this ongoing research, we are investigating EOR using nanostructured platinum electrocatalyst (of low-loading, ~ 15 wt%) supported on low-cost and corrosion-resistant titanium dioxide nanoparticles.

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One Step Electrochemical Synthesis, Characterization and Photocatalytic Activity of Mono-phase Molybdenum (IV) Oxide

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Molybdenum (IV) oxide (MoO_2) is an important transition metal oxide due to its application as a catalyst for reforming hydrocarbons and as a possible material for solid oxide fuel cell anodes and lithium ion batteries anodes. Consequently, various MoO_2 synthetic procedures, including electrodeposition, have been developed, providing the materials with various morphologies, particle size and some other features. Molybdenum oxide obtained by electrodeposition is, in general, a mixture of oxides with various valences, stoichiometry and crystal structure, depending on the deposition conditions. This work reports one step electrochemical synthesis of mono-phase MoO_2, its characterization and investigation of photocatalytic activity, towards degradaion of triarylmethane compound Crystal Violet.

MoO_2 was electrodeposited from 0.02 M $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ at pH 5 in two-electrode cell with Ti cathode as a substrate and Pt anode, at a current density of 70 mA cm^{-2} and temperature of 20.0±0.5°C, during 70 minutes. After deposition, Ti cathode covered by black MoO_2 was rinsed with deionized water and dried in air. Change of voltage during deposition was recorded. Cyclic voltammogram of Ti substrate in 0.02 M $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ electrolyte was recorded in three-electrode cell using saturated calomel electrode as a reference electrode. The same electrode setup was used for cyclic voltammetric determination of the material band gap. The obtained MoO_2 was peeled off the substrate and characterized with SEM, EDX and XRD techniques. Crystal Violet solution (50 mL of 2 mg dm^{-3}) was treated with the obtained material (1000 mg dm^{-3}) in UV chamber at 254 nm 1950 μW cm^{-2} for 60 minutes. Cyclic voltammogram showed sharp reduction peak at –0.383 V. Voltage between the working and counter electrode rapidly increases during the 1st minute of deposition, and then it remains relatively constant. SEM images revealed predominantly two-dimensional, foil-like structure, with relatively smooth surface. EDX analysis showed the average Mo:O ratio of 29:71 (close to the theoretical one for MoO_2) with relatively uniform distribution of elements on the examined surface, indicating somewhat higher oxygen content in the investigated MoO_2 compared to stoichiometric compound. XRD detected only one phase, poorly crystalline MoO_2, with its broad peaks (2θ angle) corresponding to hexagonal space group 194 (P63/mmc), parameters $a = b = 2.83890$ and $c = 4.72080$; angles $\alpha = \beta = 90.0°$, and $\gamma = 120.0°$ and V = 32.95 $Å^3$. The material calculated density is 6.45 g cm^{-3}. In spite of its relatively high calculated bang gap of 3.68 eV, the material showed certain catalytic activity in UV-photo degradation of Crystal Violet; after 60 minutes of treatment, 53% of the dye was removed under the conditions described.

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Electrosynthesis of Polypyrrole Nanowires with Enhanced Properties

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The optimization of the preparation of electrodes modified with polypyrrole nanowires, PPy-nw, accomplished directly upon the working electrode, using mesoporous silica as template [1], and only electrochemical methods is reported [2-4]. Firstly, the silica-template is prepared by potentiostatic perturbation, generating a homogeneous film over a previously deposited PPy-thin layer, so that PPy-nw grows within the nanochannels of the mesoporous silica, firmly adhered to the surface. Subsequently, the template is removed, to obtain the Pt|PPy-nw, without damage.

The original method for mesoporous silica template was intended for deposits over metallic and graphite electrodes [1]. We adapted Walcarius *et al.* process for deposition of silica template over Pt|PPy modified electrode, as described on previous studies for PEDOT deposits [6], obtaining the silica mesoporous film over the early polypyrrole layer (Pt|PPy-silica). Next, Pt|PPy-silica was used as working electrode and, by cyclic voltammetry with same conditions as described above -but considering only one cycle- the nanowires were synthesized. Subsequently, NaOH and $NaHCO_3$ solutions were used to wash and remove the mesoporous silica template as previously reported [3], leaving the PPy nanowires exposed, Pt|PPy-nw. These electrodes were subjected for studying their *p*-doping/undoping process (charge-discharge experiments) in a supporting electrolyte solution compared to bulk PPy deposits (Pt|PPy) and morphology characterization through an Inspect F50 FEI Scanning Electron Microscope.

Modified electrodes of Pt|PPy-nw show very stable electrochemical properties, with highly reproducibility and significantly superior (about 360 times higher charge capacity) response to the respective electrodes modified with PPy in it bulk form. SEM allowed appreciating a brush-type conformation of PPy-nw of 30 nm in diameter, with wires adhered to the electrode surface (Fig. 1).

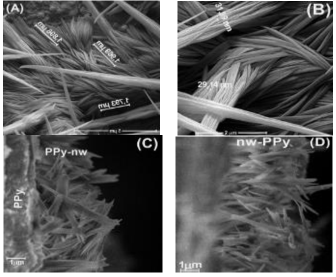

Figure 1. SEM micrographs of Pt|PPy-nw: (A-B) top views; (C-D) cross-sectional views.

Consequently, a cheap, simple, highly reproducible and repeatable method is established to prepare *in situ* electrodes modified with nanostructured polymers, using only electrochemical techniques. This can have a great impact on all likely applications of conducting polymers (examples in references [4] and [5]).

Finally, it is worth mentioning that these methods are under patent-law protection through patent-application PCT/CL2018/050116.

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Carbon/CeO_2 dual-coated NASICON-$Na_3Mn_2(PO_4)_2F_3$ cathode based materials for high-performance sodium-ion batteries

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NASICON (Sodium (Na^+) Super Ionic CONductor) based materials are amongst the well-recognized and promising electrode materials for the development of high performance sodium-ion batteries, due to their stability, safety, high sodium mobility and operating voltages.[1] Recently the interest in sodium-ion based electrode materials has grown, as the demand for cost effective, long lasting and resource abundant battery materials increases.[2] The NASICON-$Na_3Mn_2(PO_4)_2F_3$ Mn-based phosphates are known to exhibit a higher redox potential than that of Fe,[3] however Recently the commercial utilization of NASICON-based materials has been hampered by these major obstacles, intrinsic low ionic diffusivity, have low volumetric energy densities due to their low tap-density, thus leading to poor electrochemical activity.[2] Furthermore, It has been identified that strong Jahn-Teller distortion effects on Mn^{+3} exist during the process of charging and discharging, which result in lattice distortion in the coordination structure of the material and cause poor capacity retention, poor electronic and ionic conductivity affecting the materials electrochemical performance.[4] It is believed that these obstacles can be mitigated and Mn^{+3} can be highly active if properly synthesized, by reducing particle size, carbon coating and introducing elemental doping.[5] This work aims to interrogate carbon/cerium oxide (CeO_2) dual coated $Na_3Mn_2(PO_4)_2F_3$ cathode materials for sodium-ion batteries and utilizing nano-engineering methods such as microwave-assisted hydrothermal method then followed by two-step solid-state synthesis method to enhance the operating voltage, increase the tap-density, offer high structural stability, reduce particle size and Jahn-teller effects. The poster will describe key findings on our results with the synthesis and coating with CeO_2.

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Microwave-assisted synthesis of Pd/SnO_2 nanoparticles on metal organic frame-derived carbon as potential electrocatalyst for ethanol fuel cells

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Keywords: MOF-derived carbon; Pd/SnO_2 nano-electrocatalysts; Microwave-assisted synthesis methods; Ethanol oxidation reaction; Tafel slope; Electrochemical impedance spectroscopy.

Alkaline direct ethanol fuel cells (ADEFCs) represent one of the promising renewable and clean energy devices for portable, stationary and transportation auxiliary applications. The use of ethanol as fuel is due to its low toxicity, high energy density (theoretical energy density of 8 kWh^{-1} kg) and large production from sugar containing agricultural waste products[1]. Electrocatalytic oxidation of ethanol is a major parameter for viable development of these devices, but there is difficulty of ethanol crossover as a result of poisoning of intermediate carbonaceous species. Palladium based nanoparticles are commonly used to catalyse ethanol oxidation reaction (EOR) in alkaline media, because of their increased electroactivity[2]. Moreover, improved electrocatalytic activity and better tolerance to carbonaceous species poisoning can be achieved using high surface area carbon support and bimetallic electrocatalyst respectively[3].

Thus, in this research, Pd/SnO_2 nanoparticles on metal organic frameworks-derived carbon (MOFDC), abbreviated herein as Pd/SnO_2/MOFDC, has been studied as possible electrocatalyst for EOR in alkaline solution and compared with Pd/MOFDC, Pd/SnO_2/carbon black (CB) and Pd/carbon black (CB). The electrocatalysts were successfully prepared using microwave-assisted synthesis strategies and characterized using Raman. XRD, TEM, EDS and XPS. The Pd/SnO_2/MOFDC electrocatalyst exhibits superior electrocatalytic performance for EOR, relative to Pd/MOFDC, Pd/SnO_2/CB and Pd/CB electrocatalysts. The results show that the Pd/SnO_2/MOFDC electrocatalyst is promising for the fabrication of ADEFCs.

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Nanorod-like $LiMn_{1.5}Ni_{0.5}O_4$ for High-Performance Lithium-ion Batteries

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Keywords: $LiMn_{1.5}Ni_{0.5}O_4$, Spinel, Lithium-ion battery, β-MnO_2 nanorods

The commercialised cathode materials have not met the goals of the next-generation electric vehicles (EVs) in terms of cost, performance and environmental issues. Although the current lithium-ion batteries (LIBs) have been widely used to power portable devices: mobile phones and laptop computers, but their energy and power are inadequate for use in EVs to compete with the performance of vehicles powered by fossil fuel.[1,2] There are challenges in extending driving distances, increasing rate capabilities, lowering costs, and eliminating safety hazards for LIBs in EVs. It is therefore crucial to continue research works to develop high energy and power densities lithium-ion batteries that are safe and environmentally-friendly at a reduced cost.[3]

The manganese-based spinel cathode materials amongst all others are future candidates for high-energy and high-power density battery applications because of their high operating voltage, robust and fast 3D Li^+ diffusion channels. In 1983, Thackeray reported spinel $LiMn_2O_4$ and was commercialised by NEC in 1996. The spinel $LiMn_2O_4$ and its derivatives have attracted most interest due to their ease of preparation, abundance, low cost and environmental friendliness. Among the derivatives, the nickel doped: $LiMn_{1.5}Ni_{0.5}O_4$ is the most promising cathode material as a result of its high working voltage of 4.7 V, considerable high capacity: 148 mAh/g.[2,4,5] and high specific energy of 650 Wh/Kg compared to other convectional cathodes ($LiCoO_2$: 518 Wh/Kg, $LiMn_2O_4$,: 400 Wh/Kg, $LiFePO_4$: 495 Wk/Kg and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$: 576 Wh/kg). However, the commercialization of the spinel $LiMn_{1.5}Ni_{0.5}O_4$ is still a challenge because of its inferior rate capability and poor cycle stability, particularly at elevated temperatures.[5]

In this work, $LiMn_{1.5}Ni_{0.5}O_4$ nanorods have been successfully synthesised using solid sate reaction: the precursor β-MnO_2 nanorods which were first synthesised by molten salt synthetic method were impregnated with Li^+ and Ni^{2+}. The effect of morphology and phase-tuning on the spinel electrode has been evaluated by characterization: RAMAN, FTIR, SEM, TEM and PXRD and electrochemical measurements.

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Ultrasensitive electrochemical detection of microRNA based on terminus-regulated DNA hydrogelation

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In this work, a dynamic terminus-regulated fabric of DNA hydrogel was invented in debt to the reiterative catalysis of terminal deoxynucleotidyl transferase (TdT). It extended free 3’−OH end to an overhang of homopolymeric adenosine base pair, and alternated with branching from the frayed complementary seed oligo $T_{20}G_5$. The cycle of this template independent and isothermal amplification resulted in a microscale dendritic DNA fractal at first, which then gelatinized into a cohesive and intricate 3D network. Details of the complex were elucidated with gel electrophoresis, confocal and atomic force microscopy. Its well hydrated inner space could further provide plenty of biocompatible chambers for enzymatic transducers fused along the elongation. Taking merits of this neat and flexible setup, an in situ hydrogelation strategy was developed and utilized in the signal cascade of a miRNA biomarker detector on an electrode microarray, thus accomplished an ultrasensitive, selective and high-throughput sensing even for real samples. This collective manipulation of DNA-protein hydrogel ensemble on interface demonstrates its potency as a general scheme of sensitization in bioanalytical applications.

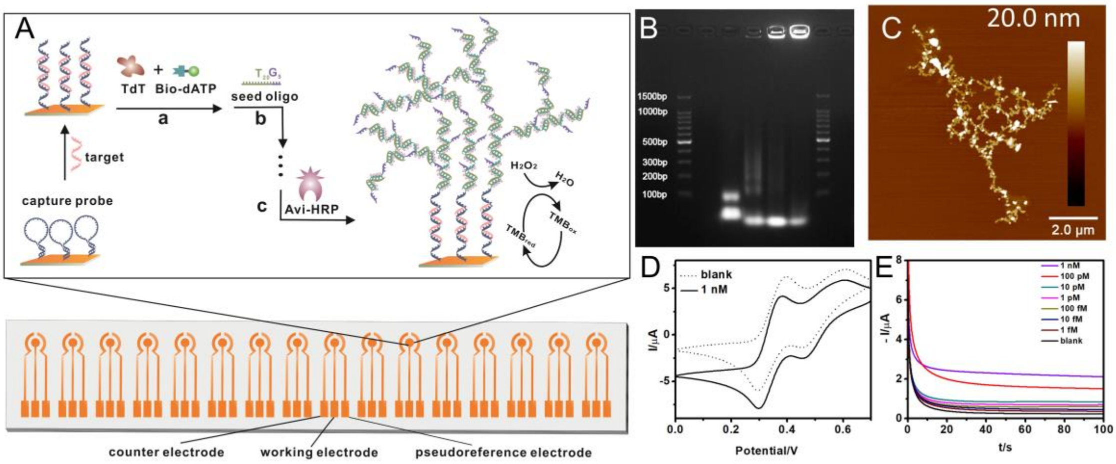

Figure. In situ DNA gelling strategy for miRNA sensing. (A) Schematic illustration of the sensing mechanism (upper panel) and the microarray platform (lower). **(B)** A snapshot about the gel electrophoresis with lanes from left to right: DNA ladder; initial oligo; products after 1st, 2nd, 3rd, and 4th round of reactions, respectively; DNA ladder. **(C)** AFM topographic scan on a clean mica sheet holding dry product after 4 catalytic cycles on AuNPs. Scale bar: 2 µm. **(D)**Typical cyclic voltammograms of the sensor during the detection of 1 nM (solid curve) and 0 M (dashed) target. Scan rate: 0.1 V/s. **(E)** The corresponding amperometric profiles at 0 (blank), 1, 10, 100 fM; 1, 10, 100 pM; and 1 nM (from bottom to top) on the potentiostatic condition (0.1 V).

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Enhanced Electrochemical Performance of Nickel(II)-tetrapyazino-porphyrazine Intercalated Two-Dimensional Titanium Carbide Nanosheets for Symmetric Supercapacitors in Aqueous Electrolyte

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Improved energy storage systems have become highly sought across the globe as the demand for efficient renewable energy set to displace fossil fuels is incessantly ever-increasing. In the recent years, *supercapacitors* or *electrochemical capacitors* have engrossed enormous research interest due the superior properties they possess. Supercapacitors store more amounts of charge than conventional capacitors, have long cycle life, and relatively high power capability when evaluated against batteries. However, supercapacitors suffer from low energy density compared to batteries [1]. MXenes, recently discovered in 2011, are found to be promising two-dimension nanomaterials for energy storage because they are chemically and mechanically stable; and can form diverse forms of layers with controllable thickness. However, their electronic functionality can be enhanced by incorporating them with possible combinations of heavy and light metals [2,3]. Also, MXenes do not have high surface area compared to other electrode materials used for electric double-layer capacitors. Currently, one of the lightest MXene, Ti_2CT_x modified with carbon nanospheres showed very improved electrochemical performance in a symmetric cell operated in an aqueous electrolyte at a relatively high voltage window (1.5V) [4].

In the current study we investigate the effects of intercalating the nickel(ii)-tetrapyrazino-porphyrazine into the 2D Ti_2C MXene. We show in this presentation the improved electrochemical performance of the material in acidic, neutral, and alkaline environment obtained as a result of this modification.

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Morphology Control of Aluminium Anodes in Secondary Aluminium Batteries

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The development of cheap and sustainable batteries with long lifetimes that can compete with lithium-ion batteries has been of great interest in recent years. A promising alternative to lithium-ion are aluminium batteries, which promise high energy density and low prices. One of the key objectives for the performance of secondary aluminium batteries (e.g. aluminium-sulfur or aluminium-ion batteries) is compact deposition of aluminium at the negative electrode with high coulombic efficiency.[1] However, aluminium, similar to lithium, is prone to dendritic growth ultimately leading to device failure.[2]

We have studied the deposition/dissolution characteristics of the aluminium electrode in two deep eutectic solvents based on the mixture of aluminium trichloride with either acetamide or urea.[3,4] The open-circuit potential after immersion in the deep eutectic solvents was monitored to obtain information about the surface state of pure aluminium in contact with the electrolyte, which indicated initial passivation of the surface. Electrochemical impedance data and electron microscopy revealed that the electrolyte attacks the native oxide film only locally. This resulted in pits of active aluminium on the surface (pitting corrosion) with most of the surface remaining in the passive state.[5] Therefore, aluminium deposited with high local current density at the pits, resulting in dendritic growth.[6] In an attempt to remove the passive layer electrochemically, current and potential controlled methods were tested. Alternating excursions to anodic and cathodic potentials led to more uniform surface depassivation. These conditioning methods, however, are not feasible for the use in batteries, because the applied potentials would cause severe damage to the cathode materials.

A promising strategy that mitigates the formation of the native oxide film on aluminium and that might also aid in the prevention of dendritic growth, is the introduction of dopant metals to form near-surface alloys.[7] Therefore, different combinations of metal dopants were introduced into the aluminium anodes, which should lower the probability of dendrite formation and effect uniform deposition of compact aluminium. The alloys were tested with respect to their charge/discharge behaviour in the deep eutectic solvents, while the surface morphology was studied with electron microscopy. The alloys showed positive effects on both the surface depassivation and the growth morphology, lowering local current densities and promoting uniform deposition of compact aluminium.

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Rechargeable Na–CO_2 Batteries: Configuration, Application, and Evolution

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Metal–CO_2 batteries have attracted much attention in recent years because of their high energy density and clean utilization of greenhouse gas CO_2. In particular, Na–CO_2 batteries show great potential for large-scale applications due to the high abundance and low cost of Na resources. However, how to realize the rechargeability of Na–CO_2 batteries is still challenging. Here we report rechargeable Na–CO_2 batteries and their further applications. We first constructed rechargeable Na–CO_2 batteries which consist of a Na anode, an ether-based electrolyte, and a designed cathode with electrolyte-treated multi-wall carbon nanotubes. The batteries showed a high reversible capacity of 60000 mA h g^{-1} at 1 A g^{-1} and good cycling stability (charge voltage $<$ 3.7 V after 200 cycles with a fixed capacity of 2000 mA h g^{-1}). In general, Na–CO_2 batteries with liquid electrolyte suffer from safety problems owing to the flammability of organic solvent and potential leakage of electrolyte. Thus, we further developed quasi-solid-sate and all-solid-state Na–CO_2 batteries. The quasi-solid-sate electrolyte contains poly(vinylidene fluoride-*co*-hexafluoropropylene) matrix, SiO_2 additive, and $NaClO_4$–tetraethylene glycol dimethyl ether plasticizer. The electrolyte could suppress electrolyte volatilization/leakage and offer high Na^+ ionic conductivity of about 1.0 mS cm^{-1} at room temperature. As a result, the quasi-solid-state Na–CO_2 batteries exhibited stable cycling performance (without obvious overpotential increase after 400 cycles with a controlled capacity of 1000 mA h g^{-1}). In addition, to further promote the practical applications, we have successfully fabricated rechargeable Na–CO_2 batteries starting from Na_2CO_3/carbon nanotubes cathode. The electrochemical decomposition of Na_2CO_3 and carbon nanotubes could take place at relatively low voltage ($<$ 3.8 V) because of the effective electron transfer and high reactivity. Moreover, pouch-type batteries could deliver a high discharge capacity of 350 mA h, corresponding to an energy density of 183 W h kg^{-1}. In summary, our work demonstrates rechargeable Na–CO_2 batteries for potential applications in the future.

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Redox behaviour 1,3-substituted-propane-1,3-diones

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β-Diketones (1,3-substituted-propane-1,3-diones), $R^1COCHC(OH)R^3$, are bidentate ligands with two oxygen atoms that can coordinate to a metal. Many β-diketones are used in the solvent extraction of metals,[1] since the β-diketones easily coordinate to many metals, such as Cr,[2] Mn,[3] Fe[4] and Rh.[5] The reactivity of metal-β-diketonato complexes is often related to the reduction potential of the un-coordinated β-diketone.[5] The reduction potential of a series of ten β-diketones, $R^1COCHC(OH)R^3$, with different substituent groups R^1 and R^3 on the β-diketone, has been reported. The measured reduction potential varies over a range of 1.1 V between -1.05 and -2.14 V *vs* FcH/FcH$^+$.[6] This contribution aims to increase the reported range of reduction potentials of these β-diketones, by adding the reduction potential of more β-diketones to this series. Electron donating groups substituted on the β-diketone should lower the reduction potential of the β-diketone to a potential below -2.14 V.

The reported reduction potentials of most of the β-diketones are irreversible. Only the cyclic voltammograms of β-diketones $R^1COCHC(OH)R^3$ of which both the substituent groups R^1 and R^3 are aromatic, showed a re-oxidation peak, only at higher scan rates, see Figure 1 left. Therefore in this study two aromatic groups are introduced in the one substituent position, to investigate the effect of the two joined aromatic groups on the reversibility of the reduction potential of this β-diketone. Results are complemented by a density functional theory (DFT) study of these β-diketones, relating DFT calculated energies such as LUMO energies (Figure 1 right), electron affinity, electrochemical potential, electrophilicity index[7], as well as the Mulliken electronegativity[8], to the experimental reduction potential.

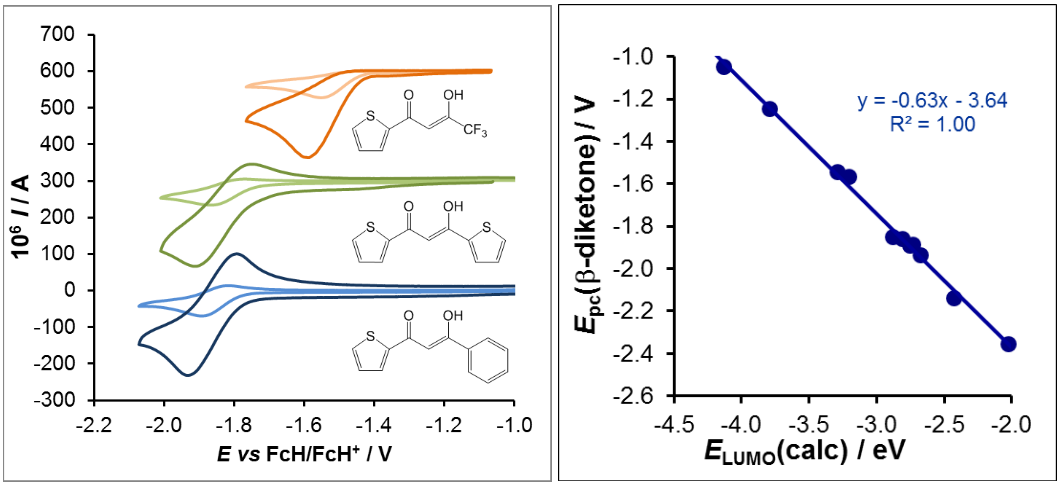

Figure 1. Left. Cyclic voltammograms of 0.003 M of the indicated three β-diketones, each at two scan rates 0.20 and 2.00 V/s, as measured in 0.100 mol dm^{-3} $[NBu_4][PF_6]/CH_3CN$, on a glassy carbon working electrode at 25 °C. Right. Linear relationship obtained between the DFT calculated energy of the lowest unoccupied orbital (E_{LUMO}) and the experimental reduction potential (E_{pc}) of the β-diketones.

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Silver-based gas diffusion electrodes for oxygen reduction reaction in alkaline electrolyte: Influence of PTFE content on pore system and electrochemical performance

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Gas diffusion electrodes (GDE) are key components for various electrochemical processes. Within the GDE, a three-phase interface must be formed at which gaseous and liquid reactants are electrochemically converted on a solid catalyst. This requires a complex pore structure with hydrophilic and hydrophobic areas in order to achieve the best possible wetting with the electrolyte, but at the same time to prevent complete flooding of the electrode. In order to optimize GDE, a general understanding of the complex overall system including the transport and reaction processes is necessary to maximize the electrocatalyst utilization.

In the present work silver-based GDE with a systematic variation of the PTFE content are produced by means of a spray process [1] and characterized by physical and electrochemical methods. The resulting pore system is analyzed using various measuring methods, supported by imaging methods such as FIB/SEM and the resulting reconstruction analysis. All techniques combined offer a clear view of the inside of the electrodes and reveal the influence of the PTFE content on the pore system.

The electrochemical performance is determined under stationary conditions in half cell experiments using linear sweep voltammetry. Particular emphasis is placed on the determination of the electrochemical kinetics and mass transport resistances. Selected electrodes are also examined in a specially designed half-cell (Fig. 1, left) under various pressure conditions to determine effects of different electrolyte intrusions [2]. An increased pressure can enhance the utilization of the electrode and therefor the overall performance (Fig. 1, right, filled triangles). In contrast, increased flooding levels impair already well performing electrodes (filled circles).

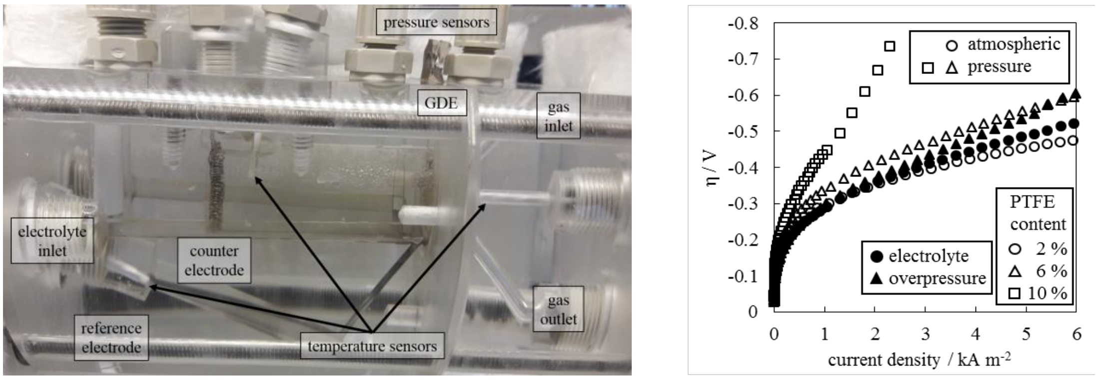

Fig. 1: Left: Half-cell setup for stationary measurements under various pressures. Right: Examples of different polarization curves for varied PTFE content and electrolyte overpressure of 200 mbar.

The contribution shows that a combination of both physical and electrochemical measurement methods is necessary to describe the pore system adequately and to develop GDE with optimal performance.

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Redox behaviour [Rh(β-diketonato)(CO)(PPh_3)] Complexes

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The Monsanto process is one of the most well-known industrial processes, using the rhodium catalyst, *cis*-[$Rh(CO)_2I_2$]$^-$, for the manufacture of acetic acid by catalytic carbonylation of methanol [1]. Rhodium triphenylphosphine complexes, [Rh(β-diketonato)(CO)(PPh_3)], are well-studied, due to their similar properties to the Monsanto catalyst [2]. The first step of the oxidative addition reaction of methyl iodide to these [Rh(β-diketonato)(CO)(PPh_3)] complexes [3], is similar to the oxidative addition reaction step of methyl iodide to the well-known rhodium(I) Monsanto catalyst. It has been shown that the experimental oxidation potentials of the irreversible Rh(I) to Rh(III) oxidation process (Figure 1) of a variety of these complexes, are linearly related to both the experimentally found kinetic oxidative addition rate constant, as well as to the theoretically calculated energy of the highest molecular orbital (E_{HOMO}) of the complex [4]. Redox potentials obtained from voltammetry were employed in these density functional theory calculations of the HOMO and LUMO levels: For these calculations, it is recommended to assume that the HOMO energy is directly related to the absolute oxidation potential [5,6,7,8]. To obtain the energy in eV, it is then sufficient to multiply the absolute oxidation potential by the electron charge (-1). The expected slope value of the graph of oxidation potential *versus* HOMO energy therefore is −1, and the intercept should then be equal to the absolute potential of the reference electrode. This contribution relates the experimental oxidation potential data of selected [Rh(β-diketonato)(CO)(PPh_3)] complexes, to the density functional theory calculated HOMO energies, obtained by various computational chemistry approaches, in order to find the best DFT method to relate the HOMO energy to the absolute oxidation potential of these [Rh(β-diketonato)(CO)(PPh_3)] complexes.

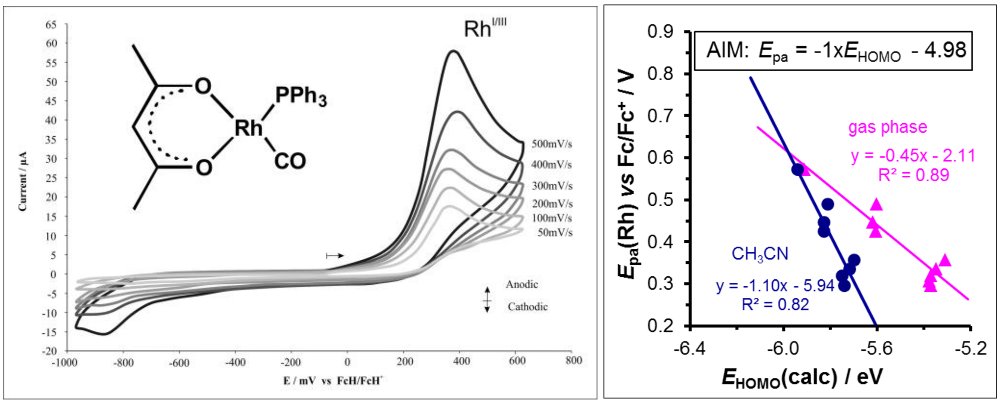

Figure 1. Left. Cyclic voltammograms of complex [Rh(acetylacetonato)(CO)(PPh_3)], at six different scan rates between 50 mV/s to 500 mV/s, measured in 0.100 mol dm^{-3} [NBu_4][PF_6]/CH_3CN, on a glassy carbon working electrode at 25 °C. Right. Graph of the experimental oxidation potential *vs* the HOMO energy.

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Investigation of electrochemical performance of the biosynthesized α-Fe2O3 nanorods

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Abstract:

This research work concerns with the development of a facile method for the biosynthesis of α-Fe_2O_3 nanoparticles nanoparticles through green method using *Persea Americana* seed extract and their electrochemical application. The sample obtained was studied by the means of by X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), Energy Dispersive X-ray Spectroscopy (EDS), Ultraviolet-Visible (UV-Vis) analysis, Fourier Transform Infra-Red (FTIR) spectroscopy, Mössbauer spectroscopy and Cyclic voltammetry. X-ray diffraction (XRD) pattern of the sample confirmed formation of α-Fe_2O_3 phase. Transmission Electron Microscopy (TEM) studies on the sample showed a nanorod-based structure with average diameter of 50 nm and length of 400 nm. FTIR spectroscopy spectrum confirmed the phase purity and chemical bond of the sample. The energy gap was estimated from UV vis spectrum of the sample and found to be 2.7 eV. Mössbauer spectroscopy investigation revealed the weak ferromagnetic nature of the sample as well as the oxidization state. Cyclic voltammetry measurements of α-Fe_2O_3 nanorods sample coated on glassy carbon electron (GCE) showed two oxidation peaks are at 0.62 V and 0.88 V associated with reversible multi step oxidation of Fe to FeO and then Fe_2O_3. Electrochemical impedance spectroscopy studies revealed minimum charge transfer resistance R_{ct} value, suggesting that α-Fe_2O_3 nanorods prepared has good conductivity and can be used in electrochemical energy storage application.

Key words: Biosynthesis, hemeatite nanorods, Cyclic voltammetry and electrochemical

Fe_3O_4@N-doped Graphene as Negative Electrode for Lithium Ion Batteries

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The use of renewable energy and efficient storage systems are topics of current interest. New generations of materials are necessary to provide practical and economical solutions for electrode fabrication in Lithium Ion Batteries (LIBs). Particularly, magnetic iron oxide, Fe_3O_4, is considered as potential material of negative electrodes due to its high theoretical capacity (934 $mAhg^{-1}$) which is almost 3 times larger than the graphite of commercial LIBs. The Fe_3O_4 negative material is abundant, presents high corrosion resistance and environment friendly. However, the practical application as negative electrode for LIBs it is still limited by the poor cycling performance, associated to the low ionic and electronic conductivity as well as the enormous variation of volume during the charge/discharge processes. To avoid these problems, the use of nanoparticles of Fe_3O_4 and conductive materials are crucial to achieve high capacities and numerous cycles of charge/discharge.

In this work, we prepared Fe_3O_4 nanoparticles coated with N-doped graphene, following a typical technique employed on the catalysis field. Firstly, we prepared de Fe_3O_4 nanoparticles by a co-precipitation method starting off Fe^{3+} and Fe^{2+} in alkaline media [1]. Subsequently, in order to synthesize the hybrid composite, we mix the as prepared Fe_3O_4 nanoparticles with 1.10 phenanthroline (60:40 in mass) in ethanol as solvent. After 12h of vigorous stirring, we dried the dispersion and finally we performed a thermal treatment in N_2 atmosphere at 800ºC for 2h [2]. In those conditions we obtained a black powder (Fe_3O_4@N-doped graphene). The electrodes used for electrochemical measurements were prepared by casting a slurry prepared with the materials synthesized, Fe_3O_4 and Fe_3O_4@N-doped graphene, PVdF as binder and carbon black C65 dispersed in NMP (80:10:10 respectively). From the electrochemical analysis performed, we obtained an improvement on the specific capacity of charge/discharge at density current of 100 mAg^{-1} for the Fe_3O_4@N-doped graphene as well as an excellent coulombic efficiency performance along the cycling (panel A). The specific capacities obtained for this hybrid material corresponding to the 91% of the theoretical capacity of the pure Fe_3O_4. Also, the hybrid material showed a great rate capability performance at high densities current of charge as can be observe on the figure (panel B). We associate this behavior to the improvement of the electrical conductivity of the magnetite material due to the shell of N-doped graphene.

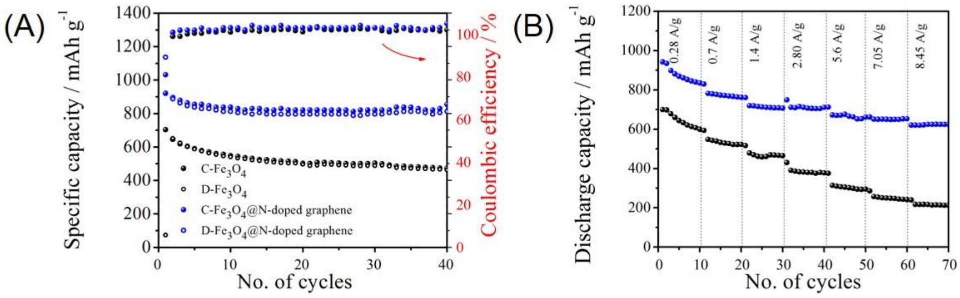

Figure 1 (A) charge/discharge cycling and coulombic efficiency, (B) rate capability performance. Color code: Fe_3O_4 (black) and Fe_3O_4@N-doped graphene (blue).

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Carbon spheres-reinforced electrospun carbon nanofiber composites for the development of supercapacitors

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Energy storage devices are a vital area of research and development across many academic and industrial disciplines. Supercapacitor is a single energy storage device which has attracted a lot of attention [1]. It has found applications in a plethora of areas portable electronics, aerospace and electric vehicles[2]. Advantages of a supercapacitor over rechargeable batteries (such as lithium-ion batteries) includes higher power density, faster charge and discharge rate, environmentally friendly, extremely low internal resistance, high efficiency and over a million charge-discharge cycles [3,4].

In this study, we focus on the utilization of hard carbons (carbon spheres) to re-enforce carbon nanofibers to improve the physical and chemical properties for supercapacitors. This PhD work is aimed at developing novel hard carbons (solid carbon spheres) and integrating them with carbon nanofiber for the fabrication of high-performance supercapacitor. In this continuing PhD work, hard carbons are being synthesized using high-temperature pyrolysis. For example, solid carbon spheres are obtained from sucrose at elevated high temperature under inert gas using a furnace, while the carbon nanofiber are being obtained via electrospinning then they are stabilized and carbonized. Hard carbon (solid carbon spheres)-reinforced electrospun carbon nanofibers composites are characterized using techniques such as XRD, Raman, TGA, XPS, SEM, TEM, EDS, BET. Electrochemistry are carried out using advanced electrochemical techniques, including cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS).

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Physicochemical Characteristics and Pseudocapacitive Response of RuO_2/Reduced-Graphene-Oxide Composites Prepared by Microwave Assisted Hydrothermal Synthesis

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Pseudocapacitive RuO_2/reduced-graphene-oxide composites were synthesized at various synthesis temperatures and pH values of precursors, using one-step microwave assisted thermal method. Graphene-oxide, previously synthesized by standard Hummers method [1], and $RuCl_3$ solution served as precursors. Obtained samples were electrochemically tested by cyclic voltammetry and electrochemical impedance spectroscopy in H_2SO_4 and Na_2SO_4 solutions. The analysis of obtained results showed that synthesized composites are of acceptable capacitive properties. Composites synthesized at 200 °C (pH 7) and 160 °C (pH 10) were obtained in a form of foam. Physicochemical properties of these samples were further investigated using TEM/EDX, TEM, FTIR, TGA and XRD techniques. TGA measurements confirmed projected RuO_2 loading of about 20 mass% in both composites, while results of XRD analysis revealed nanocrystalline structure of samples. TEM images (Fig. 1) of RuO_2/r-GO and bare r-GO synthesized in the same conditions (pH 10, 160 °C) show presence of 2-3 nm-sized RuO_2 particles uniformly distributed over graphene flakes (Fig. 1a).

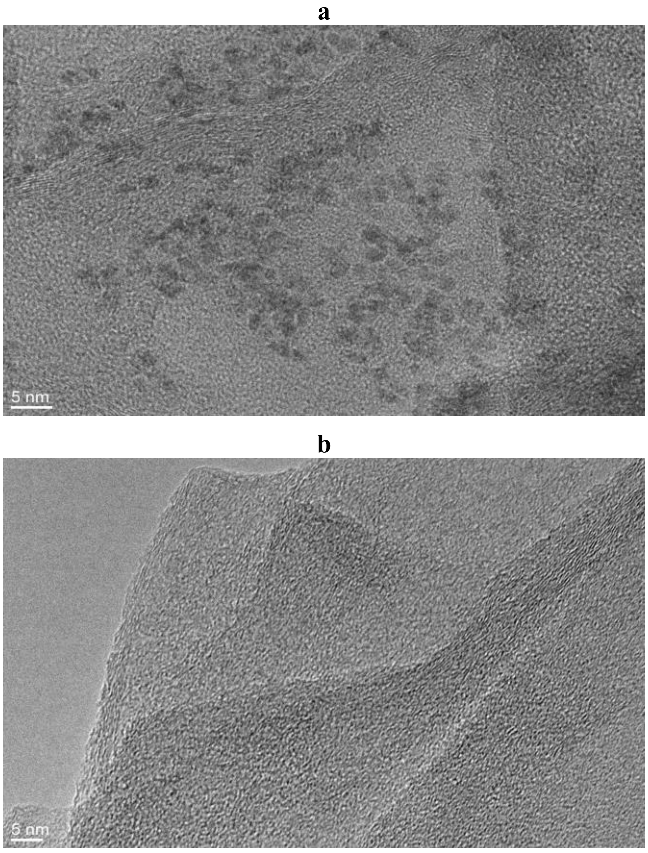

Fig 1. Comparison of appearances of: **a** - RuO_2/r-GO and **b** - r-GO samples

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A Comparative Study of the Analytical Performance of Two Aptamers for the Impedimetric Detection of *Plasmodium falciparum* Lactate Dehydrogenase in Malaria-Parasitized Blood

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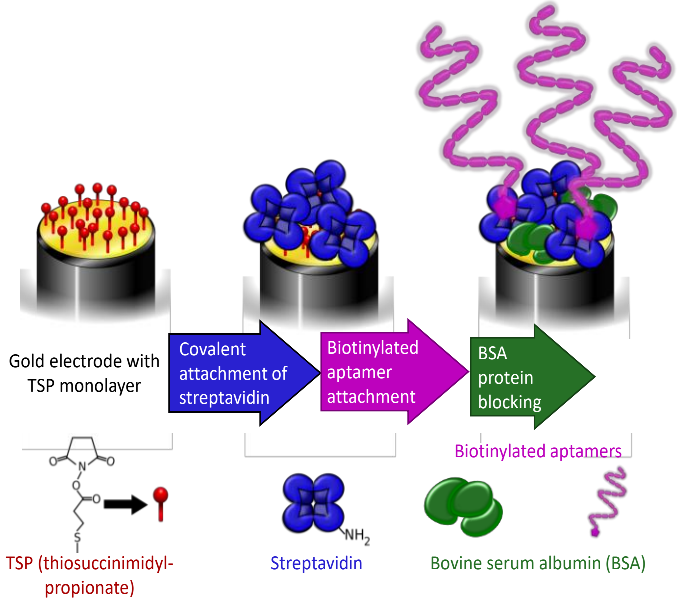
The *Plasmodium falciparum* malarial parasite is a lethal illness, causing an estimated 435 000 patient deaths during 2017. Diagnostic tests which can accurately, sensitively and specifically detect the presence of the parasite early enough during the infection can have a positive impact on patient survival. Moreover, tests that can provide a quantitative result can provide a rapid indication of treatment efficacy. We have developed two new candidate aptamers which bind with high affinity to *Plasmodium* lactate dehydrogenase [1]. Here, we report on the construction of an impedimetric aptasensor for the preferential detection of *Plasmodium falciparum* lactate dehydrogenase (*Pf*LDH) (compared to other species of malaria), both in buffered solutions of the protein and in malaria-parasitized blood samples. In this study, several aptamer immobilization strategies were tested: avidin-biotin interaction (**Scheme 1**) provided the most favourable impedimetric responses and was considered for further studies. All sensor responses were measured using Electrochemical Impedancce Spectroscopy (EIS) using 10 mM $[Fe(CN)_6]^{3-/4-}$ in PBS. Aptamers specifically recognized *Pf*LDH with significantly ($p<0.05$) increased charge transfer resistances (R_{CT}), compared to protein controls such as *Pv*LDH, HSA and hLDH. The aptamers selectively recognized *Pf*LDH in a simple protein matrix containing hsa and hLDH. The binding affinities, K_D, of the aptamer-based sensors using aptamers rLDH4 and LDHp11 were 0.48 ± 0.16 nM and 0.096 ± 0.044 nM, respectively. Limits of detection for these were 0.22 and 0.037 nM, respectively. The recognition of *Pf*LDH in both non-parasitized blood spiked with 0.365 nM r*Pf*LDH and native *Pf*LDH in parasitized blood was further tested. Aptamers rLDH4 and LDHp11 could detect the target protein at physiologically-relevant levels in both spiked and parasitized blood. The analytical performance of rLDH4 impedimetric sensor was compared to the Malstat reagent (currently used in as a standard approach in malaria research) for detection of *Pf*LDH in parasitized blood. The developed impedimetric sensor has demonstrated promising relevance as a new diagnostic test for malaria.



Scheme 1: Aptasensor assembly for the detection of *Plasmodium falciparum* lactate dehydrogenase (*Pf*LDH) in blood.

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Investigation of alternative support materials for platinum nanoparticles to be used as catalysts in PEM fuel cells.

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Keywords: fuel cells, platinum, silicon carbide, chemical deposition.

Fuel cells are a promising alternative for sustainable energy production due to their high efficiency, minimal environmental impact and wide range of applicability [1] Fuel cells have not achieved wide scale commercialisation due to the high cost of the platinum catalyst and low lifetime of the widely used carbon-supported catalyst [2]. Low lifetime of the catalyst also adds to the cost of the fuel cell as it would require very frequent replacement.

Carbon-supported catalysts are still considered to be the best catalyst for PEM fuel cell reactions because they offer not only the highest catalytic activity but also produce the highest current exchange density, are chemically stable and have a superior work function [3]. However, the carbon suffers from very low resistance to corrosion caused by electrochemical oxidation due to the acidic conditions and the high potentials during start-up and shut down processes [4,5]. Considerable work into alternative support materials to carbon has been done. This includes metal oxides such as titanium and tin-based oxides; borides nitrides and carbides [6]. Ceramic materials such as carbide (SiC) and Boron carbide (B_4C) are other alternatives to carbon being considered due to their mechanical properties, high thermal stability, high chemical inertness [7]. They are considered refractory compounds as they exhibit metallic properties and are highly chemically inert [8].

It has been shown that the properties of the support material have an influence on the activity of the Pt electrocatalyst because they determine the dispersion and distribution of the nanoparticles [9]. In addition to this, the support material also influences the metal-support interactions [6,10]. Both properties have been reported to have an influence on the performance of the catalyst. For materials such as ceramics with poor conductivity, dopants can also be used to improved conductivity [11]. Thus, the properties of a support material can be tuned using dopants towards meeting the desired catalyst requirements.

This investigation focuses on evaluating the viability of silicon carbide and doped silicon carbide as support materials for the fuel cell platinum cathode catalyst, as alternatives to carbon. The materials will be prepared in powder form with varying dopant concentrations to determine the effect of dopant concentration on conductivity and catalyst activity. On each support material variant prepared, platinum will be deposited using an in-house developed catalyst synthesis method. All catalysts will be characterised using the in-situ methods to determine electrochemical ORR activity, electrochemical surface area (ECSA), the stability of the catalysts as well as advanced surface characterisation techniques
X-ray Absorption Near Edge Structures (XANES) and Extended X-ray Absorption Fine Structure. The ex-situ experimental methods include support BET surface area, conductivity, X-ray diffraction to determine crystallite size, transmission electron microscopy (TEM) to determine particle size and advanced surface characterisation by X-ray Photoelectron Spectroscopy (XPS). These catalysts will be compared to commercial Pt/C catalysts.

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Electrochemical behaviour of Tris(β-ketoiminato)ruthenium(III) complexes

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Ruthenium complexes containing bidentate ligands with two oxygen donor atoms (e.g. β-diketones), or one nitrogen and one oxygen atom (e.g. β-ketoiminato ligands), or two nitrogen donor atoms (e.g. bipyridine and 1,3-diketimines), have previously been extensively studied for various reasons, including catalytic[1] and medical[2] applications. In order to understand the catalytic and medical properties of the complexes, it is important to study factors that influence the activity of these complexes towards oxidation, reduction, substitution, oxidative addition etc. This study focuses on the electrochemical behaviour of five tris(β-ketoiminato)ruthenium(III) complexes, see Figure 1. All these complexes exhibit two redox systems: The first redox process is on the anodic side, between 0.1 to 0.4 V *vs* FcH/FcH$^+$, and is assigned to the oxidation of Ru(III) to Ru(IV). The second redox process is on the cathodic side, between -0.8 to -1.6 V *vs* FcH/FcH$^+$, and is assigned to the reduction of Ru(III) to Ru(II), see Figure 1. Although previous experimental studies showed that for these type of complexes the *meridian* isomer is mostly favoured,[3] this study found, by density functional theory calculations as well as the experimentally observed cyclic voltammetry behaviour, that both *meridian* and *facial* isomers can co-exist in solution for some of these complexes. Therefore the two oxidation (or reduction) peaks observed for some of the complexes, is a result of the oxidation (or reduction) of the co-existing two isomers of these complexes, namely both the *meridian* and *facial* isomer.

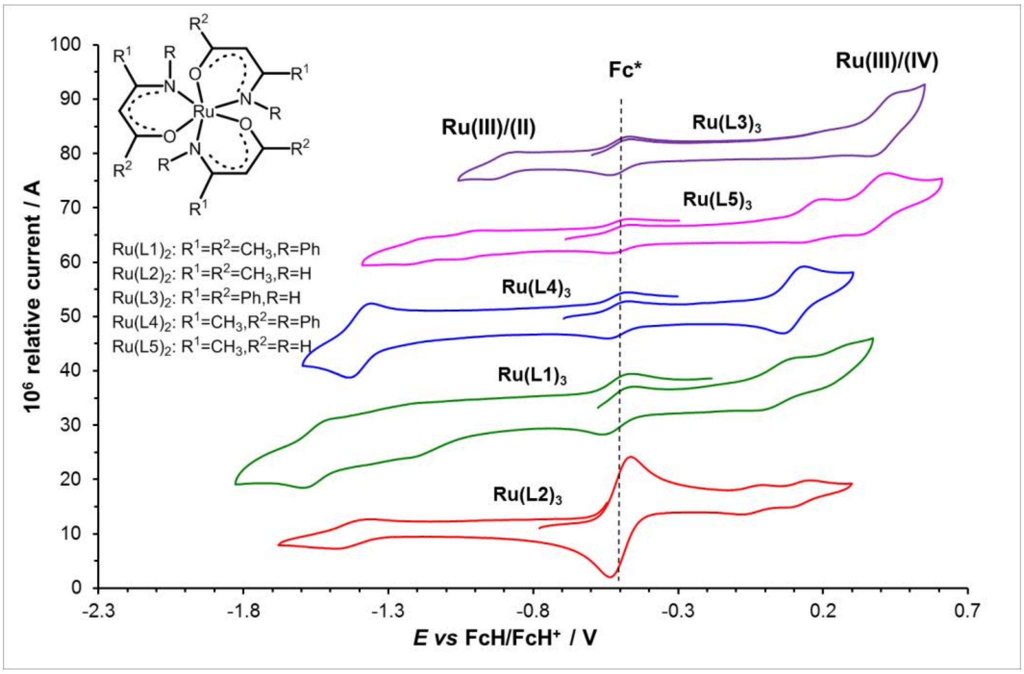

Figure 1. Cyclic voltammograms (versus FcH/FcH$^+$) of all Ru(III) complexes from this study, at a scan rate of 0.100 V s^{-1}. Fc* = decamethyl ferrocene was used as internal standard, with *E*(Fc*) = -0.508 V *vs* FcH/FcH$^+$.

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The correlation between microscopic pore structure and macroscopic water and ion mobility in fuel cell membranes

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Fuel cell proton exchange membranes (PEMs) are central to hydrogen fuel cell technology. The mechanism and optimization of proton transport in these materials are intimately linked with hydration and water transport. Studies of water transport in PEMs have previously been limited to macroscopic permeability measurements. Our work connects the macroscopic proton transport in PEMs to the microscopic molecular water arrangement and dynamics, as determined with nonlinear Raman spectro-microscopy (coherent anti-Stokes Raman scattering, CARS).

Firstly, we demonstrate the connection between the nanoscale structure of two chemically equivalent, yet morphologically distinct Nafion fuel-cell membranes and their macroscopic chemical properties. Quantification of the chemical interactions between water and Nafion reveals that extruded membranes have smaller water channels with a reduced sulfonic acid head group density compared to dispersion-cast membranes (Fig. 1, left). As a result, a disproportionally large amount of non-bulk (interfacial) water molecules exists in extruded membranes *(1)*.

Secondly, we determine that the interfacial, more weakly coordinated water species exhibits faster transit than bulk water in the membrane ionic channels. For four chemically diverse perfluorosulfonic acid PEMs, we find a linear correlation between water transport and proton conductivity (Fig. 1, right), suggesting that designing PEMs to maximize the fraction of under-coordinated interfacial water is a key, yet largely overlooked parameter, for maximizing overall transport and improving fuel cell efficiency *(2)*.

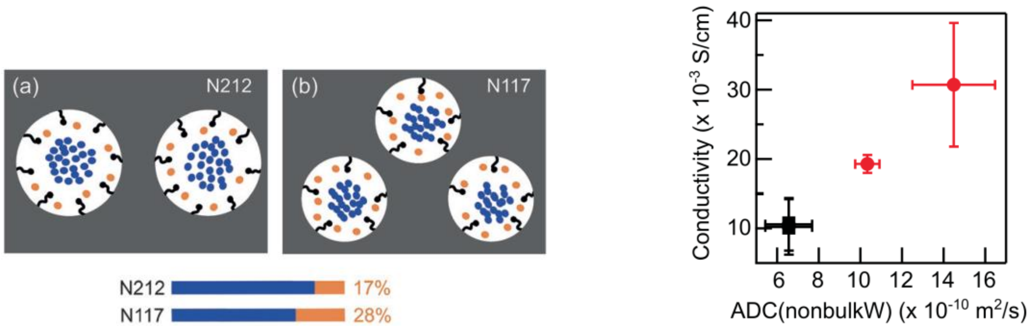

Figure 1: Left: schematic of larger (a) and smaller (b) ionic channels of Nafion N212 and N117 PEMs and relative contents of interfacial non-bulk water (yellow) compared to bulk water (blue). Right: linear correlation between proton conductivity and interfacial non-bulk water diffusivity for different PEMs.

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Rational design of Carbonate free High- and Local High Concentration Electrolytes for Lithium Metal Batteries

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Li-Ion batteries power ever more applications that were considered impractical or too expensive just a few years ago. The reason for this rapid development is the increasing energy density of the underlying chemistry. However, while anode performance has steadily improved over the last twenty years, graphite anode technology has reached its physical limit. The next leap in energy density for Li-ion technology could be made possible by overcoming the severe safety issues of the 1st generation Li-metal batteries introduced by Moli Corp. over 30 years ago and in the process unlocking the potential of Li-metal (3860mAh g^{-1}) as anode material instead of graphite (372 mAh g^{-1}) [1].

To solve the two main concerns, dendrite formation and low cycling efficiency due to side reactions with the electrolyte, High Concentration Electrolytes (HCE electrolytes with c > 2 mol/L) and Local High Concentration Electrolytes (LHCE, HCE's diluted by fluorinated solvents) of Li bis(flurosulforyl)imid and bis(trifluromethansulfon)imid (LiFSI and TFSI) have been introduced. They show a significant improvement compared to carbonate or ether-based electrolytes that use the common 1 mol/L concentration of Li salt. Their design however is not straight-forward, because many factors must be considered, including the formation of possible solvent-salt complexes. Therefore to enable a rapid iteration of possible active solvent-salt complexes a rational choice of constituents due to specific relevant parameters is necessary [2]. The rational selection of solvent-salt species and stoichiometries for a variety of candidate species and combinations of solvent-salt complexes is assisted by Density Functional Theory (DFT) with thermochemical calculations. For verification of the DFT calculations linear-sweep voltammetry (LSV), galvanostatic cycling with electrochemical impedance spectroscopy (EIS) and coulombic efficiency measurements (CE) are being combined with scanning electron microscopy (SEM) and x-ray photoelectron spectroscopy (XPS) to study the resulting morphology and lithium cycling performance.

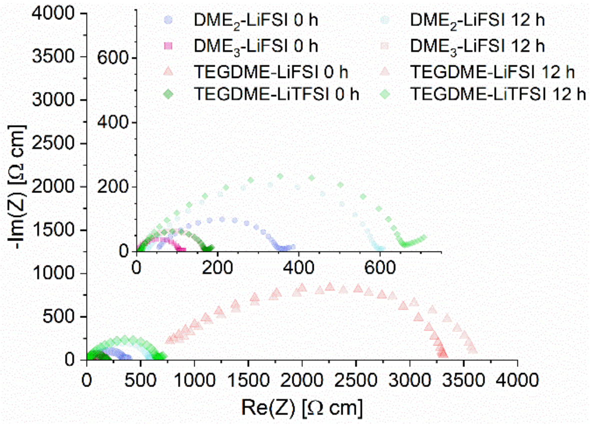

Figure 1: Nyquist Plot of each measured symmetric Cell during Li passivation of different high concentration electrolytes highlighting the stark difference between solvent (DME, TEGDME) and salt (FSI, TFSI) interaction.

Our results show, that DFT at the M11 level of theory is a very accurate approach to predict the resulting solvent-salt complex combinations. The known combinations such as DME$_3$-LiFSI and SL$_3$-LiFSI are compared with the alternatives of DME$_3$/SL$_3$-LiTFSI DME$_2$-LiFSI and DME-TEGDME-LiFSI/TFSI (SL = Sulfolan) in terms of Li-metal plating efficiency and SEI resistance after initial passivation (Fig. 1) and cycling. Functional principles of the complexes and their probable origin and physical parameters will be discussed, compared and correlated with obtained LSV, EIS and CE results. Significant anion decomposition rates as a function of complex structure and/or anion type and resulting shift in redox potential can be observed and the resulting SEI stability and chemical make-up can be correlated to electrochemical performance.

The results for Li-complexation energy, Nernst potential and reduced species show correlation with expected lithium cycling performance and have led to the identification of the HCEs DME$_2$-LiFSI and TEGDME-DME-LiFSI as electrolytes for Li-metal plating and stripping. The developed procedure shows great promise for fast and rational design of promising (L)HCEs.

The financial support by Umicore N.V. for this project is gratefully acknowledged.

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The Electrocatalytic Cleavage of Carbon-Halide Bonds on Ag, Au and Cu electrodes: from aprotic and protic traditional solvents to ionic liquids

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In the last years we have showed in detail how the electrocatalytic cleavage of carbon-halide bonds is modulated by *(a)* the stepwise or concerted nature of the DET mechanism, (as a function of the electrode surface, of the nature of the halogen atom, and of the molecular structure of RX) and *(b)* the double layer structure (as a function of the nature and bulkiness of the supporting electrolyte ions).

To both complete and support our interpretative scheme we are now concentrating on the solvent role.

Comparing aprotic with protic organic solvents after appropriate intersolvental normalization, interesting peculiarities emerge concerning protic media. Solvent proticity deeply affects both the reaction mechanism (on both non-catalytic and catalytic electrode surfaces) and the extent of the catalytic effects [1]. We will also present a first extension of this study to room temperature ionic liquids (RTILs), which are currently arising considerable interest on account of their advantages over traditional organic solvents. In this context, the electrochemical reduction of a series of aliphatic and aromatic bromides has been investigated in 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIMBF_4$).

$BMIMBF_4$ behaves like molecular solvents such as acetonitrile and dimethylformamide but, in general, both Ag and Cu are less active in the ionic liquid than in polar aprotic solvents [2].

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Electrochemical oxygen reduction and evolution on graphene supported Au nanoparticles in ionic liquid

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Oxygen reduction and evolution reactions (ORR and OER) are essentially important to the performance of rechargeable metal–air batteries. The design and fabrication of highly active, durable and low-cost electrocatalyst toward ORR and OER is considered to be the key to solve the bottle-neck of the rechargeable metal-air batteries development.[1]

Au is considered to be a promising alternative to Pt catalyst for ORR due to its high activity and high resistance to CO poisoning as well as cheaper price. In order to enhance the catalysis activity of Au, hybrid of AuNPs with graphene has attracted significant attentions. Novel properties of graphene have attracted much interest in employing graphene as an excellent substrate for hosting functional nanomaterials as electrocatalysts. Enhanced electrocatalytic activity is largely attributed to the improve in charge transfer rate from the nanoparticles to the graphene substrate as well as the existence of abundant active sites for ORR on the surface.

Electrolyte also plays crucial role in determining the overall performance of metal-air batteries. Rechargeable metal-air batteries functioning with traditional alkaline electrolytes always suffer from severe problems such as dendrite formation, solvent evaporation and carbonation with CO_2. As novel electrolyte, room temperature ionic liquids (RTILs), featured with a number of ideal novel properties like high thermal stability, negligible vapor pressure and wide electrochemical window, have attracted wide interest in electrochemical system researches. Employment of ILs as electrolyte toward rechargeable metal-air battery avoids the volatilization and carbonation issues of alkaline media, and likely suppresses the growth of metal dendrite as well. Elia et al. have reported that ionic liquid-based electrolytes are suitable for operation in a full Li−O2 battery, offering unique properties in terms of reversibility and particularly energy efficiency. However, electro-catalyst toward ORR and OER in ILs system has been rarely reported. Study on highly active catalysts toward ORR and OER processes in ILs system is one of the most urgent needs for the development of rechargeable metal-air batteries.

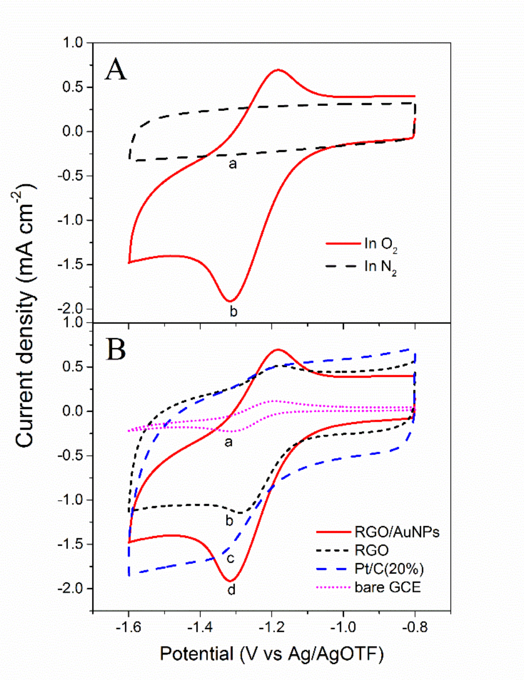

Fig 1. CVs of (A): RGO/AuNPs-GCE in N_2 (a) and O_2-saturated (b) [Bmim]BF_4; (B): (a) bare GCE, (b) RGO-GCE, (c) Pt/C-GCE and (d) RGO/AuNPs-GCE in O_2-saturated [Bmim]BF_4. Scan rate: 50 mV/s.

The previous catalytic studies on Au strongly inspired us to research the ORR performance of the monodisperse Au NPs in IL. Herein, we report a facile strategy for the synthesis of reduced graphene oxide (RGO) sheets/gold nanoparticles composite, which is prepared by in situ growing Au nanoparticles from $HAuCl_4$ precursor solution in the presence of graphene oxide (GO) sheet. The Au nanoparticles with an average diameter of 8 nm are highly dispersed on the graphene sheets. Electrochemical studies show high electrocatalytic activity of the hybrids toward reversible ORR and OER processes in IL, while the reversibility of ORR process (i.e. OER) is fairly poor in alkaline medium.[2]

Acknowledgements

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Investigation of lithium polysulfide encapsulation mechanism in porous carbons derived from organic sources

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The new era of communication and mobility would not be possible without efficient solutions for energy storage systems. Commonly commercially used Li-ion batteries have almost achieved their limits in terms of energy densities. Among various types of prospective rechargeable systems, lithium-sulfur batteries are widely regarded as one of the most promising. By utilizing metallic lithium as anode and elemental sulfur as cathode, Li-S batteries can potentially reach unparalleled gravimetric and volumetric energy densities of 2500 Wh kg^{-1} and 2800 Wh L^{-1}. Apart from the theoretical potential, the lithium-sulfur system still suffers diverse challenges. Lithium polysulfides shuttle is one of those aspects as it results in low charge efficiency, fast capacity loss as well as severe anode corrosion. For this reason the suppression of the redox shuttle mechanism is a high priority task.

Incorporating active sulfur into carbon frameworks with good electrical conductivity and diverse nanostructures, such as micro/mesoporous carbons, have been regarded as one of the most effective strategies to enhance the electrochemical performance of lithium sulfur batteries.

In our study active carbon materials with developed surface area and defined pores from biomass precursors have been synthesized and applied as cathode additive and host for lithium polysulfides. Among the investigated materials were: carbon from mandarin peels (MAC) and carbon from humic acids (HAMC). Both materials have been obtained by pyrolysis of appropriate organic waste in argon atmosphere. The materials have been characterized by means such techniques as XRD, Raman spectroscopy, nitrogen adsorption isotherms and SEM/TEM. Electrochemical testing involved constant current charge/discharge tests, cyclic voltammetry and EIS techniques performed in Swagelok-type two-electrode cells with lithium counter/reference electrodes and electrolyte comprising $LiSO_3CF_3$ dissolved in a mixture of DOL and DME, with 0.5 M addition of $LiNO_3$. The obtained materials appeared to be very effective as conducting components of the sulfur cathode, enabling trapping sulfur and intermediate polysulfides within the carbon network, thus contributing to a very high initial capacity and good cycling stability.

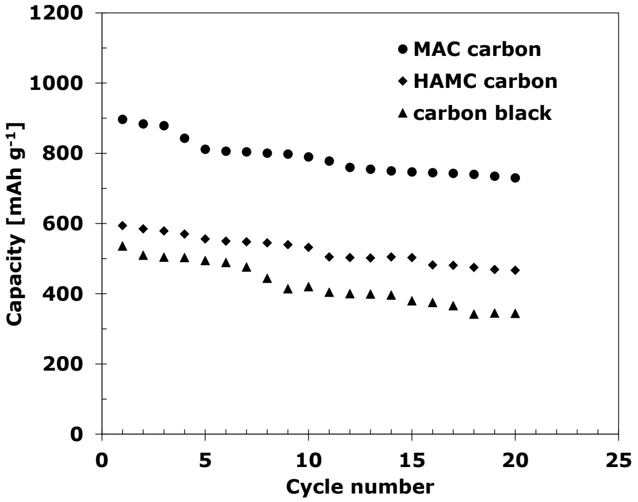

Fig. 1. Cycling stability of Li-S battery with different carbon as cathode additive.

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Study of the charge/discharge mechanism of lithium-sulfur cells using operando UV/Vis spectroscopy

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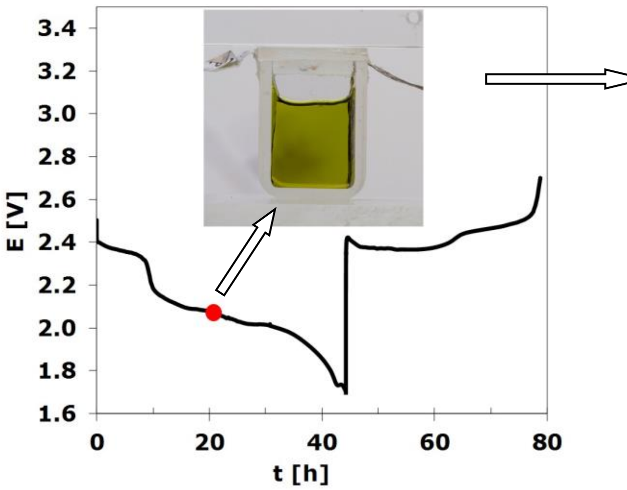
The on-going electrification of the transport sector is one of the major driving forces for energy storage breakthroughs. Current Li-ion battery technology has fundamental limitations hampering to fulfil the need of future electric cars with long driving ranges. Therefore alternative chemical power sources with high energy density are continuously developed. Beside high energy density, the new system needs to be safe, environmentally friendly and cheap.

One of the most promising alternatives is the family of lithium-sulfur batteries, working through multi-step reaction between lithium and sulfur. During discharge sulfur is reduced to lithium polysulfides species with different chain length. Lithium polysulfides dissolve in the organic electrolyte. Dissolved polysulfide species may easily diffuse back and forward between the two electrodes, giving rise to a characteristic mechanism of Li/S system, so-called "redox shuttle". The high-order polysulfides migrate toward the anode, react with the lithium metal, reduce to low-order polysulfides, migrate back to the cathode, form high-order polysulfides again, and so on. Severe shuttle behavior can lead to an infinite recharge and poor charge efficiency. The detailed charge/discharge mechanism of a lithium-sulfur cell is still not fully investigated. This includes a better understanding how different battery components influence the conversion of sulfur to polysulfides throughout discharge.

In order to identify the solution phase intermediates in an operating lithium-sulfur battery, we designed a transmission UV/Vis spectro-electrochemical cell. In the operando measurement, the Li-S cell was placed in a UV/Vis spectrometer and first discharged with a constant current of C/10 to 1.7 V and then cycled at C/10 in the potential range 1.7–2.7 V by using a Biologic VMP-3 galvanostat/potentiostat. During the charge and discharge of the cell, the UV/Vis spectra were recorded every 15 min from 900 nm to 200 nm. The experiment enabled us to gain insight into the processes of lithium polysulfide creation and transport between the electrodes. It has been found that kinetics of polysulfide release strongly depends on the morphology and porosity of the carbon component of the cathode.



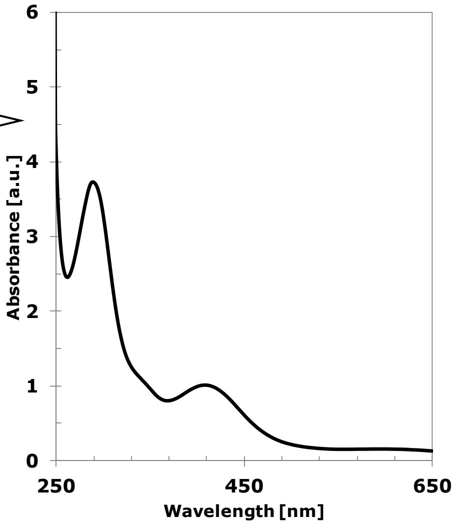


Fig. 1. Galvanostatic charge/discharge curve of Li-S cell.

Fig. 2. UV/Vis spectrum of lithium polysulfides.

Acknowledgment: This work was supported by the National Science Centre, Poland grant No. UMO-2016/23/D/ST4/01539

Chrome Plating Using $CaCl_2$ Hydrate Melt-Based Trivalent Chromium Baths

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Electrochemical chromium (Cr) plating is an important finishing for both metallic and non-metallic parts due to the excellent decorative, anticorrosive, and wear-resistant properties. Conventional aqueous Cr plating baths, however, utilize hexavalent chromium salts that places a heavy burden on the environment. As an alternative to the hexavalent chromium, trivalent chromium plating baths have been developed, but their commercial use is not sufficiently advanced to displace hexavalent ones especially in hard coating applications [1]. Most of the trivalent baths contain organic acid(s) as a complex former, which makes the resulting Cr layers amorphous by carbon inclusion and reduces some physical properties, such as corrosion and wear resistance of thicker coatings [2]. Since the concentration of Cr^{3+} ion is generally low (*e.g.* 5–20 g L^{-1}), plating rates of trivalent chromium baths are still unsatisfactory for producing Cr coatings with the thickness of several microns. The lifetime and manageability of the baths also have room for improvement.

Calcium chloride hexahydrate, $CaCl_2·6H_2O$, is a low-temperature melting salt (m.p. 29 °C), and was recently applied for the electrodeposition of UO_2 [3]. Such hydrate melts with a high Cl^- activity can dissolve various metal chlorides, and we reported a dendrite-free displacement plating of silver using the melts [4,5]. In the present work, we tried the hydrate melts as novel baths for trivalent chromium plating. The absence of *bulk* water molecules could suppress hydrogen evolution during the electrodeposition of less-noble metals like Cr.

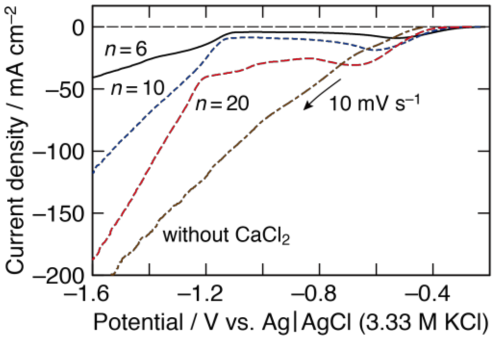

Figure 1. Cathodic voltammograms for three $CaCl_2$-H_2O melts (n = 6, 10, 20) and normal water each containing 52 g kg^{-1} H_2O of Cr^{3+} ion, where n is $H_2O/CaCl_2$ molar ratio.

Solubility of $CrCl_3$ in $CaCl_2$-H_2O melt (50 °C) at the $H_2O/CaCl_2$ molar ratio (n) of 6 exceeds 150 g kg^{-1} H_2O (*i.e.* [Cr^{3+}] = 49.3 g kg^{-1} H_2O), being sufficient to use for electroplating bath. A set of cathodic linear sweep voltammograms (Figure 1) for four different solvents, each of which contains [Cr^{3+}] = 52 g kg^{-1} H_2O, shows that hydrogen evolution onset at around –0.4 V *vs.* Ag-AgCl (3.33 M KCl) is depressed in the presence of concentrated $CaCl_2$. Potentiostatic electrodeposition of Cr on a nickel-plated brass substrate was carried out at –1.2 V using the melt (50 °C) with n = 10. Current density during the deposition for 30 min was in the range 30–40 mA cm^{-2}. Although the current density was lower than either of the existing hexavalent and trivalent chromium plating, the thickness of the resulting Cr layer was 10 µm, suggesting that the current efficiency was much higher than the existing methods; the deposition rate was about 0.3 µm min^{-1}. X-ray diffraction (Figure 2) shows the Cr layer is polycrystalline with a random orientation. The appearance of the Cr layer was blackish; therefore, it is necessary to find brightening additive(s) to obtain a lustrous surface. Alternatively, the blackish layer can be used as is as a novel black chromium plating.

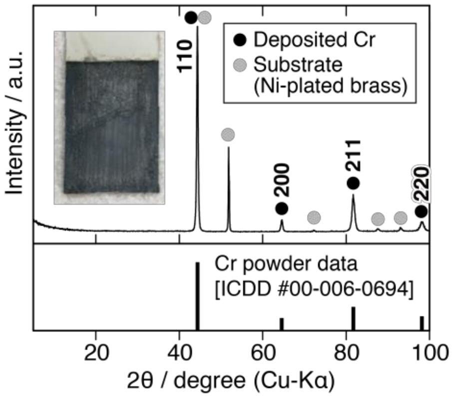

Figure 2. Photograph and X-ray diffraction pattern of Cr layer electroplated from $CaCl_2$-H_2O melt (n = 10) in Figure 1.

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$NiFeP_4$ semi-hollow nanocages as high performance electrocatalysts for hydrogen evolution reaction

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Hydrogen (H_2), due to its high power density, rich resource and recyclability, has been identified as one of the most promising alternatives to traditional fossil fuels. The open structures could provide a larger surface area which facilitates the contact among the active sites and electrolyte and species of reaction. NiFe-PBA was selected as both a precursor and a morphological template to prepare an open-typed structure by a directional etching method. In this work, we prepared $NiFeP_4$ and $NiFeP_4$ semi-hollow nanocages ($NiFeP_4$-SHNC), which showed a highly uniform and well-defined cubic structure with anaverage diameter ofaround 180 nm.

From Fig. 1 we can observe that the inner space of $NiFeP_4$-SHNC is enlarged obviously which may provide more active sites and gas transmission path for the hydrogen evolution reaction (HER). From Fig. 2 we can be observed that the $NiFeP_4$-SHNC presents an overpotential (η) of 128 mV (vs RHE) at the current density of 10 mA cm^{-2}, which is similar than that of Pt/C-JM (120 mV), and far greater than that of $NiFeP_4$ (194 mV), implying superior HER activity. More interestingly, $NiFeP_4$-SHNC is pretty outstand on driving high j = 50 mA cm^{-2}, generally needed in practical electrolysis, with greatly lower overpotential (195 mV) than that of Pt/C-JM (326 mV), which indicates a promising future for $NiFeP_4$-SHNC in industrial applications. The enhanced HER activity of $NiFeP_4$-SHNC can be attributed to the result of improved mass transfer rate during the hydrogen evolution reaction process owing to the open structure and improved active sites produced by the directional etching method. In addition, this synthetic approach provides strategies and horizons to design and synthesize other types of porous binary metal oxides, sulfides, phosphides and selenides which are beneficial for energy conversion and storage.

This work was supported by National Science Foundation of China (Grant No. 21773198 and U1705253).

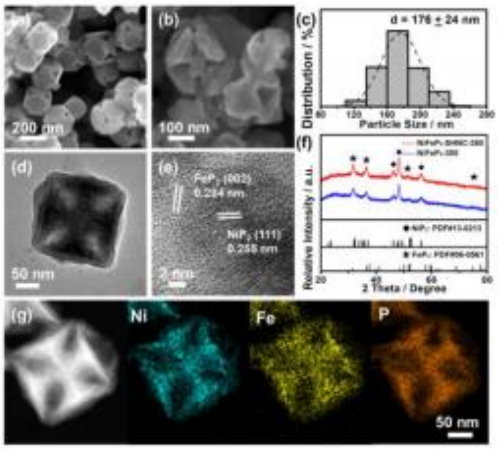

Fig. 1 (a-b) SEM images, (c) size histogram; (d) TEM and (e) HRTEM of $NiFeP_4$-SHNC-350; (f) XRD patterns of $NiFeP_4$-SHNC-350 and $NiFeP_4$-350; (g) STEM and corresponding elemental distribution of $NiFeP_4$-SHNC-350.

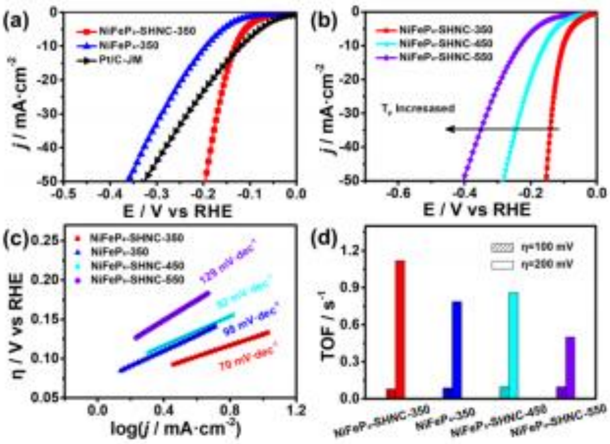

Fig. 2 Electrocatalytic HER activities of catalystsmeasured in 1.0 M KOH. (a) LSV curves of NiFeP4-SHNC-350, NiFeP4-350 and commercial Pt/C-JM; (b) LSV curves of NiFeP4-SHNC prepared at 350, 450 and 550 °C; (c) corresponding Tafel plots; (d) TOFs values measured at η = 100 and 200 mV.

Enhanced electrochemical property of graphite decorated with Mn_3O_4 thin films towards achieving high energy storage capacity

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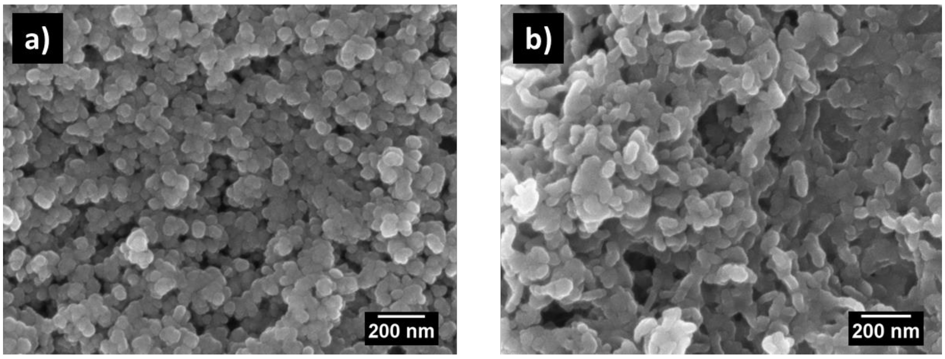
Abstract

Manganese oxide thin films were successfully synthesized and decorated on graphene via a chemical bath deposition method. The morphological, structural, optical and electrochemical properties of the deposited films were respectively studied using scanning electron microscopy (SEM), x-ray diffractometry (XRD), UV-vis spectrophotometry and a 3-electrode potentiostat. Decorating the graphene with manganese oxide film improved the morphological, structural, optical and electrochemical features of the deposited films. SEM image reveals irregularly fused capsule-like nanoparticles while the structure of the film improved from amorphous to crystalline after decoration on graphene. The transmittance and optical band gap values of the films recorded an increase upon decoration on the graphene. The undoped manganese oxide thin films had band gap energies ranging from 2.0 eV to 2.3 eV. Electrochemical studies showed good cyclic voltammograms and a recorded maximum specific capacitance value of $194 Fg^{-1}$. The films find application in optical devices owing to its high transmittance and in electrochemical storage devices.

Keywords: manganese oxide, thin films, doping, band gap, cyclic voltammograms, specific capacitance.



Effect of porosity enhancing agents on the electrochemical performance of high-energy ultracapacitor electrodes derived from peanut shell waste

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This study reports the synthesis of porous activated carbon nanostructures from peanut shell waste (PSW) via a two-step carbonization and activation process at elevated temperature using potassium based salt as porosity enhancing agents (PEA) with varying mass concentrations (CPSW:PEA).

The textural properties obtained were depicted with relatively high specific surface area values 1457 m^2 g^{-1}, 1625 m^2 g^{-1} and 2547 m^2 g^{-1} for $KHCO_3$, K_2CO_3 and KOH respectively at a mass concentration of 1 to 4 which were complemented by the presence of a blend of micropores, mesopores and macropores. The structural analyses confirmed the successful transformation of the carbon-containing waste into an amorphous and disordered carbonaceous material.

The electrochemical performance of the material electrodes tested in a 2.5 M KNO_3 aqueous electrolyte depicted its ability to operate reversibly in both negative and positive potential ranges of 0.90 V. The activated carbon with a CPSW:PEA mass ratio of 1:4 yielded the best electrode performance for all featured PEAs. The porous carbons obtained using KOH activation displayed a higher specific capacitance and the lower equivalent series resistance as compared to others. The remarkable performance further corroborated the findings linked to the textural and structural material properties. The assembled device operated in a neutral electrolyte at a voltage of 1.80 V, yielded a ca. 224.3 F g^{-1} specific capacitance at a specific current of 1 A g^{-1} with a corresponding specific energy of 25.2 Wh kg^{-1} and 0.9 kW kg^{-1} specific power. This device energy was retained at 17.7 Wh kg^{-1} when the specific current was quadrupled signifying an excellent supercapacitive retention with a corresponding specific power of 3.6 kW kg^{-1}.

Improvement of Cycling Stability of Lithium Metal Cell by employing the Coated Mesh Interlayer for Selected Lithium-ion Deposition

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The demand for rechargeable lithium batteries with high energy density is increasing in various applications such as electric vehicles and energy storage systems. Lithium metal with high theoretical capacity and low operational voltage have been considered as one of the promising anodes for high energy density lithium batteries. However, the development of rechargeable lithium metal batteries has been hindered by the high reactivity of lithium metal toward liquid electrolytes and the occurrence of dendrite growth during charge and discharge cycles. In addition, the non-uniform current distribution on the lithium metal electrode, which arises from the heterogeneous composition of solid electrolyte interphase (SEI) layer formed on lithium by the reductive decomposition of organic electrolyte, results in a low cycling efficiency and gradual capacity loss with repeated cycling. The high propensity of lithium dendrite during cycling is related to inhomogeneity on the lithium surface layer. In this work, we investigate an efficient interlayer that suppresses lithium dendrite growth. The uniform shape of mesh interlayer effectively improved the surface homogeneity on the lithium surface, which resulted in suppression of lithium dendrite and stabilization of lithium surface. The role of coated mesh was compared and investigated by various analyses such as dc polarization, electrochemical impedance spectroscopy and surface analysis.

High Voltage Cycling Performance of Lithium-Ion Cells Employing a Functional Additive

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Lithium-ion batteries (LIBs) have been widely used in many applications such as mobile electronics, drones, electric vehicles and energy storage systems because of their high energy density and stable cycle life. As there is always need of more capacity for using LIBs for longer time, high voltage operating is essential for increasing energy density of LIB. However, there are several issues in high voltage operation of LIBs, such as, dissolution of transition metal from cathode material and oxidative decomposition of electrolyte. Among the strategies for improving the high-voltage performance, an addition of functional additive is one of the most promising methods. Functional additives can form cathode electrolyte interphase (CEI) on the cathode surface, which suppress the oxidative electrolyte decomposition and the dissolution of transition metal from cathode. In our study, we investigated effective additives for forming the uniform CEI layer and applied them to the LIB composed of graphite anode and $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cathode. Electrochemical characterization and evaluation were performed to examine how these additives could improve the high-voltage performance of LIBs.

Highly Porous N-doped Carbon Nanofibers as Support Materials of Platinum Catalysts for Ammonia Electrooxidation

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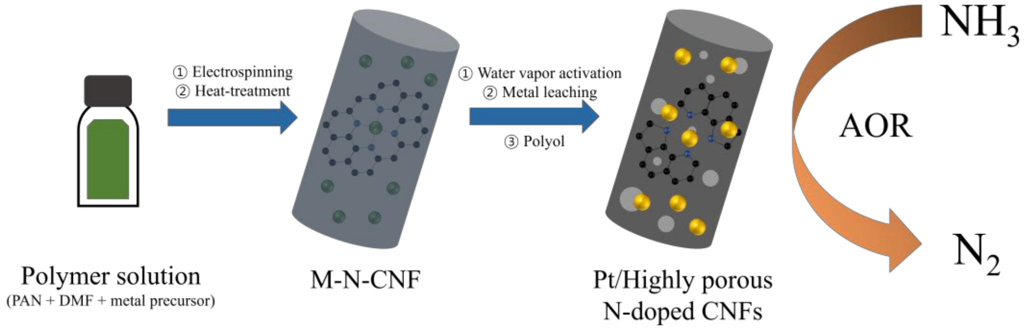
For the further development of renewable hydrogen economy, there still remain numerous technical issues, such as hydrogen transportation and storage. Ammonia is regarded as a potential energy carrier because of its' high volumetric energy density and easier transportation/storage. Production of hydrogen fuel by ammonia electrolysis has attracted great attentions as a low-cost and carbon-free technology. Especially, it is possible to produce high purity hydrogen through the ammonia electrolysis process.

Ammonia electrooxidation, which is the anodic reaction of ammonia electrolysis, has been investigated mostly on platinum (Pt) or iridium (Ir) catalysts. Due to the sluggish kinetics of ammonia elelctrooxidation reaction (AOR) as compared to the hydrogen evolution reaction (HER) at the cathode, it is required to design and develop more active catalysts for AOR.[1] For achieving the high activity of catalysts for AOR, it is also important to understand the reaction kinetics and poisoning mechanism.

In this study, ammonia electrooxidation have been investigated on Pt catalysts supported on highly porous N-doped carbon nanofibers (CNFs). Highly porous N-doped CNFs were prepared by electrospinning a metal contained polymer solution and subsequent heat-treatments/metal-leaching processes. As a result, platinum-nitrogen-carbon nanofibers structures provided higher activity for AOR than platinum supported on untreated carbon nanofibers.



Reference
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Stationary-Potential CO_2 Reduction on Pt/C Occurs at a More Positive Electrode Potential than H_2 Evolution

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CO_2 electroreduction, in which CO_2 is converted electrochemically into useful compounds, has attracted intensive research. When using a Cu electrocatalyst, the reduction current efficiency for hydrocarbon production has been reported to be as high as ~60% [1]. However, it experimentally requires a very large overpotential of >1 V, which is a significant obstacle for practical application. To overcome the issue, we have proposed an approach that uses a polymer electrolyte single cell containing a Pt/C electrocatalyst, which enabled to reduce CO_2 at an electrode potential close to the theoretical CO_2 reduction [2]. Remarkably, we also demonstrated that CO_2 is reduced to CH_4 with a high efficiency and high selectivity by controlling the CO_2 concentration to be fed. However, the CH_4 generation quickly decreases within ~10 s. If the reaction continuance at a stationary potential can be achieved, the system stabilization of CO_2-reduction technology will be realized. In this study, we investigated the stationary-potential CO_2 reduction on the Pt/C electrocatalyst.

We prepared the polymer electrolyte single cell equipped with a Nafion-based membrane electrode assembly containing the 46.2 wt% Pt/C as the working and counter electrodes (WE and CE). Fully humidified H_2 and Ar/CO_2 (CO_2 partial pressure: 0.04 atm) were supplied to the CE and WE, respectively. The experimental setup in this study is drawn in Fig. 1. The WE potential was stepped 13 levels a measurement in a negative direction every 2 min in the potential range between 0.4 V and 0.05 V. At the same time, in-line mass spectrometry (MS) was conducted to analyze the products in real time. All the potentials are shown with the reference to reversible hydrogen electrode (RHE).

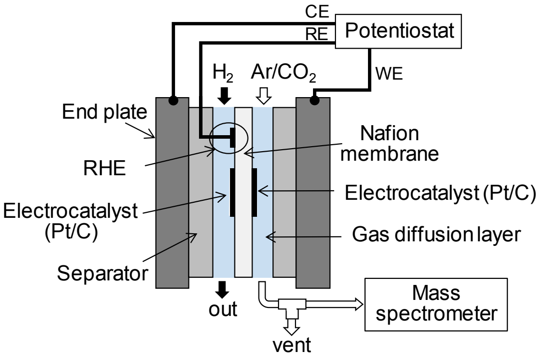

Fig. 1. Schematic diagram of the experimental setup in this study.

Fig. 2 shows MS signals of *m*/*z* 2 (for H_2) and 15 (for CH_4) with applied potential program. The signal of *m*/*z* 15 is observed in the potential range between 0.25 V and 0.1 V. On the other hand, the signal of *m*/*z* 2 is observed only at the potential of 0.05 V. Hence, it is found to reduce CO_2 at a more positive electrode potential than H_2 evolution in this system. Significantly, the observed *m*/*z* 15 signals in each potential scarcely decrease within 2 min, which is indicative of the steady CH_4 generation at a stationary potential. The maximum *m*/*z* 15 signal intensity is observed at 0.16 V, at which the Faradaic efficiency was calculated to be ~3.3%. Consequently, this work reveals that the steady CH_4 production from CO_2 reduction at a stationary potential with a high efficiency occurs on the Pt/C electrocatalyst at a more positive electrode potential than H_2 evolution.

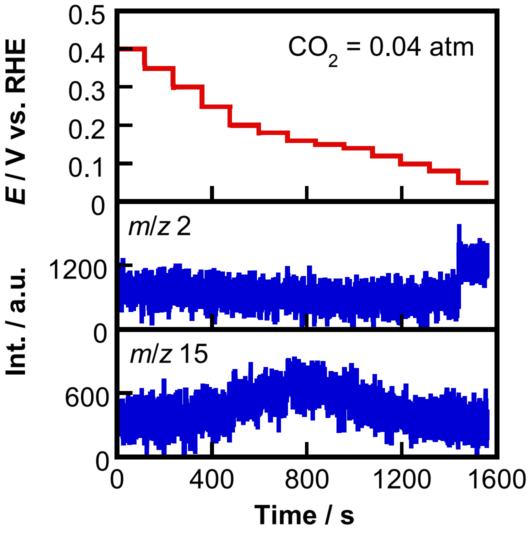

Fig. 2. Potential program applied to the working electrode and MS signals (*m*/*z* 2 and 15) measured simultaneously at Pt/C by feeding 0.04 atm CO_2 at 40°C.

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Pd$_1$Nb$_1$ electrocatalyst supported on Printex 6L carbon black with improvement performance for ADEFC

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A possible source of renewable energy is alkaline direct ethanol fuel cells (ADEFC) because it can reach high current densities with minimal pollutant production and using bioethanol as fuel [1]. Here, we report the synthesis of Pd$_x$Nb$_y$ (20% wt) electrocatalysts in the Pd:Nb metal mass ratio (1:0; 3:1; 2:1; 1:1) supported on Printex 6L carbon black (80% wt) by the chemical reduction method to be used in ADEFC anode [2]. These synthesized electrocatalysts were physically characterized by XRD, ICP-MS, XPS, Raman spectroscopy, and TEM techniques. The electrocatalytic activity for ethanol oxidation reaction (EOR) of the prepared electrocatalysts was studied by Cyclic Voltammetry (CV) and Chronoamperometry (CA). Besides, the electrocatalysts were evaluated their performance in a single cell ADEFC.

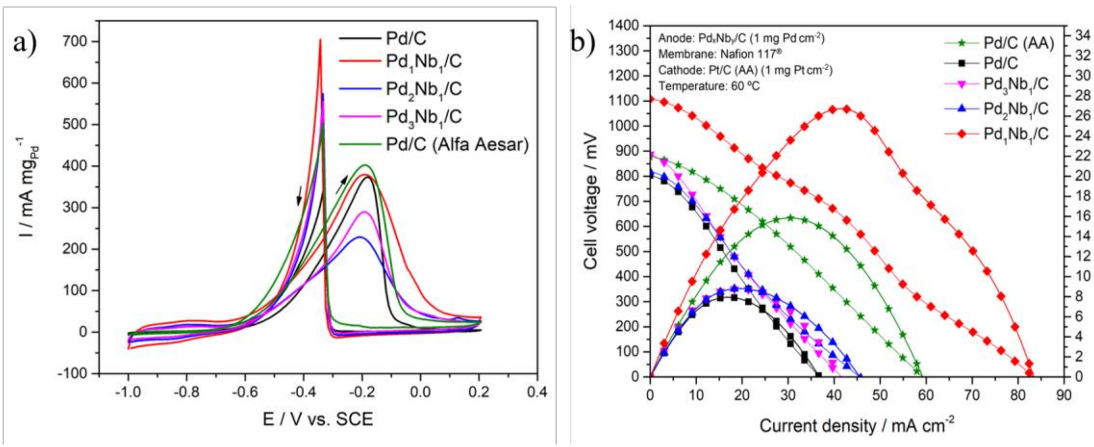

Figure 1. (a) Cyclic voltammograms using 1.0 mol L^{-1} ethanol and 1.0 mol L^{-1} KOH, measured in the potential range from −1.0 to +0.20 V vs. SCE, at a scan rate of 20 mV s^{-1}. (b) Polarization and power density curves in the ADEFC. The temperature was set at 70 °C for the fuel cell and 85 °C for the oxygen humidifier. The fuel, 2.0 mol L^{-1} ethanol (in 1.0 mol L^{-1} KOH), was delivered at 1.0 mL min^{-1}, and the oxygen flow was regulated at 200 mL min^{-1}.

The results of XRD showed the presence of metallic Pd and the absence of crystalline face of Nb and its presence in ICP-MS and TEM suggest the presence of adsorbed amorphous Nb in the support Printex 6L. The oxidation current normalized by mass in CV was the highest for ethanol oxidation using Pd$_1$Nb$_1$/C (Figure 1a). In addition, Pd$_1$Nb$_1$/C has a lower positive onset potential for EOR -0.37 vs. NHE while Pd/C (AA) -0.35 vs. NHE. In Figure 1b, we can see that Pd$_1$Nb$_1$/C also showed superior performance in the single ADEFC experiment reaching the maximum power density of 27 mW cm^{-2}. That performance is 1.8 times higher than that one of Pd/C (AA) with 15 mW cm^{-2}. The results of the ADEFC experiment residue analysis results by FT-Raman showed a lower amount of acetaldehyde in the residue for the catalyst with higher Nb ratio (Pd$_1$Nb$_1$). We suggest that Nb improves the electrocatalytic activity of Pd by two mechanisms: bifunctional and electronic [3-4]. Therefore, Niobium is a promising alternative co-catalyst to Pd for EOR in alkaline medium.

Acknowledgments: The authors are grateful to FAPESP (2015/10314-8, 2017/00819-8, 2017/22976-0, 2017/21846-6, 2017/26288-1, 2017/10118-0, 2018/26307-9), CNPq (406612/2013-7, 429727/2018-6), CEM-UFABC, and CAPES.

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Modification of Carbon Nanomaterials with Organoimido-Polyoxometalates: Electrochemical Evaluation

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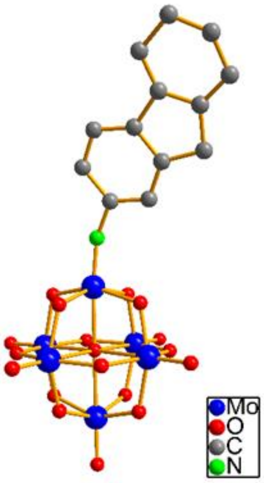
One of the important areas in materials science is the development of new hybrid organic/inorganic molecules forming part of nanostructured composites. Polyoxomolybdates are an interesting family of inorganic polyanions made of molybdenum and oxo ions forming different discrete systems showing high symmetry. These polyoxomolybdates present two type of oxo ions in the structure, bridging and terminal oxo atoms. The terminal oxo atoms can be replaced by an aromatic organic imido substituent giving rise to a hybrid system presenting a strong acceptor inorganic fragment and an aromatic donor fragment. The aromatic fragment of the molecule can interact by pi-stacking with a nanostructured carbon system such as nanotubes of graphene sheets, whereas the inorganic fragment is exposed to the environment being able to interact with different species.



In this work we present the electrochemical characterization of modified electrodes with hybrid POM-imido systems. Two different organic fragments have been used, aminofluorene (see figure 1) and 3-methylpyridine and the inorganic fragment is the Lindqvist type hexamolybdate (see figure 1). Both hybrid molecules have been immobilized on two different carbon nanomaterials (CNM), multiwalled carbon nanotubes (MWCNT) and graphene (GR). The glassy carbon electrode (GCE) modification was done by two different methods, i) modification of the surface by drop coating with a suspension of the CNM and then the dried electrode is immersed in a solution of the POM-imido molecules and ii) drop coating of the surface of the GCE with a suspension of the CNM with the POM-imido. The resulting electrodes were evaluated by cyclic voltammetry using the molybdenum electrochemical signal Mo^{VI}/Mo^{V}. The results show that the POM-imido systems are more efficiently immobilized on the MWCNT than GR. On the other hand, the method using a mixture of the CNM and the POM-imido for drop coating produces a more intense, stable and reproducible electrochemical signal.

Figure 1: chemical structure of the POM-AF.

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L-cysteine modified MoS_2/reduced graphene oxide-based electrodes: Synthesis and Electrochemical Characterization

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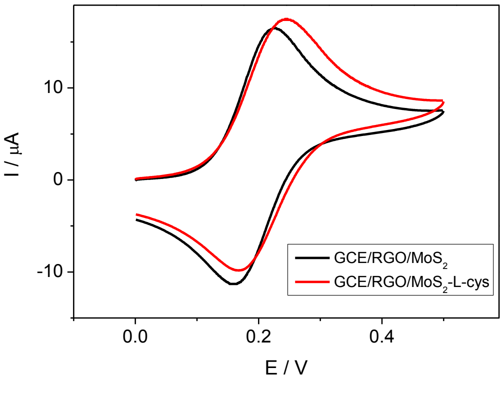
Molybdenum disulfide (MoS_2) is a 2D layered nanomaterial that has attracted an increasing number of scientists' interests because of its unique properties and graphene-like structure. MoS_2 is a semiconductor, which has an interesting indirect-to-direct bandgap transition (from 1.2 to 1.9 eV), depending on its thickness. This phenomenon may offer a valuable solution to overcome the shortages of graphene. So, the increasing potential uses of MoS_2 is going to develop sensing combined with fluorescence, electrochemistry, and surface-enhanced Raman scattering techniques. On the other hand, there is a growing interest in generating MoS_2/graphene hybrids to produce advanced multifunctional materials with effectively great performances in the electrochemical biosensors field.

In this work, we prepared a novel modified electrode based on the conjugation of L-cysteine amino acid with the layer-structured MoS_2 nanosheets and its posterior combination with reduced graphene oxide. MoS_2 nanosheets were successfully prepared by liquid phase exfoliation method in N,N-dimethylformamide (DMF) or isopropanol below ultrasound and then modified with L-cysteine. The materials were characterized using powder X-ray diffraction, SEM, DLS and FTIR-Drift.
The glassy carbon electrodes (GCE) were modified by drop coating methodology starting with a volume of RGO dispersion followed by a volume of MoS_2 or MoS_2-L-cys dispersion. The resulting electrodes were electrochemically evaluated by cyclic voltammetry using ferrocene as redox mediator.

The results show that the exfoliation using isopropanol produces lower sizes and more homogeneous nanostructures, therefore was the solvent selected to proceed with the L-cysteine modification.
From the electrochemical point of view, the incorporation of L-cysteine on the MoS_2 surface did not modify the electrochemical response of the redox mediator compared to the bare MoS_2 (see figure). 5 and 10 µL volumes were evaluated to prepare the electrodes being the use of 10 µL which produces the better reproducibility of the redox signal. Several layers of RGO/MoS_2 were incorporated with a good response which permits to incorporate more L-cysteine residues on the surface which will be used for a further platform to covalent attach biomolecules such us the acetylcholinesterase enzyme to develop organophosphorus insecticides biosensors.



Acknowledgements
The authors acknowledge to CONICYT-FONDECYT (CHILE) 1161225 and 1161255 and Financiamiento Basal FB0807 (CEDENNA) for the financial support.

H-doped TiO_{2-X} Nanoparticles for Hydrogen Generation and Environmental Remediation.

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Photocatalysis is considered an ideal route for effectively utilizing the sun's energy for hydrogen generation from water and for environmental remediation [1–3]. Titanium dioxide (TiO_2), the gold standard photocatalyst is limited in its inability to utilize the abundant 46% visible-light portion of the sun's energy reaching the earth [4–6]. Its wide energy band gap value of 3.2 eV, makes it only sensitive to the approximately 4% Ultra-Violet (UV) light portion of the sun's radiation [7]. In addition, an external energy source is required to generate UV light which makes UV-induced photocatalysis very expensive [8].

To make solar mediated catalysis industrially feasible, demands making TiO_2 visible-light active. Some techniques used to achieve this purpose includes dye sensitization, semiconductor coupling, metal and non-metal doping [7–9]. The present research therefore focuses on the synthesis and characterization of Hydrogen-doped titanium dioxide (H-doped TiO_{2-X}) nanoparticles for application as photocatalysts in water-splitting devices to generate hydrogen fuel from water, and also for environmental remedy applications.

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ENERGY MANAGENENT TECHNIQUES FOR SELF RELIANCE AND SUSTAINABLE DEVELOPMENT IN NIGERIA

By

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ABSTRACT

Energy is the tripod on which civilisation, urbanisation and advancement of any nation stand and is the ability to perform work. The optimum energy management and utilization of any firm, institution or a nation can lead to energy efficiency and overcoming the challenges of the energy trillema of energy access, energy security and energy affordability. This paper focuses on the energy management techniques such as Supervisory Control and Data Acquisition System SCADA, Power plant maintenance, Automatic General Control, Fuel management, Load management, Security Control, Distribution Automation System and metering and billing. Critical analysis of Nigerian energy sector were made that governing energy required strong energy politics and policy at the highest level. Finally, conclusions were also made that Public Private Partnership is required for smooth energy management.

Key words: SCADA, Energy policy, Energy efficiency, Energy trillema and energy banking

Understanding the Lithium Storage Mechanism in Core-Shell Fe_2O_3@C Hollow Nanospheres Derived from Metal-Organic Frameworks: An In situ diffraction using synchrotron radiation and in situ X-ray absorption spectroscopy (XAS)

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The aim of this research is to gain a comprehensive understanding of the lithium storage mechanism in Fe_2O_3@C by *in situ* diffraction using synchrotron radiation, in situ X-ray absorption spectroscopy (XAS) and complementary electrochemical techniques (such us cyclic voltammetry and galvanostatic charge/discharge) [1-4]. Obtained diffraction patterns demonstrate that the intermediate phases $Li_xFe_2O_3$ (*R-3c*, hexagonal) and $Li_xFe_2O_3$ (*Fd-3m*, Li-lean) are formed and subsequently converted to $Li_xFe_2O_3$ (*Fd-3m*, Li-rich), which finally transforms to metallic Fe and Li_2O at the end of lithiation. During the de-lithiation process, the "Li-lean phase" can be regenerated. The phase transition and the formation of Fe^0 during lithiation are confirmed from the in situ XAS experiment.

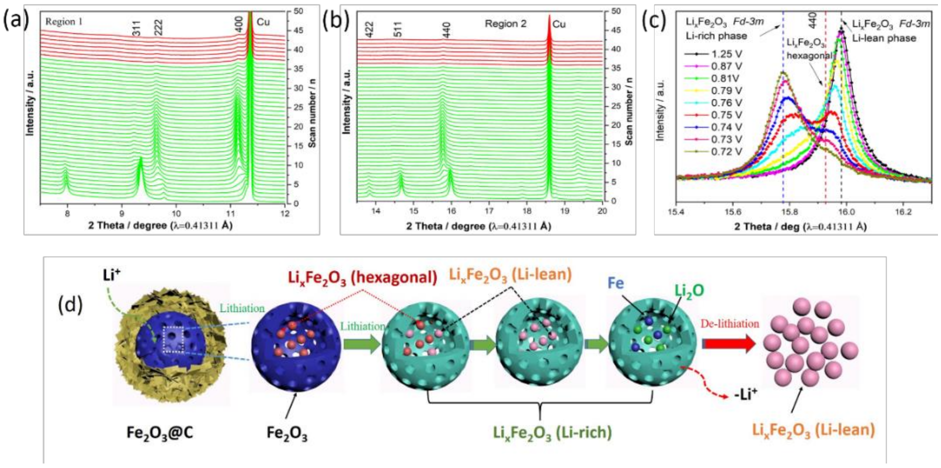

Fig. 1 In-situ XRD of Fe_2O_3@C during the initial lithiation (green lines) and de-lithiation (red lines) process.

Acknowledgments:

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Monitoring of the Evolution of the Patina Layer Formed on Weathering Steel Exposed for up 2 Years to the Atmosphere of São Paulo City

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Weathering steels (WS) have higher resistance to atmospheric corrosion than the others structural steels and with the best cost-benefit ratio. For this reason, it benefits an outstanding reputation in a wide range of architectural and structural applications. In order to develop a protective and beautiful patina, its use is recommended in urban atmospheres. To understand the mechanism of **protective rust formation** on WS, representative industrial samples (produced by Brazilian steelmaking companies according to the standard ASTM A242), were exposed at the urban atmosphere in São Paulo, Brazil, with quarterly data monitoring. In the present work, results referring to the growth of the surface patina formed on WS after 3, 12, 15, 18, 21 and 24 months of atmospheric exposure are reported. The electrochemical properties of the patina layer were investigated by means of open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and electric equivalent circuit (EEC) fitting. SEM, XRD and thicknesses evaluation were used to characterize the patinas. The thickness measurements of the patina layer indicate a high dependence on the exposure time and it tends to steady stage of corrosion after 1.6 months. Considering the first year of exposure, lepidocrocite (γ-FeOOH) and goethite (α-FeOOH) are still the main crystalline phases determined by XRD. OCP measurements show that the potential becomes nobler with exposure time, which is usually associated with improved protective properties of the patina layer [1]. EIS diagrams (Figure 1) showed that the impedance modulus increases with exposure time, pointing to progressive consolidation of the patina layer. Moreover, data interpretation pointed to a porous electrode behaviour, which was interpreted based on the model of de Levie [2].

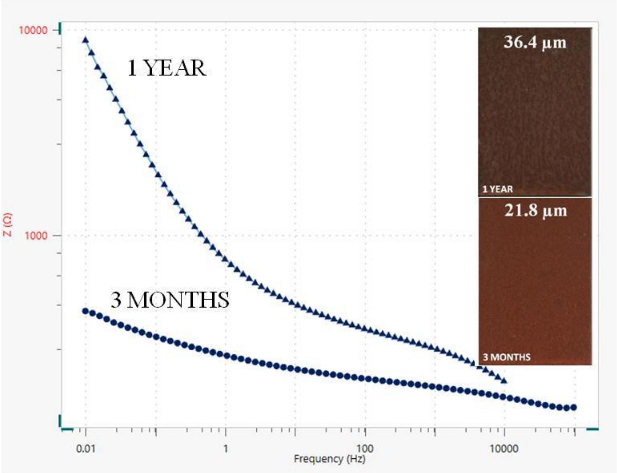

Figure 1 – EIS diagram for WS after 3 months and 1 year of atmospheric exposure

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Amorphous Electrolytic Deposits (Re–Ni, Co–Mo, Ni–Mo etc.) as Efficient Catalysts for Hydrogen Evolution Reaction in Alkaline Solutions: Structure and Electrocatalytic Properties

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Search for new non-platinum catalysts for hydrogen evolution reaction (HER) and elucidation of the mechanism of their catalytic activity are important for enhancement of the process of electrolytic hydrogen production. From this point of view, of interest are systems containing an iron-group metal (typically, Co or Ni) and a refractory metal (Re, Mo, or W). Electrodeposition is a simple and convenient method for preparation of these alloys.

It was previously found that X-ray amorphous deposits immediately after their electrodeposition possess the highest catalytic activity towards HER. Heat treatment of such materials in vacuum accompanied by their recrystallization results in a decrease in the catalytic activity of alloys. Therefore, data on the structure of electrolytic deposits and their chemical and phase composition are necessary for understanding the causes of catalytic activity.

Both XPS and EXAFS methods are applied for determining the composition and structure of Re–Ni, Co–Mo, and Ni–Mo electrolytic deposits. It is found that these materials are amorphous. The metals in Co–Mo and Ni–Mo systems are in a metallic state; however, Re–Ni deposits contain both metallic and oxidized rhenium.

The catalytic activity of electrolytic deposits generally decreases in the following row: Re–Ni ≥ Co–Mo > Ni–Mo, although their catalytic activity strongly depends on the refractory metal and iron-group metal percentages. The Tafel slope in voltammetric dependences of HER also depends on both the chemical composition and structure of the cathode material. It increases from *ca*. 80 mV dec^{-1} for Re–Ni cathodes to *ca*.120 mV dec^{-1} for Ni–Mo cathodes. The results of the investigations are discussed.

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The development of prototype lithium-sulfur battery for autonomous unmanned platforms

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Lithium-sulfur (Li-S) batteries are widely regarded as one of promising candidate for the next generation electrochemical energy storage devices, replacing commonly applied today Li-ion battery chemistries. Due to a large theoretical capacity of sulfur, this type of batteries is expected to provide significantly higher energy densities, approaching 2500 Wh/kg, as compared to the maximum of ca. 400 Wh/kg featured by conventional Li-ion batteries. This is particularly important in light of the emergence of novel demanding application such as electric vehicles, grid storage and energy consuming portable electronic devices.

While there is an increasing number of scientific publications on the Li-S technology, the number of studies on prototype cells is rather low. Commercialization of Li/S batteries still cannot be realized due to many problematic issues, such as poor electronic conductivity of sulfur, solubility of lithium polysulfides in organic electrolytes and the use of highly reactive metal lithium as anode.

In this project we are trying to implement our knowledge of lithium-sulfur batteries and develop prototype Li-S pouch cell. We will present key manufacturing aspects in the pouch cell preparation. Prototype lithium-sulfur pouch cell will be finally tested as energy source for autonomous unmanned platform.

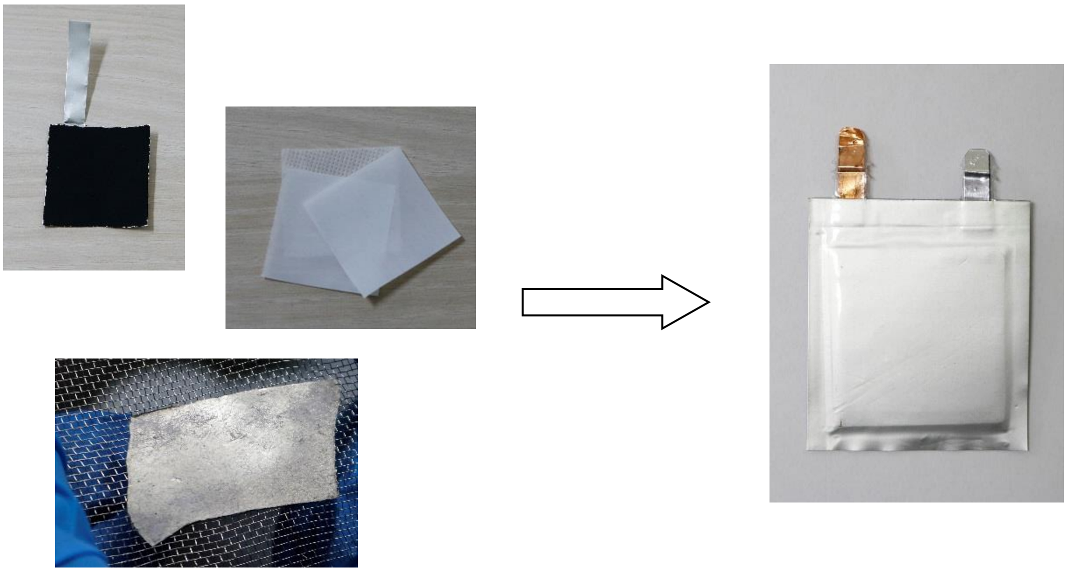

Fig. 1. Manufacturing of prototype Li-S pouch cell

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Nanocomposite Materials Comprising MnO_2 and Activated Expanded Graphite (AEG) as Electrodes for Electrochemical Capacitors

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Abstract

Nanocomposite material comprising MnO_2 and activated expanded graphite (MnO_2-AEG) was successfully synthesized via a simple two-step method. The as-synthesized material was characterized by using scanning electron microscope (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy, and N_2 physisorption to ascertain its morphological, structural and compositional and textural characterization. Electrochemical characterization of the composite was performed in both three- and two-electrode set-ups using three different aqueous electrolytes (1 M Na_2SO_4, 1 M Li_2SO_4, and 1 M K_2SO_4). The composite showed improved specific capacitance in comparison to some other similar materials in the literature. Notably, the fabricated symmetric supercapacitor (SC), MnO_2-AEG//MnO_2-AEG from the material and tested in 1 M Li_2SO_4, displayed an enhanced specific capacitance, high energy and power densities that favorably compare with those obtained for similar composite materials in the literature. The assembled SC showed an impressive stability over a long-term 100000-cycle cycling test, which enable the possible adoption of such MnO_2-AEG//MnO_2-AEG devices in high performance energy storage applications.

Optimizing Phthalocyanine Based Dye-Sensitized Solar Cells: the Role of Reduced Graphene Oxide

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Dye-sensitized solar cells (DSSC) were fabricated by incorporating graphene materials as catalysts at the counter electrode, Fig. 1. Platinum was also used as a catalyst for comparison purposes. Different phthalocyanines: hydroxyl indium tetracarboxyphenoxy phthalocyanine (**1**), chloro indium octacarboxy phthalocyanine (**2**) and dibenzoic acid silicon phthalocyanine (**3**) were used as dyes. Complex **3** gave the highest power conversion efficiency (η) of 3.19% when using nitrogen doped reduced graphene oxide nanosheets (NrGONS) as a catalyst at the counter electrode, and TiO_2 containing rGONS at the anode. The value is close to 3.8% obtained when using Pt catalyst instead of NrGONS at the cathode, thus confirming that NrGONS is a promising candidate to replace the more expensive Pt. The study also shows that placing rGONS on both the anode and cathode improves efficiency.

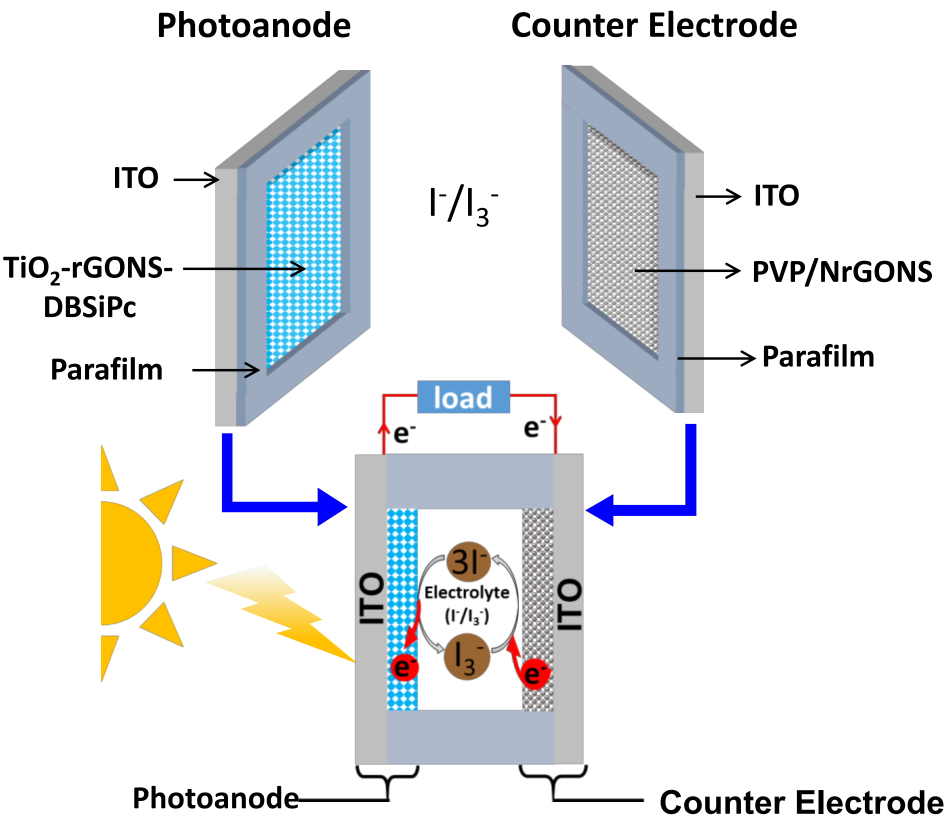

Figure 1: Schematic representation of dye-sensitized solar cell employed

Study of the Corrosion Resistance of a Magnesium Alloy Containing Rare Earth Elements for Orthopedic Implants

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Orthopedic surgeries are heavily dependent on the development and use of biocompatible implants for fracture fixation and joint replacement. In this field, biomaterials contribute to improving the health and well-being of humankind. Thus, there is a need to optimize and develop new materials to enhance the performance and function of implants, as well as to achieve the goal of tissue regeneration. In some types of injuries, the human body has the ability to regenerate and heal, exempting the use of permanent implants after recovery and avoiding the need of a second surgery to remove them. Therefore, a class of material that is in ascension is the biodegradable implants. These implants remain inside the body only during tissue regeneration, being naturally degraded over time. Magnesium alloys are promising biomaterials for application in non-permanent orthopedic implants due to their good biocompatibility, biodegradability and similar mechanical properties to those of human bone (e.g. Young's modulus, fracture toughness and bending resistance). Despite of many advantages, the main issue about the use of Mg alloys as biodegradable materials is the high corrosion rate, which leads to undesirable consequences, such as loss of mechanical integrity before total tissue restoration, hydrogen generation and pH change in the implant region. Therefore, the addition of rare earth elements to magnesium might improve its mechanical properties and mainly its corrosion resistance, leading to potential materials for biomedical applications. This work compared the corrosion resistance of a final forming Mg-4.8Y-2.8Gd-0.7Zr wt.% alloy aged at different times with a hot rolled pure Mg. Rectangular samples were cut, mechanically ground and properly cleaned. EIS measurements and potentiodynamic polarization curves were carried out in 0.9% NaCl solution at 37±0.5°C. The microstructure and morphology of the samples were characterized before and after electrochemical tests by LOM, SEM /EDS and XRD. By adding rare earth elements to Mg alloys, it is expected to achieve a promising material in terms of corrosion resistance for biomedical applications in the area of orthopedic implants.

Electrochemical and Surface Analysis Studies on Corrosion Inhibition of Mild Steel by Thiophenium-Based Ionic Liquids in Hydrochloric Acid Solution

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The thiophenium-based ionic liquids namely, 5-(Trifluoromethyl)dibenzothiophenium tetrafluoroborate (TDTB) and 5-(Trifluoromethyl)dibenzothiophenium trifluoromethanesulfonate (TDTM) were investigated as corrosion inhibitors for mild steel in 1.0 M HCl solution. The investigations were done by electrochemical techniques [potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS)] and SEM surface analysis. The results from both PDP and EIS studies (at 303 K) showed that the inhibition efficiency significantly increased with an increase in the concentration of the inhibitor. The PDP study revealed that both inhibitors are mixed-typed inhibitors. An impedance to electrochemical corrosion through the formation of a protective film was suggested by the increase in charge-transfer resistance (R_{ct}) and decrease in the double layer capacitance (C_{dl}) with an increase in inhibitor concentration. Results from the EIS and PDP measurements were further supported by SEM analysis which showed an improvement in the surface morphology of mild steel when the inhibitors were introduced to the HCl solution. The adsorption behaviour of the ionic liquids on mild steel obeyed the Langmuir adsorption isotherm. The ΔG°_{ads} values suggested that the adsorption was spontaneous and occurred through a physisorption mechanism. Both inhibitors showed similar inhibitive behaviour which suggests that inhibition was mainly due to the cation.

Keywords: Mild steel, HCl, thiophenium-based ionic liquids, PDP, EIS, adsorption, SEM

High-performance asymmetric supercapacitor based on vanadium dioxide/activated expanded graphite composite and carbon-vanadium oxynitride nanostructures

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Abstract

In this work, we report vanadium dioxide/activated expanded graphite (VO_2/AEG) composite and carbon-vanadium oxynitride (C-V_2NO) porous web-like structures. These materials were successfully synthesized by chemical vapor deposition (CVD) method. The X-ray diffraction analysis of the VO_2/AEG composite revealed the diffraction peaks of the monoclinic VO_2 and hexagonal AEG structures respectively while for the C-V_2NO material, a cubic crystal structure was observed. The Raman spectroscopy analysis of VO_2/AEG composite and C-V_2NO depicted vibration brands linked to vanadium dioxide with the distinct D, G, and D' peaks confirming the presence of disordered carbon into the main vanadium-based matrix.The electrochemical performance of the electrode material (VO_2/AEG//C-V_2NO) was evaluated in a two-electrode asymmetric device with the VO_2/AEG composite as the positive electrode and C-V_2NO as the negative electrode operating in a 6 M KOH electrolyte. The asymmetric device exhibited a specific energy of 41.6 Wh kg^{-1} with a corresponding specific power of 904 W kg^{-1} at a 1 A g^{-1} specific current in a large operating voltage of 1.8 V. The specific energy was still retained at 9 Wh kg^{-1} at an amplified specific current of 20 A g^{-1} with a specific power of 18 kW kg^{-1}. The supercapacitor showed a 93% capacity retention for up to 10,000 constant gravimetric current cyclic stability test at a specific current of 10 A g^{-1} with a good rate capability.

Cytochrome P450 biosensor for the detection of TB drugs in a cocktail format in synthetic urine and environmental waters

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Keywords: Tuberculosis, CYP2E1, rifampicin, pyrazinamide, ethambutol, isoniazid, nanoparticles

Abstract

Tuberculosis (TB) is a potentially serious infectious disease that mainly affects the lungs. Many strains of TB resist most of the drugs used to treat the disease. The main reason TB remains a major problem is the increase in drug-resistant strains of the bacterium. Studies have shown that some of the pharmaceuticals drugs administered during the treatment of human diseases such as TB may be excreted in unmetabolized forms. The poor disposal of human excreta containing drugs can contaminate both surface, rivers and underground water [1]. Since residual drugs are resistant to conventional water treatment strategies employed by sewage treatment plants, the presence of unmetabolized drugs in water can contribute to creating resistant bacteria. Therefore, there is need to develop cheap and readily available methods to detect these residual drugs at trace levels in water. We have demonstrated with the glassy carbon electrode polyamic (GCE/PAA) acid GCE/PAA silver nanoparticles (GCE/PAA/AgNPs) platforms that TB Mycobacterium 85B antigen (Ag85B) can immobilized on GCE/PAA and cytochrome P450-2E1 (CYP2E1) can also be immobilized on GCE/PAA/AgNPs to detect TB anti-Ag85B antibodies and ethambutol (ETH), respectively. The detection limit (LOD) of TB antibodies with GCE/PAA/Ag85B was 8 µg/mL (Fig. 1A). Meanwhile the LOD of ETH with GCE/PAA/AgNPs/CYP2E1 was 0.75 ng/mL (Fig. 1B). This platform will be improved and used to detect the other 3 TB drugs; rifampicin, isoniazid and pyrazinamide. These drugs will be detected individually and in a cocktail form to evaluate the selectivity and sensitivity of the biosensor.

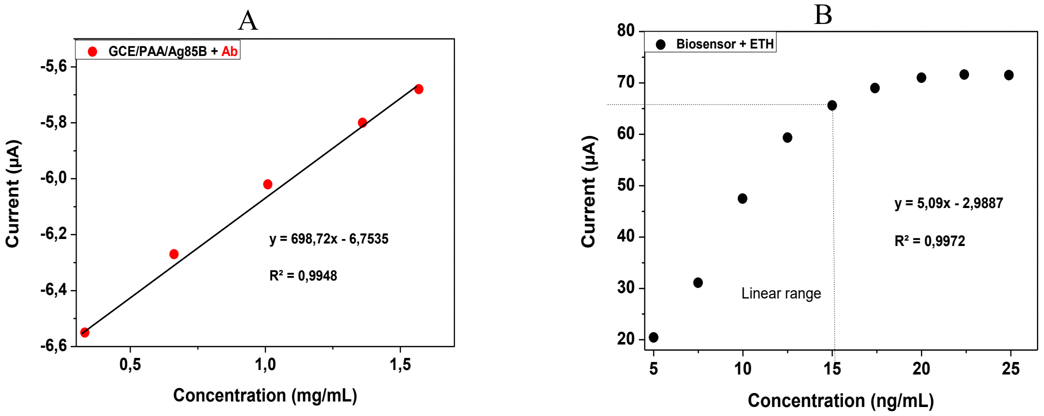

Figure 1: Calibration curve of Ag85B antibody at GCE/PAA/Ag85B sensor (A) and calibration curve of ETH at GCE/PAA/AgNPs/CYP2E1 biosensor (B)

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The Detrimental Impact of Sodium Metal Electrodes on Electrochemical Experiments

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In order to probe the electrochemical properties of sodium-ion-batteries (NIBs), sodium metal is frequently applied as reference and/or counter electrode in state-of-the-art literature [1-3]. However, the high reactivity of sodium and its impact on the electrochemical performance keeps neglected. We demonstrate that sodium spontaneously reacts with organic electrolytes and contaminates those. This can end up in wrong conclusions on the stability of active materials. We prove that the cycling stability is highly affected by these electrolyte contaminations by comparing sodium metal free with sodium metal containing cells. When replacing the Na metal counter and reference electrodes by activated carbon (AC) electrodes, the cycling performance of the $Li_4Ti_5O_{12}$ half-cells is massively improved. We attribute this difference to the impact of the electrolyte contaminations on the surface chemistry of the solid electrolyte interphase. Additionally, we propose the AC-half-cell setup as a suitable alternative for performing electrochemical experiments in NIBs.

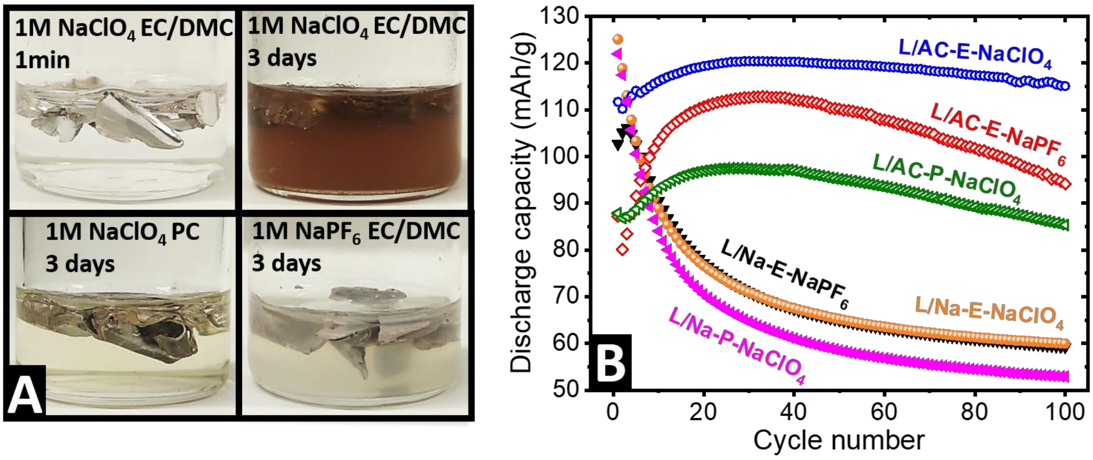

Fig. 1: (A) Na metal in 1M $NaClO_4$ in EC/DMC right after Na addition (representative for all electrolytes) and Na in different electrolytes after 3 days. (B) Comparison of the electrochemical stability of AC-half-cells and Na-half-cells

Acknowledgments:

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Effect of Prior Austenite Grain size (PAGS) on Passive Layer Properties of Fully Martensitic Steels

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In the past decades, great advances have been achieved in understanding the grain size - mechanical properties relation, but we are still seriously lacking knowledge of grain size - passivity relations that are needed to predict corrosion behaviour. This mainly stems from the fact that microstructural features, e.g. dislocation density, crystallographic orientation, inclusions, different phases, chemical composition, have a synergistic effect with grain size on passive layer properties. Hence, it is crucial to work with well-controlled model microstructures to understand the individual effect of grain size on passive layer properties. In this work, controlled fully martensitic steels were employed since martensitic steels are widely used in many applications including infrastructure, oil and gas production as a result of their beneficial mechanical properties. However, they exhibit poor passive layer properties. The effect of prior austenite grain size (PAGS) of martensitic steels on passive layer properties was investigated in 0.1 M NaOH solution. Designed fully martensitic steels with prior austenite grain size varying from 65 to 5 μm were produced with different heat treatments, applied through dilatometry. Microstructures with the same chemical composition and very similar dislocation density, as characterized by Electron backscatter diffraction (EBSD), were employed to avoid the synergistic effect of these features with PAGS on passive layer properties. Electrochemical measurements - potentiodynamic and potentiostatic polarization, electrochemical impedance spectroscopy (EIS) - showed that the overall electrochemical properties of passive films deteriorate with PAGS refinement until reaching a grain size of approximately 5.3 μm. Further refinement leads to an improvement of the passive layer properties. This behaviour can be explained with the trend in defect density and chemical composition of the passive layer obtained with Mott-Schottky analysis and X-ray photoelectron spectroscopy (XPS), respectively.

Gravimetric and adsorption studies of organic synthesized derivatives of carboxylic acids as corrosion inhibitors of zinc metal in acidic environment

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Keywords: N-phenylglycine, 2-phenoxyacetic acid, Inhibitors, Zinc, Weight loss, inhibition efficiency.

Metals such as zinc are used as raw materials in areas such as fabrication, electrical, electrochemical, structural etc [1]. Zinc is used particularly for coating metals such as steel and iron because it has several characteristics that make it appropriate for metallic coating and improves the resistance of iron and steel against corrosion [2]. However, under favourable/suitable conditions zinc can degrade by a process known as corrosion [3]. Several studies have shown that corrosion inhibitors that evidently carry minimal toxicity while exhibiting good inhibition efficiency are advantageous when it comes to the control of corrosion [4].

The present study focused on the derivatives of carboxylic acid namely, N-phenylglycine (NPG) and 2-phenoxyacetic acid (POA) which were successfully synthesized to be evaluated as corrosion inhibitors for zinc metal in acid medium.

The corrosion inhibitory effects of the compounds on zinc metal in 1.5 M HCl at 30-60°C were investigated using gravimetric analysis. The results obtained from the gravimetric analysis indicate that the addition of NPG and POA decreases markedly the corrosion rate of zinc and a linear relationship of weight loss and concentration, temperature and time in the uninhibited and inhibited 1.5 M HCl was observed. The trend of the weight loss was found to decrease and %IE to increase as the concentration of the inhibitors is increased and is almost similar for all the inhibitors utilized at all temperatures studied. The studied carboxylic acid derivatives attained the maximum inhibition efficiency at $12x10^{-3}$ M. between the two inhibitors, NPG attained the highest inhibition efficiency of 89.22% at the concentration of $12x10^{-3}$ M, this NPG served as a better inhibitor in comparison to POA for zinc metal. Thermodynamic and kinetic parameters such as ΔG^{o}_{ads}, E_a, ΔS^* and ΔH^* were calculated from the data collected and the values of E_a and ΔH^* suggested a mixed-type adsorption process observed in the Langmuir isotherm plots.

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Theoretical and Experimental Study of Adsorption and Photon-Driven Charge Transfer of 4-Mercaptopyridine on Silver and Gold Electrodes of Nanostructures

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Electrochemical Surface-enhanced Raman spectroscopy (EC-SERS) has high detection sensitivity at the molecular level. This is due to the surface plasmon resonance (SPR) from the collective oscillation of conductance electrons on silver and gold electrodes of nanostructures. The strong SPR effect can amply the Raman signal to a million fold compared with that of the same molecule in vacuum or aqueous solution. However, the Raman signal of EC-SERS also strongly depends on the contribution of the adsorption interaction and some low-lying excited electronic states when molecules adsorbed on nanoscale electrodes. In the case theoretical investigation plays very important role on understanding the relationship of surface adsorption configuration and electronic structures

The work explored the relationship of SERS signals to surface structures, binding interaction, and low-lying excited charge transfer states of p-mercaptopyridine (4MPY) adsorbed on silver electrodes. The probing molecule can form self-assembly monolayer, interfacial pH probe, and Raman chiral probe at interfaces. Our simulated Raman spectra were closely associated with specific adsorption configuration of 4MPY interacting with silver clusters in pure molecules, adsorption states solvated by water and protonated by hydronium ion, as well as double-end adsorption configurations. Figure 1A presents a modeling structure in double–end adsorption configuration. We considered the influence of the hydrogen bonding interaction on relative Raman intensity of 4MPY though its thiol group binding to silver clusters. Our finding shows that the protonation significantly change the position of specific SERS peaks, which can be used as an indicator to infer surface adsorption structures of 4MPY on metal electrodes. Our results also proposed that there are a double-end adsorption configuration of 4MPY on silver electrodes due to the low-lying charge transfer states. The charge transfer has a direction from the silver cluster binding to the nitrogen atom of pyridine ring to the pyridine moiety. This causes the significant enhancement of the specific-mode with vibrational Raman peak at 1215 cm^{-1}, as shown in Figure 1B.

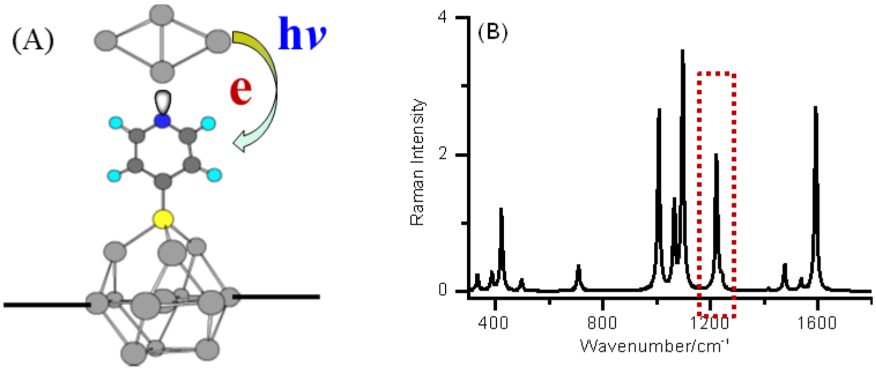

Figure 1 Theoretical models (A) and simulated Raman spectrum (B) of p-mercaptopyridine (4MPY) in a double-end adsorption configuration Ag_x-4MPY-Ag_4

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Nanozyme Integrated Paper Electrode Sensing Platform for DNA Oxidative Damage Assessment

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Exposure of toxicants such as PM2.5 causes oxidative stress, leading to generation of reactive oxygen species (ROS) that results in cellular and DNA damage. The oxidized guanine is excised from the DNA via glycosylase activity, released into the blood and excreted via the urine. Because 8-OHdG in urine is stable and the measurement is relatively easy, urinary 8-OHdG is commonly measured in the laboratory setting; elevated urinary 8-OHdG levels are associated with environmental toxicant exposure. Levels are also sensitive to occupational exposure and therapeutic drug dosing. Rapid monitoring of 8-OHdG following suspected exposure to dangerous agents is critical to identifying pre-symptomatic (not ill) states, high risk situations, and early stages of illness.

In this lecture, we will introduce a smart phone integrated paper based analytical device by combining a disposable glucose sensor and nanozyme modified sensing strips for real time monitoring urinary 8-OHdG biomarker. . Different to the traditional design of later flow strips, we integrated an on-strip enzymatic reaction by which the analyte can be converted to be glucose and therefore can be detectable by a conventional smartphone enabled glucose meter. Our approach yields results comparable to commercial diagnostic ELISA kits at a substantially reduced cost and reaction time. Therefore, the smartphone-enabled blood glucose meter can be used as a novel point-of-care (POC) device for quantitative detection of non-glucose biomarkers.

The technology will especially benefit the people who are working daily at areas with high risk of toxicant exposure and do not have easy access to the clinical laboratory. This technology can provide gap filling measures for the evaluation of toxic exposures and their long term effects on public health.

Resolution of mixtures of vitamins by electrochemical Surface-enhanced Raman spectroelectrochemistry (EC-SERS).

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Detection of single molecules and traces by Raman spectroscopy is an overwhelming subject that has received growing attention from the scientific community in a wide variety of fields, such as chemistry, biology, petrochemistry, food industry, pharmaceutical applications, etc. [1-3]. Development of new procedures based on the combination of electrochemistry and Surface-Enhanced Raman Scattering (SERS) effect has allowed the improvement of Raman spectroelectrochemical features. Enhancement of the Raman signal displayed by Electrochemical Surface-Enhanced Raman Scattering (EC-SERS) is associated with the interaction of the species with the electrode surface as well as with the in-situ generation of fresh nanostructures with SERS properties.

In this work, EC-SERS response for the resolution of mixtures of different vitamins using metallic screen-printed electrodes (SPEs) is evaluated. Gold and silver SPEs display very interesting results not only for the detection of vitamins, but also for discriminating the presence of each vitamin in mix samples. Vitamin B1 (thiamine), B2 (riboflavin), B3 (nicotinamide) and B6 (pyridoxine) were selected to demonstrate the great features of EC-SERS in this field. Furthermore, changes of the Raman intensity shows that EC-SERS effect is concentration-dependent (Figure 1a) [4] and the enhancement of Raman signal depends on each vitamin (Figure 1b).

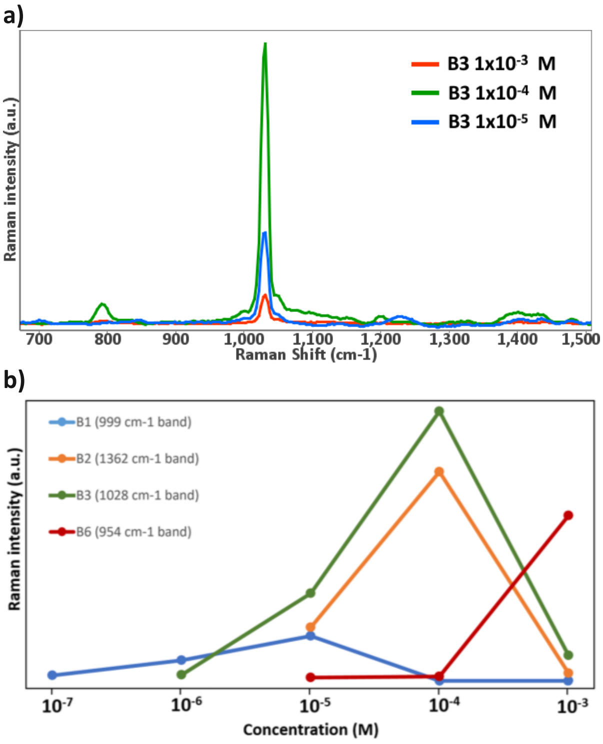

Figure 1. (a) Raman spectra of vitamin B3 obtained with different concentrations. (b) Variation of Raman intensity of vitamins B1, B2, B3 and B6 with concentration.

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New alternatives to overcome the water limitation in NIR spectroelectrochemistry.

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NIR spectroscopy has been traditionally limited due to the water absorption in this spectral range. In this way, the well-known water restriction has limited the development of new applications for NIR spectroelectrochemistry because the high absorption of water produces that NIR bands cannot be distinguished in consequence of enough light does not arrive to the detector. Although organic solvents are an alternative to the aqueous solutions, the volatility of some of these solvents does not ensure the good reproducibility of the electrochemical response and new procedures should be developed.

In this work, two interesting alternatives are proposed in order to minimize or even to remove the aqueous contribution in this spectral range. The first one consists of using screen-printed electrodes with one thin channel that allows us to minimize the absorption of water. As can be noticed in Figure 1a, this configuration displays NIR spectra only slightly limited at 1450 nm and a bit more at 1950 nm, the wavelengths at which water shows the highest absorption. Furthermore, another outstanding strategy is based on using ionic liquids (ILs). ILs are salts widely used in electrochemistry due to their excellent properties such as wide electrochemical potential window, good ionic conductivity and high thermal stability [1-3] and are considered as one of the most competitive alternatives to volatile organic compounds. Hence, these environmentally friendly solvents allow us to overcome the aqueous restriction at NIR spectroscopy, and as can be observed in Figure 1b, they display NIR spectra not limited to the water absorption.

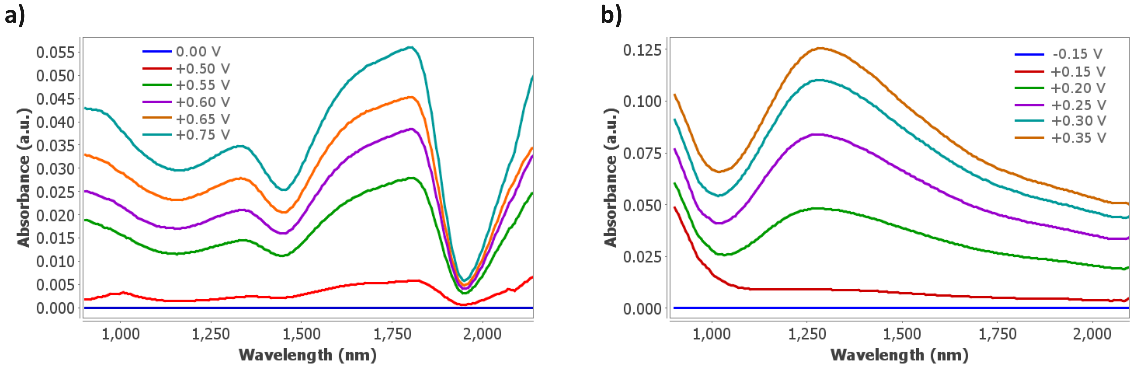

Figure 1. NIR spectra obtained during a linear sweep voltammetry using (a) screen-printed electrodes with one thin channel in aqueous solution and (b) screen-printed electrodes in ionic liquid.

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Testing Protocol for Reversal Tolerant Anodes under Cell Reversal by Simulated Fuel Starvation

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Due to the rapidly depleting global fossil fuel reserves and the drive towards sustainable and ethically conscious power solutions, the need for sustainable energy generation and alternative energy conversion technologies has increased significantly over the last several decades. Hydrogen is a promising energy storage medium and fuel due its high energy density by weight. This points towards the need for alternative energy conversion technologies capable of utilizing hydrogen as a fuel. One such technology is the polymer electrolyte membrane fuel cell (PEMFC). PEMFCs generate electricity through the electrochemical oxidation and reduction of hydrogen and oxygen respectively, over a platinum electrocatalyst producing water as a by-product. PEMFCs are particularly promising for portable and transport applications due to their high power density, high efficiency, low operating temperatures, rapid start-up times, and good power-to-weight ratios (Liang et al., 2009; Zhang et al., 2018).

Reliability and lifespan are key factors currently preventing the large-scale commercialization of PEMFCs. One crucial degradation issue is cell reversal under fuel starvation. Fuel starvation refers to the undersupply of fuel to the PEMFC and can occur during start-up and shutdown, sub-zero operation, or rapid load changes (Liang et al., 2009). Fuel starvation can lead to the undesirable reversal of the overall cell potential. Under cell reversal, the carbon support material of the platinum electrocatalyst experiences high rates of corrosion causing irreversible damage to the fuel cell within seconds or minutes. Carbon corrosion results in a decrease in electrocatalyst surface area and activity causing a loss of overall fuel cell performance. It is thus crucial to be able to effectively simulate cell reversal under fuel starvation and characterise the effects thereof, in order to effectively evaluate cell reversal mitigation strategies such as reversal tolerant anodes which utilize alternative electrocatalysts and electrocatalyst support materials.

This study was aimed at developing an in-house testing protocol to reproducibly simulate cell reversal under fuel starvation for in-situ single cell membrane electrode assembly (MEA) testing, as well as setting up a suite of in-situ and ex-situ characterization procedures. A protocol was developed consisting of cyclic fuel starvation by N_2 dosing, with an intermittent H_2 recovery period. The period of the overall accelerated stress test, and the period of N_2 dosing were experimentally determined based on the dynamic response of the fuel cell under complete fuel starvation. In-situ characterization consisted of potential profiles to monitor the dynamic response of the fuel cell to fuel starvation, electrochemical impedance spectroscopy (EIS) to quantify changes in ohmic and charge transfer resistance, and polarization curves to analyze overall performance. On-line mass spectroscopy was successfully incorporated into the fuel cell test station hardware to analyze CO_2 evolution resulting from carbon corrosion. Ex-situ characterization consisted of scanning electron microscopy (SEM) imaging of cross-section samples prepared from MEAs which had undergone cell reversal degradation testing in order to quantify the changes in catalyst layer thickness and structure. Both in-situ and ex-situ characterization produced results which indicated a high level of reproducibility of the developed protocol. Results using the developed protocol were consistent across 3 independent single cell tests in terms of: 1) the dynamic potential response of the cell to fuel starvation, 2) changes in ohmic and charge transfer resistance determined through EIS, 3) overall performance based on polarization curves, 4) CO_2 evolution profiles determined through on-line MS, and 5) reduction in anode catalyst layer thickness.

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Effect of Carbonization Time on Compactivated Samples from Plant Biomass Waste for Electrochemical Device Electrodes

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The formation mechanism of the porous framework in nanostructured carbon materials is important in a wide variety of applications such as in supercapacitors, gas storage, adsorbents and catalyst supports. The accessibility to the pore sites by electrolyte ions and gases are highly determined by the precise synthesis techniques adopted for these materials. As such, biomass waste materials are a good choice for synthesis as they are available in abundance and cheap, while containing high carbon content and giving high specific surface area for electrochemical supercapacitor applications.

In this study, activated carbon (AC) was synthesized from renewable plant biomass waste using a chemical vapour deposition (CVD) technique via a pre-hydrothermal conversion step and compactivation along with the fine-tuning of key growth parameters, including activation time.

The textural, structural and morphological features were investigated by the Brunauer-Emmett-Teller (BET) technique, X-ray diffraction (XRD), and Scanning/Transmission electron microscopy (SEM/TEM) characterization. The material tested in a three-electrode configuration exhibited electric double-layer capacitor (EDLC) behaviour and working comfortably in KNO_3 aqueous electrolyte in both negative and positive operating widow of 0.80 V. The material also exhibited higher gravimetric energy of over 40 Wh.kg^{-1} and gravimetric power of 700W.kg^{-1} at 0.5 A.g^{-1} gravimetric current in ionic liquid electrolyte. The results from this study provide the pathway into designing hierarchically porous materials from cheap and sustainable sources suitable in high power and energy storage devices.

Electrochemical detection of serotonin in food at green mediated PPy/Fe$_3$O4NPs nanocomposites modified electrodes

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Serotonin one of the major neurotransmitters found in central nervous system (CNS), gastrointestinal tracts of the digestive system, blood, platelets has a great impact in the general well- being of humans as it plays a key role in in healing of wounds, sleep, appetite, sexuality and mood[1.] When inadequate it could result to eating disorders, depression and fibromyalgia[1]. Level of serotonin in the body can be boosted by exercise, high water intake and eating tryptophan containing food such as bananas[2]. Earliest methods used in detection of serotonin in human, aquatic and plants samples are chromatographic methods which are time demanding and labour intensive especially when derivitization of analytes of interest is needed[3]. There are current reports on the use of electrochemical sensor in detection of serotonin since electrochemical sensors are reliable, fast, cost effective, and highly sensitive with simple instrumentation[1,4].

A novel comparative study on the electrochemical detection of serotonin (SE) using polypyrrole (PPy) doped with iron (III) oxide nanoparticles synthesized from leaves (Fe$_3$O$_4$NpL) and flowers (Fe$_3$O$_4$NPsF) extracts of callistemon viminalis at modified electrode is reported. The working electrode used for the detection of serotonin was glassy carbon electrode (GCE). Modified electrodes displayed good electrocatalytic activities in detecting 5-HT. Cyclic voltammetry (CV) was used in detecting serotonin at electrode modified with PPy/Fe$_3$O$_4$NPsL and PPy/Fe$_3$O$_4$NPsF with peaks observed at 0.3664 V (16.689μA) and 0.35874 V (37.736μA) respectively. Square wave voltammetry (SWV) was used in concentration study of serotonin detection at electrode modified with PPy/Fe$_3$O$_4$NPsL and PPy/Fe$_3$O$_4$NPsF given limit of detection values of 8.6900 μM and 3.4436 μM (S/N =3) and limit of quantification LoQ values of 28.966 μM and 11.478 μM for PPy/Fe$_3$O$_4$NPsL and PPy/Fe$_3$O$_4$NPsF respectively. Both modified PPy/Fe$_3$O$_4$NPsL and PPy/Fe$_3$O$_4$NPsF electrodes gave better regression values at 0.99547 and 0.96226 respectively. Simultaneous detection of ascorbic acid (AA) and serotonin (SE) at the modified electrode was achieved by using differential pulse voltammetry (DPV). GCE/PPy/Fe$_3$O$_4$NPsF exhibited an excellent selectivity towards AA and SE with peaks 0.0583 V (2.8052 μA) and 0.3721 V (2.0638 μA) respectively than GCE/PPy/Fe$_3$O$_4$NPsL which showed only the SE peak at 0.4451 V (3.6881 μA). The proposed electrodes were applied in the detection of SE in selected food.

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Synthesis and Characterizations of GO/Mn_3O_4 Nanocomposite Film Electrode Materials for Supercapacitor Applications

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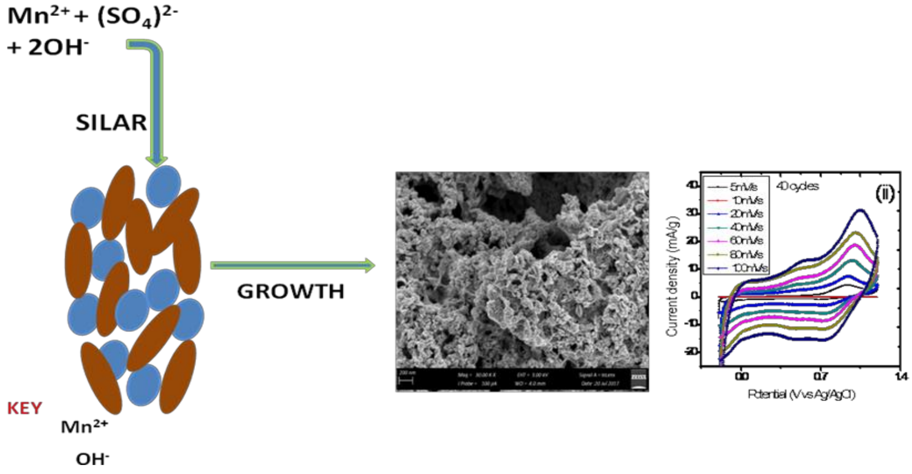
Abstract

We have, in this study, used simple, inexpensiveand environmentally-friendly successive ionic layer adsorption and reactions (SILAR) deposition procedure to successfully grow GO/Mn_3O_4 thin film electrode materials.The deposited films were examined for their surfacemorphology using scanning electron microscopy (SEM). X-Ray diffraction (XRD) was used to study their structural properties while their supercapcitive studies were done usingcyclic voltammetery (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) techniques.All deposited films were scanned in 1 M solution of Na_2SO_4 electrolyte.The SEM imagesof the deposited films revealed highly porous interconnected morphology with Mn_3O_4densely dispersed among GO. Individual peaks of Mn_3O_4 and GO compoundsindicatinguniform spread of Mn_3O_4 inside the porous matrix of GO were observed from the XRD. The film deposited at 40 cycles yielded themaximum specific capacitance of 532.54Fg^{-1}at 5mVs^{-1}scan rate. The results of the electrochemical studies show that the GO/Mn_3O_4 composite filmssynthesized by SILAR could be very suitably used as a promising materials for pseudocapacitors.



Studies on the Effects of Methylammonium Lead Iodide on Nickel Oxide as A Hole Transport Material For Perovskite Solar Cells

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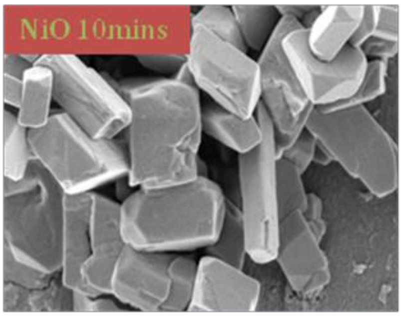
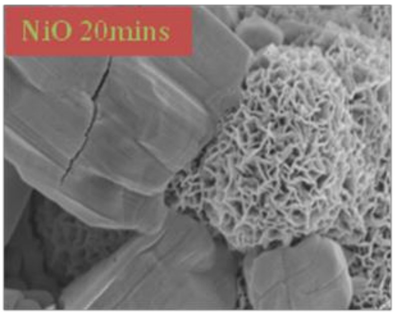
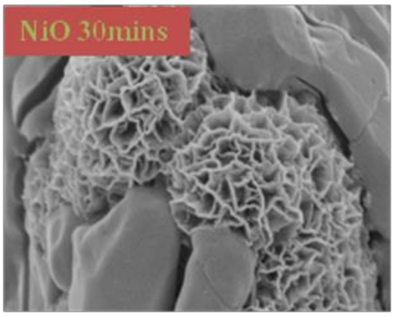
Abstract

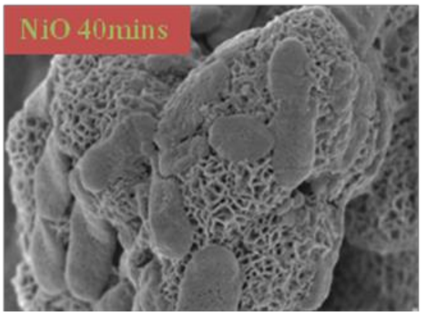
The continuously improving efficiency of perovskite device has attracted great research interest in this trending solar cell generation. Several research studies have been conducted on this device with different hole and electron transport materials incorporated in a bid to obtaining highly efficient perovskite devices. Nickel oxide is one of the few hole transport materials that have been shown high stability and efficiency in recent years. A simple chemical bath deposition method was employed in depositing nickel oxide films at different deposition times and afterward spin coated on by an already synthesized perovskite solar cell in an inverted planar architecture. The XRD results reveal an amorphous and a crystalline nature respectively for nickel oxide films without and with perovskite spin coated on the surface. SEM results show nested and large compact clusters of oval-shaped grains while the EDX analysis confirmed the elemental composition of nickel and oxygen in the deposited films. The optical results show good optical properties with a bandgap energy ranging from 3.21eV to 3.30eV while the electrochemical studies revealed maximum specific capacitance of the films at 2000Fg^{-1}. The stability of the perovskite device on inclusion of nickel oxide as a hole transport material makes it a good material in the production of highly efficient perovskite devices.

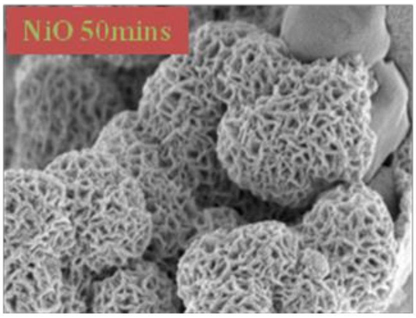
Keywords: perovskite, nickel oxide, chemical bath deposition, bandgap energy, electrochemical studies, specific capacitance.











Electrochemical Stability research on chain ether-based electrolyte with LiTFSI salt

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The electrochemical stability of the [Li(Triglyme)]$^+$[TFSI]$^-$ electrolyte is characterized and the experimental results strongly suggests the tendency of the [Li(Triglyme)]$^+$[TFSI]$^-$ electrolyte, which is an independent type of the current collector, to oxidize and decompose under an operating voltage over 3.8 V. Moreover, polyethylene oxide (PEO) with of similar chain ether structure with triglyme was further investigated, and it is confirmed that PEO-based polymer electrolyte is limited under 3.8 V as well, so we believe that chain ether-based electrolyte is difficult to use under high voltage conditions over 3.8 V without appropriate modifications.

Experimental methods. The [Li(Triglyme)]$^+$[TFSI]$^-$ (LiG3) electrolyte was prepared by dissolving a stoichiometric amount of LiTFSI into anhydrous triglyme with stirring for 10h. Triglyme was dried in vacuum at 60°C before use. The PEO-LiTFSI polymer electrolyte film was prepared by solution casting method. PEO and LiTFSI (EO: Li = 18: 1, molar ratio) were mixed into anhydrous acetonitrile solvent and stirred for 12 h, and the obtained homogeneous solution was casted in a Teflon disk and then naturally volatilized for 24 h to remove the majority of volatile solvent, following with a vacuum drying for 12 h at 60℃ to evaporate the residual solvent.

Results. LSV measurements were characterized with Li/LiG3/Al and Li/LiG3/carbon cloth cells, and the results were presented in Fig. 1a and 1b. Independent of aluminum current collector or carbon cloth current collector, both of them exhibit oxidation tendency lower than 4.0 V, specifically, oxidation potential (vs. Li$^+$/Li) of cell with aluminum current collector occurs at 3.9 V, cell with carbon cloth current collector exhibits an obvious oxidation peak at 3.9 V. And it is observed that the oxidation degree of LiG3-C is fiercer than that of LiG3-Al, which may be due to the larger specific surface area of carbon cloth. More important, the results indicate that the ESW of LiG3 electrolyte is around 3.8 V and the oxidation reaction has no connection with aluminum or carbon cloth. Considering the similar structure of LiG3 with PEO-LiTFSI polymer electrolyte, the oxidation characterization was performed as well, as showed in Fig. 1c and 1d. Due to the increase of molecular weight, the oxidation degree of PEO-LiTFSI polymer electrolyte was greatly decreased. However, As Fig. 1 presents, the oxidation potential of PEO-C and PEO-Al are similar to that of LiG3-C and LiG3-Al, respectively. The oxidation degree of PEO-C is lower than that of PEO-Al, carbon coated aluminum foil was used here, so the specific surface area of aluminum and carbon coated aluminum is analogous. The results suggest that the oxidation reaction occurs not only in liquid chain ether-based electrolyte, but also in solid-state chain ether-based polymer electrolyte.

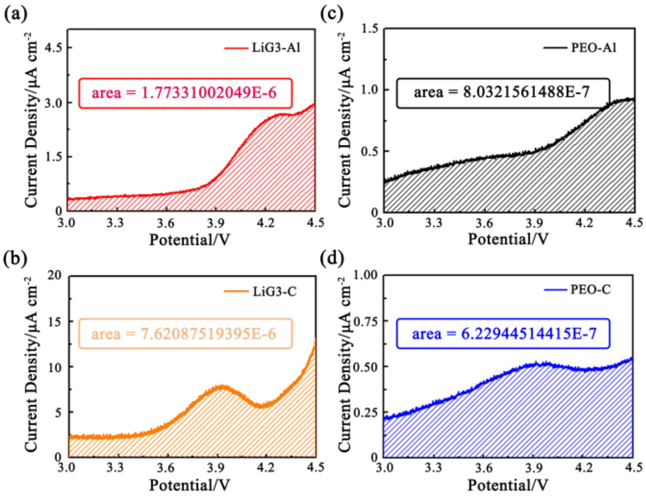

Figure 1 Linear sweep voltammetry (LSV) test of LiG3 and PEO-polymer electrolyte with Aluminum and carbon current collector at 0.1 mV/s. (a) LiG3-Al, (b) LiG3-C; (c) PEO-Al and (d) PEO-C.

Conclusions. [Li(Triglyme)]$^+$[TFSI]$^-$ electrolyte of similar structure to PEO-LiTFSI polymer electrolyte was examined and the ESW of chain ether-based electrolyte was confirmed to be 3.8 V, which is an independent type of the current collector. The oxidation degree of PEO-LiTFSI polymer electrolyte was characterized much lower than that of [Li(Triglyme)]+[TFSI]- electrolyte, but the oxidize and decompose indeed exist.

Evaluation of Highly Active PtGa Nanoparticles, Synthesized via the Galvanic Replacement of Liquid Metal Galinstan with Platinum

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When considering the human quest for an improved standard of living, fossil fuel consumption has tremendously intensified and adversely depleted beyond the rate at which they are renewed within the earth crust. Besides, the combustion of fossil fuels has been directly implicated in the imbalance of the carbon cycle (anthropogenic CO_2 emission) leading to global warming and environmental degradation. Hence, urgent attention is required to address the aforementioned challenges, such that a greener, sustainable, renewable, highly efficient energy conversion and storage system could serve as an alternative to fossil fuels. Renewable energy technologies which utilize energy sources such as solar, and biofuel (for example, bio-ethanol produced sustainably) are considered as a suitable alternative [1]. Advanced Oxidation Processes (AOPs) including electrocatalysis and photoelectrocatalysis are currently topics of significant interest for fuel generation and energy conversion. To implement these technologies, many nanocatalysts have been engineered and evaluated. Precious metal (Platinum, Pt) based catalysts have been intensively investigated for alcohol oxidation reactions related to direct methanol and ethanol fuel cells, and they have shown excellent performance, nonetheless, Pt exhibits low resistance to carbon monoxide, leading to catalyst poisoning and degradation in performance. Furthermore, Pt is expensive and sparsely distributed in the earth crust. Incorporation of low-cost metals such as liquid metal galinstan could improve Pt utilisation and decrease cost. The catalytic activity of multi-metallic electrocatalysts are largely influenced by size, morphology, stabilizing agents, proportions of active sites and therefore exhibit different electronic structures, crystallinity as a result of the interplay of geometric, ligand and electronic effects [2]. The catalytic activity of liquid metal-based composites is in its infancy but may be an opportunity to create new materials that are active for specific types of reactions. Therefore, engineering and surface modification of galinstan with platinum could provide synergy between Ga and Pt, and be a way to create a nanostructured PtGa catalyst. Till date, few reports are available on alloying liquid metal galinstan and other precious metals. To the best of our knowledge, no such investigation has been carried out on galvanic replacement reaction of galinstan with Pt at room temperature. Herein, we report the synthesis of PtGa nanoparticles (NPs), based on the galvanic replacement reaction of the liquid metal galinstan, such that gallium is surrounded by PtGa NPs. The as-prepared PtGa NPs were characterized using scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy and transmission electron microscopy for a physiochemical characterization. TEM result suggests that the alloy is polydisperse with particle sizes ranging between 1.0 and 60.0 nm, while the HRTEM shows that the NPs are crystalline. Furthermore, oxidation of methanol and ethanol were carried out, where the electro-oxidation experiments showed that the PtGa NPs have a higher activity for methanol than ethanol in alkaline media. This indicates a promising application of PtGa NPs in alkaline direct methanol fuel cells.

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Degradation analysis of SOFC performance (6)

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In the R&D for improving reliability of SOFC, Central Research Institute of Electric Power Industry (CRIEPI) has operated several types of Solid Oxide Fuel Cells (SOFCs). New basic R&D has been initiated in the NEDO's projects, "development of system and elemental technology on SOFC" (FY2008-FY2012) and "Technology development of SOFC commercialization promotion, Basic study on rapid evaluation method of SOFC durability (FY2013-FY2019)". In these studies, we operated several types of SOFCs and stacks, which are developed by MHPS, Kyocera, TOTO, NTK, NGK, Murata and DENSO, in order to understand their performance under the various conditions (temperature, current density and gas conditions) and the behavior during long term operations.

For instance, flattened tubular type SOFC stacks fabricated by Kyocera were operated. CRIEPI has been developing an electrode polarization model for SOFC performance which is able to express SOFC performance under various conditions with high accuracy. SOFC durability has been analyzed by the developed electrode polarization model. Voltage drops by performance factors such as Nernst loss, ohmic potential drop and polarizations of the anode and cathode, were determined by electrode model which is derived by using electrochemical consideration. Other types of SOFCs have been operated for long time. Same performance factor analysis was performed for obtained data.

Long-term durability tests lasting from 5,000 to 30,000 h and performance factor analyses of seven types of SOFCs were performed by applying performance factor analysis. As a result, the dependency of the electrode polarization on the gas partial pressure was determined and the voltage decay rates for all of the performance factors of each SOFC were revealed.

Acknowledgement

This work has been carried out under a contract research with the SOFC developing project of the New Energy and Industrial Technology Development Organization (NEDO), Japan. We would like to express our gratitude to NEDO, MHPS, Kyocera, TOTO, NTK, NGK, Murata and DENSO, as well as to the National Institute of Advanced Industrial Science and Technology (AIST).

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Graphene Loaded Iron Oxide nanoparticles as a new tool for electrochemical and naked-eye detection of global DNA methylation

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DNA methylation is a significant epigenetic mechanism that plays an important role in various biological processes, such as DNA repair, gene transcription, and embryogenesis [1]. DNA methylation naturally occurs within the CpG dinucleotides at the fifth carbon of cytosine base and aberrances in the methylation pattern can result in genomic instabilities, leading to the development of various human diseases including cancer. DNA methylation is considered as one of the promising epigenetic biomarkers and recent studies show that abnormalities in DNA methylation patterns present a signature for disease diagnosis, prognosis of outcome and therapeutic interventions. Therefore, the development of detection techniques that are rapid, sensitive and specific are of great importance for the detection and quantification of DNA methylation. Bisulphite treatment (BT) based methods are regarded as the gold standard for DNA methylation assay, but they have several drawbacks which include longer processing time, DNA degradation etc. Apart from these limitations, BT enriches the analyte DNA thymine which consequently complicates the design of specific probes for PCR amplification [2].

Recently, we synthesised a new class of metal-loaded, highly porous, superparamagnetic nanoparticles and have used these particles as (*i*) dispersible capture agents [3], (*ii*) electrocatalysts [4], and (*iii*) nanozymes [5] (they possess peroxidase-like activity) for the detection of circulating biomarkers [6] [e.g., cell-free DNA, tumour DNA, microRNA, autoantibodies, exosomes, tumour cells, etc.] in body fluids. Herein, we report a rapid and sensitive bisulphite treatment free global DNA methylation assay using electrochemical and colorimetric methods. Graphene loaded iron oxide nanoparticles (GO-Fe_2O_3 NPs) are modified with the gene-specific 5-methylcytosine (5-mC) antibody for the capture of the methyl group containing single-stranded DNA (ssDNA). The surface bound GO-Fe_2O_3 shows an intrinsic peroxidase mimetic performance in the presence of TMB and H_2O_2 substrate solution. The variation in methylation level was reflected with the colour intensity produced by the TMB oxidation reduction reaction due to the presence of GO-Fe_2O_3. Amperometric transduction at the screen-printed gold electrodes (SPGE) was carried out after stopping the oxidation reduction of TMB using 2.0 M of HCl (stop solution). Naked eye detection (qualitative) enabled detection of methylation levels as low as 10%, whereas electrochemical response showed a LOD 5% of methylation level in the target DNA. This assay shows an excellent reproducibility for three subsequent readouts for both colorimetric and electrochemical analysis. Use of a portable potentiostat, disposable screen-printed gold electrodes and mesoporous NPs in this assay gave the freedom to develop a low cost miniaturised platform for DNA methylation detection. Ultimately, this assay has successfully been applied in the analysis of two ovarian cancer cell lines along with one non-cancerous cell line.

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Studying the interaction of NPs at the electrode surface by bipolar electrochemistry

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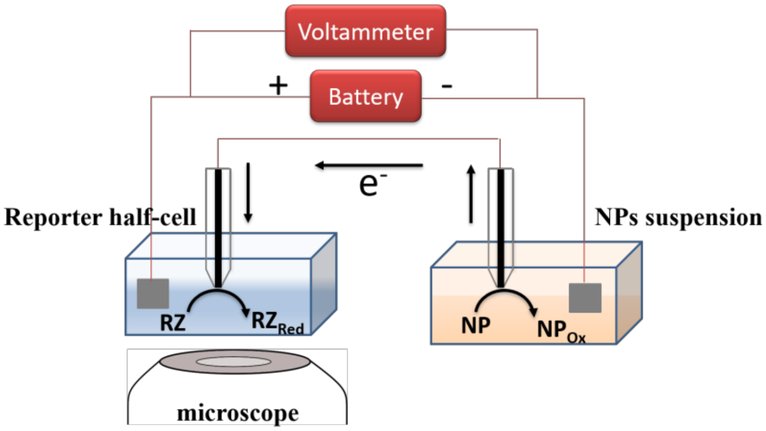
In the last decades, the precise characterisation of single nanoparticles (NPs) has become a requirement because of their application in numerous fields and applications. Although the characterization of NPs has progressed greatly, the accurate inspection is still challenging. Even for narrow NP size distributions, subtle effects may substantially alter the reactivity of individual NPs. Therefore, results obtained from bulk measurements allow only limited conclusion for individual NP. For this reason, a several tools were established to study the reactivity of single NPs at the electrode surfaces, either by immobilizing NPs at the substrate or by single NP collision experiments. When the transmitted charge is caused exclusively by single NP transformation as observed during NP collision events, electrochemical methods suffer from the limited signal-to-noise ratio(SNR) [1]. Bipolar electrochemistry may be a reasonable method to study the events of single NPs at the electrode surface. Guerrette et al. [2] studied the electrochemical coupling of a fluorogenic reduction reaction and conventional oxidation reactions such as the oxidation of dopamine on closed bipolar microelectrodes. The electrochemical current caused by electron transfer at spatially separated reduction and oxidation sites was correlated to the derivative of fluorescence intensity. Using this idea, we studied the electron transfer kinetics of NPs at the electrode surface via the reduction reaction of a suitable organic dye on the other side of a bipolar microelectrode arrangement. At sufficient potential difference between both feeder electrodes, the oxidation and reduction reaction occurs simultaneously. For a proof of concept and for calibration of current measurements via fluorescence detection, the oxidation of a compound with precisely known electrochemical properties like ferrocenemethanol was coupled to the reduction of resazurin as fluorogenic reporter molecule. With this information, the charge which is transferred from NPs was determined. In a more advanced setup, single molecule spectroscopy is coupled with bipolar electrochemistry for obtaining a higher sensitivity in fluorescence detection. In this method, one pole of the bipolar electrode is adjusted 1 μm above the center of the confocal volume and the other pole is immersed in the NP suspension. Depending on the interaction between NPs and the electrode surface, the luminescence intensity in the confocal volume will changed, which was followed by fluorescence correlation spectroscopy and emission decay measurements.



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A PEO/LLZO Solid Composite Electrolyte for Solid State Lithium Ion Battery

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The PEO/LLZO solid composite electrolyte with high ionic conductivity and low interfacial resistance was prepared by solution casting method. The electrochemical properties such as lithium ion conductivity, lithium ion transference number, electrochemical stability and compatability with lithium metal anode of PEO/LLZO solid composite electrolyte were investigated. The results showed that the addition of LLZO could effectively improve the ionic conductivity, electrochemical stability window, transference number, and compatibility with lithium metal of composite electrolytes. The LLZO 45% content of the PEO/LLZO solid composite electrolyte showed the lowest activation energy and the electrochemical stability at 4.75V (vs Li/Li^+). In addition, when the thickness of the PEO/LLZO solid composite electrolyte was 130 μm or more, The behavior of Li^+ plating/stripping on lithium symmetric cell was greatly enhanced. The NCM622/Li solid-state lithium ion battery assembled with the PEO/LLZO solid composite electrolytes had good cycling performance. At current rate of 0.5C, the discharge specific capacity remained about 148mAh/g after 100cycles at 60℃.

Hybrid Electrochemical Supercapacitor Based on Birnessite-type MnO_2 as the Cathode and Carbonized Iron-Polyaniline/Nickel Graphene Foam as an Anode

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ABSTRACT

In this work, a hybrid electrochemical supercapacitor based on birnessite-type MnO_2 hierachical nanostructures as the cathode and carbonized iron-polyaniline/nickel graphene foam as an anode was demonstrated to have an enhanced capacitive performance and the long-cycling stability. The electrochemical characterization was carried out in both three and two-electrode cell configurations using 2.25 M KNO_3 electrolyte. The as-fabricated asymmetric device exhibited a maximum energy density of 34.6 W h kg^{-1} and high power density of 1100.0 W kg^{-1}, at a specific current of 1.0 A g^{-1} and maximum cell potential of 2.2 V. The device further displayed long-term cycling stability with capacitance retention of 98% over 10 000 galvanostatic charge-discharge cycles at 10 A g^{-1}. The stability of the device was also tested using voltage holding at a maximum operating potential of 2.2 V over 80 h, and displayed excellent stability.

Cathodic Electron Transfer of *Shewanella* Strains Revealed by Electrochemical Technologies

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Extracellular electron transfer (EET) in metal-reducing bacteria has attracted interest in recent years, because the process was found to be important to biogeochemical cycling, as well as iron corrosion, biosynthesis, and bioelectrochemical technologies. The capacity for electron exchange between cells and electrodes includes both anodic and cathodic reactions[1, 2]. As a typical microorganism associated with EET, *Shewanella oneidensis* MR-1 has the ability to directly transport electrons from cytoplasmic oxidative reactions to extracellular electrodes *via* membrane-bound cytochrome *c*. However, the feasibility and directionality of electron flow from electrodes into *Shewanella* remain vague[3]. Here, we designed a series of electrochemical experiments to study the redox behavior of *S. oneidensis* cells for direct electron transfer. Electrochemical voltammetric tests (Figure 1A) and scanning electrochemical microscopy profiles (Figure 1B) were carried out to elucidate the roles of cytochrome *c* in electron exchange between electrodes and *S. oneidensis* MR-1. Our results suggest the possibility that cathodic electron transport is between redox proteins in the cell membrane and among different contacting cells. This work not only provides new insights into reduction reactions at the microbe-electrode interface, but also facilitates the design and fabrication of new bioelectrical devices.

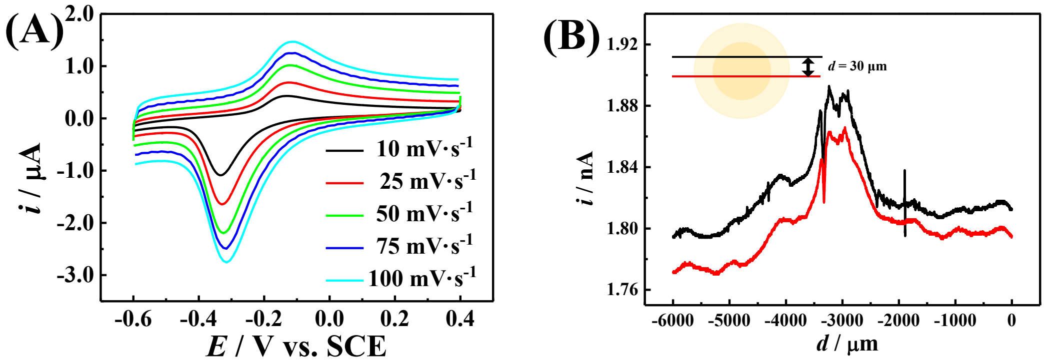

Figure 1 (A) Cyclic voltammetric curves at different scan rates for *S. oneidensis* MR-1 on ITO plates in 0.1 mol·L^{-1} PBS. (B) Schematic diagram and probe-scan curves from an SECM X-direction over the "T" shape of *S. oneidensis* MR-1 (yellowish) coated on agar plates. The scan rate was 25 μm·s^{-1}.

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Versatile semimetallic core-shell TiO_2 nanotubes: a sustainable high conductivity scaffold for energy conversion and storage application

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An ideal 1D electrode should provide an optimized ion diffusion path through the electrolyte and into the solid – such as a 1D conducting nanotubular or nanowire array [1]. An example of a highly controllable 1D array is given by self-ordered anodic TiO_2 nanotubes (TNTAs). Usually, such TNTAs are obtained by self-organizing electrochemical anodization of Ti and offer a well-controlled morphology, vertically aligned on the substrate. These structures have been previously explored for photoelectrochemical energy conversion and energy storage applications [2], however TiO_2 has generally insufficient conductivity, for using it as an electrode and/or photoelectrode. Additional efforts towards increasing the conductivity of TiO_2 nanostructures have been investigated, e.g. doping, surface engineering (decoration), and particularly self-doping by reduction, forming Ti^{3+} donor species including reduction in H_2 [3]. However, Ti^{3+} species formed on the surface of the nanostructure are highly unstable (reoxidation by O_2, air, or water) [4]. Therefore, long term stability is a crucial issue if self-doped TNTAs are used as a conductive electrode in cycling applications.

In this work, we present a simple and effective strategy to provide conductivity by buried Ti^{3+} centers, and use the material as scaffold for energy application. Here, we combine the advantages of the reduced TNTAs including high surface area, charge directionality, and stable Ti^{3+} states to form a stable, conductive and high surface area electrode. In a first step, a TiO_2 nanotube array is grown on a Ti metal substrate by self-organizing anodization. Then the tubes are self-doped through an optimized annealing in an Ar/H_2 reductive environment. Under these optimized conditions, electron paramagnetic resonance (EPR) and electron energy loss spectroscopy (EELS) results confirm the formation of a stable Ti^{3+} core structure within the tube wall. Then, we showed that by optimizing the reduction treatment such a platform can be used for enhanced photoelectrochemical water splitting photoanode. To further confirm the stability of this reduced scaffold we used it as an electrode for supercapacitor application. Decorating the reduced scaffold with a small amount of RuO_2 a 3D supercapacitive platform with specific capacitance of 1297 Fg^{-1} was obtained.

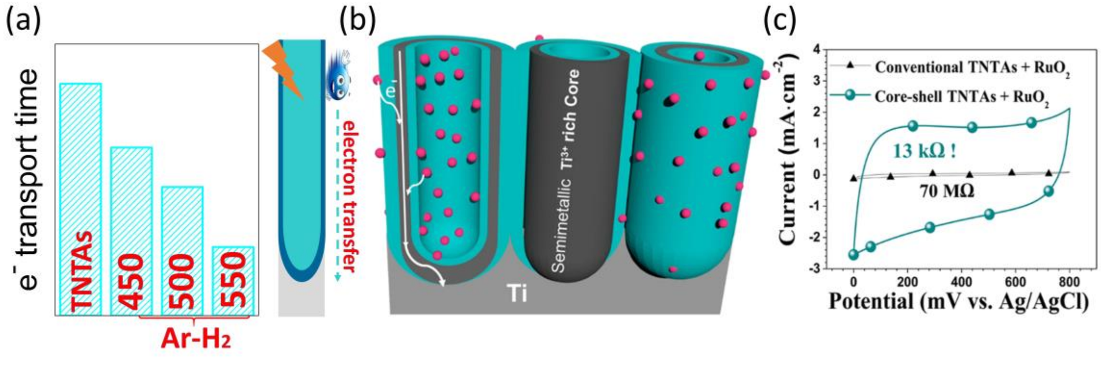

Figure 1. (a) electron transport time of pristine TiO_2 nanotubes compared to Ar/H_2 treated TiO_2 nanotubes in different temperature, (b) schematic graph of the core-shell structure of the stable reduced TiO_2 nanotubes decorated with RuO_2 nanoparticles for supercapacitor application, and (c) CV result of the conventional TiO_2 nanotube compared to the Ar/H_2 treated (core-shell) TiO_2 nanotube.

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Intrinsic Au-decoration on anodic TiO_2 nanotubes grown from metastable Ti–Au sputtered alloys—High density co-catalyst decoration enhances the photocatalytic H_2 evolution

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TiO_2 has received large attention due to its ability to "photocatalytically" generate H_2 from H_2O.[1] Classically, photocatalytic reactions are carried out using semiconductor particle suspensions, such as TiO_2 nanoparticles floating in aqueous environment. In order to overcome the kinetic hindrance of the electron transfer at the solid-liquid interface, usually the TiO_2 nanoparticles are decorated with a so-called co-catalysts, typically Pt, Au, Pd. More recently, TiO_2 1D nanostructures have gained increasing attention for photochemical and photocatalytic applications, due to their unique electronic and optical properties and directional charge transfer.[2] One of the most straightforward synthesis approaches is self-organizing electrochemical anodization of a metallic Ti sheet. When a Ti-X alloys are used for self-organizing anodization instead of pure Ti sheet, and X is e.g. a noble metals such as Au: the noble metal is not oxidized during the anodization process but forms, via self-diffusion and agglomeration, noble metal clusters at the TiO_2 nanotube surface[3]. Recent work demonstrated that intrinsic Au nanoparticle decoration of TiO_2 nanotube arrays (NTs) can be achieved by electrochemical anodization of Ti–Au alloy substrates. However, for a Ti–Au cast alloy produced by melt-alloying, the Au concentration cannot exceed the solubility limit of Au in Ti of 0.2 at.% – this sets constraints on the intrinsic Au nanoparticle loading on anodic TiO_2 NTs[3].

Here we explore "metastable" Ti–Au metal substrates that are produced by Ti and Au cosputtering and we establish Au concentrations that far exceed the solubility limit in cast Ti–Au alloys. We show the use of these "metastable" Ti–Au sputtered layers for the anodic formation of TiO_2 NTs with a much higher density of Au nanoparticle loading than using classic alloys. Under optimized conditions (Au nanoparticle density) photocatalytic H_2 production from such Au@TiO_2 platforms provides a 15 times higher photocatalytic H_2 evolution rate than the best rates achieved with conventional Ti-Au alloys.

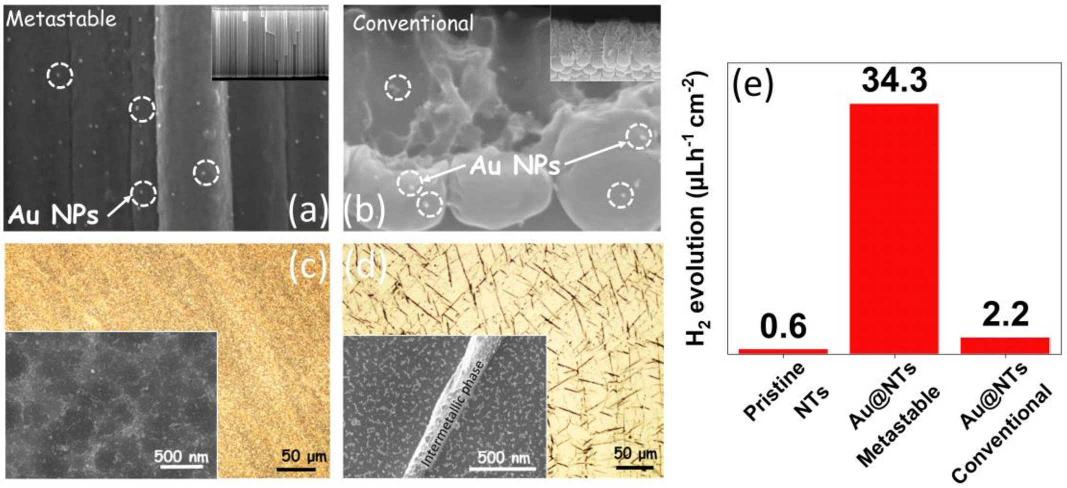

Figure 1. (a) and (b) cross sectional SEM images of TiO_2 nanotubes grown on the metastable alloy and the irregular oxide grown on the conventional alloy, respectively; (c) and (d) metallographic images of the metastable alloy and the conventional alloy, respectively; (e) hydrogen evolution rate of pristine TiO_2 and Au@TiO_2 nanotube grown on metastable and conventional alloy.

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Co-precipitation Synthesis of cobalt phosphate material as electrodes for supercapacitor application

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Cobalt phosphate $Co_3(PO_4)_2$ nanograin and its composite of graphene foam ($Co_3(PO_4)_2$/GF) materials are synthesized via different mass loading of graphene foam (GF) through a co-precipitation method. Structure, morphological and chemical bonding of the samples are confirmed by using various techniques. The electrochemical test of the pristine and composite samples is done in 1 M KOH aqueous electrolyte. The specific capacity of $Co_3(PO_4)_2$/GF composites is found to increase with increasing mass loading of the GF up to 20 mg, and then decreased when the loaded mass of GF was 30 mg. The Co3(PO4)2/20 mg GF electrode shows a maximum specific capacity of ~ 57 mAh , which is much higher compared to 21 mAh g^{-1} for the pristine $Co_3(PO_4)_2$ at a specific current of 0.5 A g^{-1}. Furthermore, a hybrid asymmetric device fabricated by adopting the $Co_3(PO_4)_2$/20 mg GF as positive electrode and an activated carbon (AC) as the negative electrode could deliver an energy density of 21 Wh kg^{-1} with a corresponding power density of 266 W kg^{-1} at a specific current of 0.5 A g^{-1}. The device exhibited an exceptional cycling stability showing a 94% capacity retention over 10,000 charge-discharge cycles at 5 A g^{-1}. Based on these results, this material is of great interest in supercapacitor energy storage device application.

Electrochemical functionalization of AISI 304 stainless steel coupons with conducting polymers: A comparative study of their performance against corrosion

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In the last three decades, research on the anticorrosion properties of intrinsically conducting (or semiconducting) polymers (CPs), has led to the development of a wide variety of CP-based protective coatings with specifically designed properties. Then, the basic principle behind the idea to apply CPs for metal protection is related to an electron transfer process and passivity, by which nature has predicted the prevention of metal degradation, such as stainless steel [1]. In this sense, several heteroatom containing organic molecules such as pyrrole, carbazole and indole have received increasing attention as material coatings, because they are easily electrografted to the surfaces forming conductive films. As a modifier compound, indole family has received more interest because of its advantages of having fairly good thermal stability and high redox activity [2]. In the present work, the electrodeposition of n-aminoindoles (n = 4, 5, 6 and 7) onto AISI 304 stainless steel surfaces was done in order to generate a protective film towards corrosion. The films were obtained through cyclic voltammetry at 80 mVs^{-1}. The obtained materials were evaluated in terms of morphology by using FE-SEM, and in terms of spectroscopy by using FT-IR, ATR and RAMAN techniques. Additionally, contact angle was calculated with the aim of analyzing the hydrophobicity of the resulting materials *versus* the initial substrate. Then, electrochemical performance of the resulting materials were evaluated by measuring the open circuit potential (OCP), polarization curves and electrochemical impedance spectroscopy (EIS) in a 3.5% NaCl solution and at 0 h, 12 h and 24 h of exposure time. It is found that all the modified substrates behave differently over the bare material in terms of all the characterizations abovementioned, as well as between all formed materials.

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Low Detection Electrochemical Immunosensor to Proteasome 20S based on Poly-indole-6-carboxylic acid

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Electrochemical immunosensors based on antigen-antibody interaction have received great interest due to their high sensibility and possibility of miniaturization for mass production with low costs. Nanotechnology plays a very important role in the biosensors field allowing to improve the performance of these devices and increasing the possibility of reaching very low detection limits. One of the most import steps in developing an immunosensor is the oriented immobilization of the antibody necessary to facilitate and favor the antigen-antibody interaction for an increase sensibility and selectivity. Among several possibilities to achieve oriented immobilization is the use of boronic acid derivatives, which interacts with oligosaccharides present in the Fc region of an antibody [1]. In order to achieve this objective, functionalization of electrode surface is essential. Proteasome 20S is part of 26S proteasome complex, which have a barrel shape structure with four stacked rings, two outer α rings which recognize and facilitate the entry of the substrate proteins into the two inner β rings with catalytic activity [2,3]. Proteasomes are important molecular machinery with direct influence in cellular cycle regulation, protein hydrolysis responsibility and antigenic peptide production [4], and currently it is a great target of study to fight against to many different cancers disease [5].

In this work, an electrochemical immunosensor based on poly-indole-6-carboxylic acid (6-PICA) capable to detect low concentrations of 20S proteasome (P20S), is described. The electro-polymerization reaction leads to a nanowire structure of the conductive polymer. On the other hand, direct interaction with 4-aminophenylboronic acid (APBA), allows a specific orientation of the antibody (mAb) at the electrode surface, increasing the efficiency of the device by favoring antigen-antibody interactions. The functionalized electrode surface was characterized by square wave voltammetry (SWV) and electrochemical impedance spectroscopy (EIS). The figure shows SWV and Nyquist diagrams of the step-by-step modification of electrode surface where can observed a systematic increase of charge transfer resistance in each step 6-PICA, APBA, mAb or P20S, respectively, over the electrode by EIS, and a decrease in current by SWV as expected from the non-conductive nature of the antigen-antibody complex.

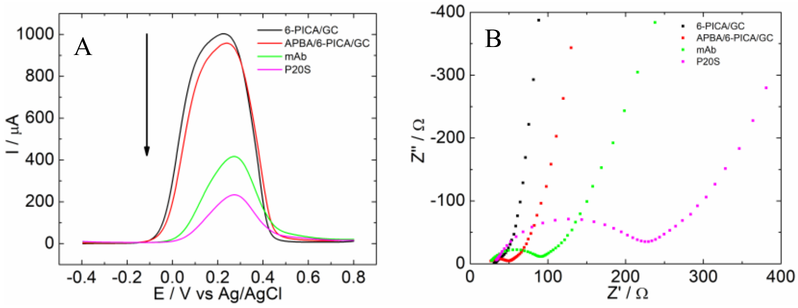

Figure 1. A) SWV and B) Nyquist diagram in 1M HAc/Ac$^-$, between 100 kH – 0.01 Hz for: 6-PICA/GC, APBA/6-PICA/GC, mAb/APBA/6-PICA/GC and P20S/mAb/APBA/6-PICA/GC, respectively.

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Very Stable Cycling of Ni-rich Cathodes with Practical Loading in the Cells with Lithium Metal Anodes in Fluoroethylene Carbonate-Based Organic Electrolyte Solutions.

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High theoretical specific capacity (3860 mAh g^{-1}) and low negative redox potential make lithium metal an ideal anode for high-energy-density Li batteries. However, dendrite growth and side-electrolyte solution reactions limit the cycling life of the batteries with Li metal anode and cause severe safety problems, hindering practical use of these anodes.

We demonstrate excellent cycling performance of Li metal anodes in ethylene carbonate EC-free fluoroethylene carbonate (FEC) based organic carbonate electrolyte solutions, which were shown to be the most promising electrolyte solutions for high energy-density and high-voltage rechargeable Li batteries. Symmetric Li|Li cells demonstrated an extremely long cycle life and a stable voltage profile for more than 1100 cycles at a current density up to 2 mA cm^{-2} and an areal capacity of 3.3 mAh cm^{-2} with a minimal amount of electrolyte solution, sufficient for wetting the separator in coin cells (50 µl/cell or 22 µl cm^{-2}). The use of the FEC-based electrolyte made it possible to obtain stable cycling of Li|NMC 622 cells for hundreds of cycles with high loading of active cathode material with areal capacity of 3.3 mAh cm^{-2}.

Besides, we demonstrate a highly stable Li | $LiNiO_2$ prototype cells with practical areal loading of the electrodes in FEC-based electrolyte solution. $LiNiO_2$ is one of the most promising cathode materials for high energy density Li ion batteries because of its high theoretical capacity (275 mAh g^{-1}) and reasonable cost. However, cathodes comprising pure $LiNiO_2$ suffer from intrinsic instability problems which lead to their capacity fading during cycling. Li | $LiNiO_2$ cells with practical cathode loading (4 mAh cm^{-2}), low amount of the electrolyte solution (33 µl cm^{-2}) and Li metal anodes were cycled at 0.8÷1 mA cm^{-2} for more than 750 cycles with excellent capacity retention.

We attribute the high performance of the Li anodes to the formation of a stable and efficient SEI on the surface of the Li metal electrodes cycled in FEC-based electrolyte solutions. The composition of the SEI is analyzed by Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy.

Photo-assisted Electrochemical Micro-patterning of Gold Film

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Gold is widely used in electronic devices and electrochemical sensors owing to its good ductility, conductivity and excellent stability. Developing convenient and efficient ways for the micro-patterning of gold film is thus of significance for boosting their applications in these fields. Electrochemical etching is a powerful and popular method for producing micro-patterns in Au films. Localized electrochemical etching of Au film is required for micro-patterning, which was achieved either by the introduction of a pre-patterned insulating layer on top of the substrate (i.e., mask) or bringing in a scanning micro-electrode to generate reactive reagent around the scanning probe. However, cumbersome procedures of the mask fabrication and unmanageable reproducibility due to the diffusion of the etching agent as well as the structure of the probe electrode limits their applications in micro-patterning of the Au film [1].

Here, we employed photo-assisted electrochemical method to selectively etch gold film with sub-micron spatial resolution by combining the electrochemical potential and light irradiation. When comparing with masks and microelectrodes, light beam exhibits superior controllability and reliability because of the utilization of confocal imaging system and scanning galvanometer mirrors. Etching kinetics and mechanism were also studied by monitoring the dynamic evolution of optical transparency with a conventional Bright-field microscope, together with characterizations on the as-obtained patterns with atomic force microscopy and electron microscopy. This study is anticipated to not only advance the fundamental understanding on the interfacial electron transfer in the photo-assisted nanoelectrochemistry, but also contribute a feasible method for the micro-patterning of gold film with implications for nanoelectronics and electrochemical sensors.

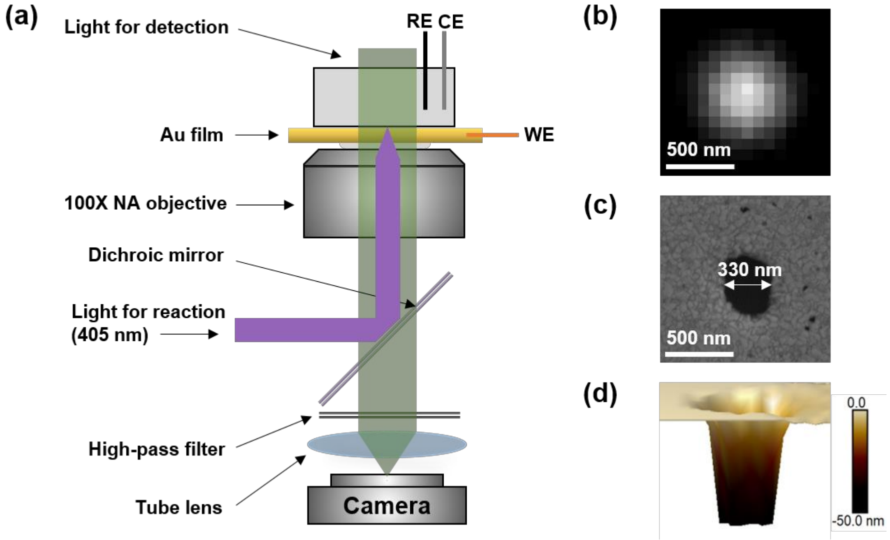

Figure 1. (a) Schematic diagram of the experimental set-up; (b-d) characterizations of one representative patterns of Au film by BF (b), SEM (c) and AFM (d).

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The Effects of CO_2 Contamination on Reaction Mechanism in Non-aqueous Na-air Batteries: A DFT Study

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Metal–air batteries become promising candidates for modern energy storage due to their high theoretical energy density in comparison to other energy storage devices. The low cost, low overpotential and abundance of Na compared with Li makes Na–air batteries more attractive. Here, we apply density functional theory (DFT) calculations to study the effect of CO_2 contamination on reaction mechanisms and resulting electrochemical overpotentials on stepped surfaces of NaO_2 and Na_2O_2, the discharge products at the cathode of rechargeable non-aqueous Na-air batteries (NASAB). Adsorption energies of CO_2 at various nucleation sites for both surfaces were determined and their corresponding binding energies show that CO_2 adsorbs strongly at various sites of the surfaces, it would preferentially bind at the step valley (-1.31 eV) and front step valley (-4.39 eV) sites of step (001) NaO_2 and $(1\bar{1}00)$ Na_2O_2 surfaces, respectively (see figure 1). We also investigate the reaction mechanisms with and without CO_2 on stepped surfaces of the NaO_2 and Na_2O_2 systems, result reveals significant increase in discharge overpotentials on NaO_2 surface, $\eta_{\text{dis}} = 0.14$ V to 0.48 V. Similarly, the results of CO_2 contamination on Na_2O_2 surface also revealed remarkable increase in both discharge and charge overvoltages, 0.69 V to 1.26 V and 0.68 V to 0.92 V, respectively. Moreover, the equilibrium potential is decreased by 0.13 V in the presence of CO_2 on Na_2O_2 surface. In general, the DFT calculations show that in both cases, with and without CO_2, the cells that discharge with NaO_2 exhibit low overpotentials while the Na_2O_2 exhibit higher over potentials. The growth/depletion mechanisms are strongly influenced by CO_2 contamination, and exhibit increased overpotentials and hence affect the performance of the Na-air battery.

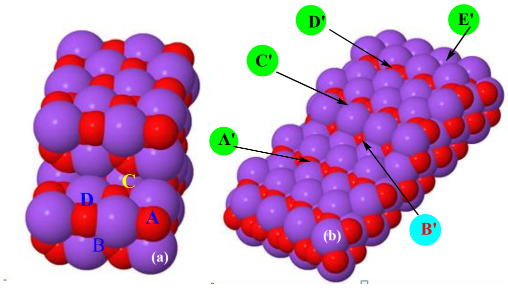

Figure 1: CO_2 adsorption at various sites of stepped (a) (001) NaO_2 and (b) $(1\bar{1}00)$ Na_2O_2 surface.

Key Words: NaO_2, Na_2O_2, Na–O_2 Batteries, DFT, CO_2 Contamination, Overpotential

Electrochemical sensor of CO_2 based on surface modification of halloysite nanotube

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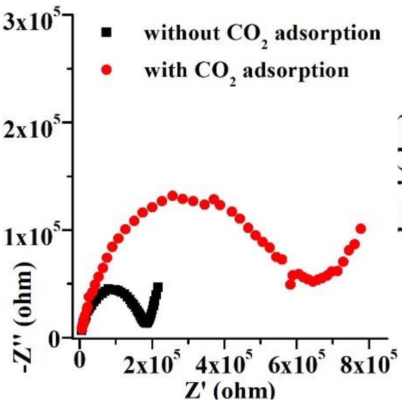
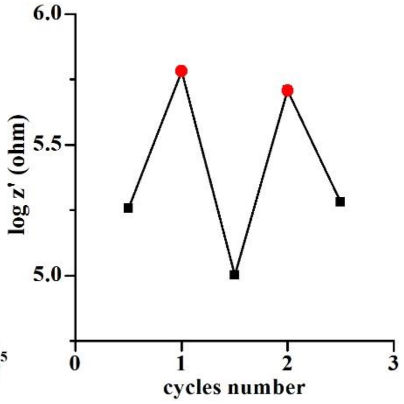
Alteration of the surface by self-assembled monolayer (SAM) has emerged as the excellent strategy to tune the surface of the materials for interested applications. This paper describes the fabrication of plate electrode by selective modification of the outer surface of halloysite nanotues (HNTs) with 3-aminopropyl triethoxysilane for CO_2 detection. This ammonium surface functionalized HNTs has been revealed to selectively capture and release CO_2, permitting for the measurement of the amount of CO_2 by electrochemical impedance spectroscopy. We found that the proton conductivity of SAM-modified HNTs was dropped upon CO_2 binding within 3 minutes. Further measurements of cycling CO_2 adsorption and desorption revealed that this modified material can be reused by heating at low temperature within 30 minutes. Current efforts are being made to correlate the percentage of CO_2 in the gas mixture and proton conductance of surface modified HNT. The results we demonstrate here offer a new path to produce a low-priced material for CO_2 electrochemical sensor





Tracking the Optical Mass Centroid of Single Electroactive Nanoparticles Reveals Electrochemically Inactive Zone

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Energy density is one of the most critical factors in the evaluation and optimization of electrode materials for ionic batteries because it determines the maximal work a battery can provide with a unit volume ($Wh \cdot m^{-3}$). While the theoretical energy density of a particular type of materials sets an upper limit by assuming complete and effective use of all the electroactive sites within the structure, the practical performance could be significantly compromised due to poor crystallinity and limited ion/electron conductivity. Inevitable microstructural defects, including cracks, grain boundaries and dangling bonds, could make a portion of the material inaccessible to electrons or ions, resulting in electrochemically inactive zones. These inactive zones not only reduced the effective energy density and the charging rate, but also could expand their territories during charge-discharge cycles, causing the capacity fading.

Here in, we employed 2D Gaussian fitting to track the migration of the optical mass centroid (OMC) of single Prussian blue (PB) nanocubes during electrochemical cycling. Any shift in the optical mass centroids (OMC) during charging, however, implied the partial transformation and therefore suggests the existence of inactive zones. PB was selected as a model material because individual PB crystals with nicely cubic shape can be obtained with a simple synthesis procedure, facilitating the interrogations on the relationship between electron accessibility and morphological crystallinity.

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Two-stage method of producing thin films based on copper-bismuth complex oxide system

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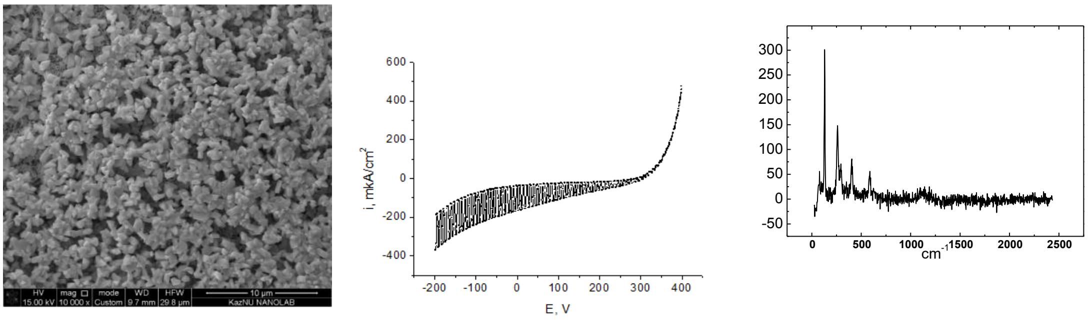
Semiconductor films of $CuBi_2O_4$ (p-type conductivity) are interest as an active photocathode for producing hydrogen fuel from water.

The paper presents a two-stage method for creating $CuBi_2O_4$ thin films, which consists in obtaining BiOI bismuth oxoiodide by electrochemical deposition (Stage 1) followed by deposition of copper (I) CuI iodide on its surface by heat treatment of the resulting BiOI / CuI film heterostructures at 450 °C (Stage 2).

Studies of the structure (SEM, XRD, Raman spectroscopy) and photoelectrochemical parameters (PEC, solution 10 mmol / dm^3 H_2O_2 + 0.1 mol/dm^3 Na_2HPO_4 + 0.1 mol/dm^3 NaH_2PO_4 + 0.3 mol/dm^3 Na_2SO_4, pH 7) showed that the obtained $CuBi_2O_4$ nanocrystalline films have a developed surface and demonstrate high photoelectrochemical activity (i^{ph}≈200 µA/cm^2).



a b c

Fig. 1. Micrograph of $CuBi_2O_4$ surface (a), photopolarization curve of $CuBi_2O_4$ electrode (b), Raman spectrum (c).

As can be seen from the obtained dependence, the $CuBi_2O_4$ electrode exhibits the flow of an exclusively cathodic photocurrent, which begins to flow at 300 mV and increases with increasing cathode polarization of the electrode. In this case, the cathode dark current is almost absent, up to a potential of about minus 200 mV

High values of photocurrent in complex oxide $CuBi_2O_4$ films obtained by this method allow us to consider this material as promising for use in photoelectrochemical solar cells and photoelectrochemical water decomposition devices.

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Improving the photocurrent in electrodeposited polyaniline / $Cu_2ZnSn(S,Se)_4$ structures

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Electrodeposition of polyaniline (PANI) and four-component semiconductor chalcogenide $Cu_2ZnSnSe_4$ (CZTSe) was performed at room temperature and photoelectrochemical properties of the resulting composition formed on Mo or FTO glass substrates were studied. This structure was designed to improve the photocurrent in the hybrid photocell. The PANI layers with a thickness of 20 and 60 nm were obtained by anodic oxidative polymerization of aniline in galvanostatic mode. One-stage electrodeposition was usedforthe preparation of the CZTSe films (1900 nm in thickness) from aqua electrolyte.The films were washed with distilled water, dried in air and finally annealed in Ar atmosphere at 450°C for 30 min. For comparison, five-component $Cu_2ZnSn(S,Se)_4$ compound was prepared by sulfurization of the electrodeposited $Cu_2ZnSnSe_4$ films in sulfur atmosphere at 500 °C. The structure and phase composition of the films were confirmedusingthe XRD method and Raman spectroscopy.

Table 1. Photocurrent in chalcogenide structures

	Mo/CZTSe	Mo/CZTSSe	FTO/PANI/CZTSe
Photocurrent, μA/cm^2	3	15	60

The photoresponse signals of the structures under study were recorded under white-light illumination of 80 mW/cm^2 with a halogen lamp at a constant potential of -10 mV applied to the Mo or FTO electrode with respect to the Pt counter electrode in 0.1M Na_2SO_4 electrolyte at room temperature. The photocurrent for samples of the FTO/PANI/CZTSe structure is seen to be much higher than that for samples without the PANI layer (Table 1).Themeasurements were carried out in air so oxygen molecules served as a redox mediator (O_2/O_2^-) collecting electrons from conductive band of the chalcogenide and transporting them to the counter electrode. In a cell without PANI, the rate of hole transfer between the chalcogenide layer and the cathode seems to be low because the corresponding energy levels match poor (Fig.1). In a cell with PANI, the polymer layer serves as a means to improve the collection of holes on the FTO cathode since the polymer HOMO level matches well with the valence band of CZTSe facilitating the easy transfer of holes from the CZTSe layer (Fig.1). Thus, the recombination of electrons and holes in the bulk of CZTSe decreases. Moreover, the PANI layer blocks electrons to transfer from the conductive band of CZTSe to FTO. These behaviors of the polymer layer leads to improving the photocurrent. It is proposed to use electrodeposited PANI thin layers as a buffer layer in hybrid solar cells with multicomponent chalcogenides.

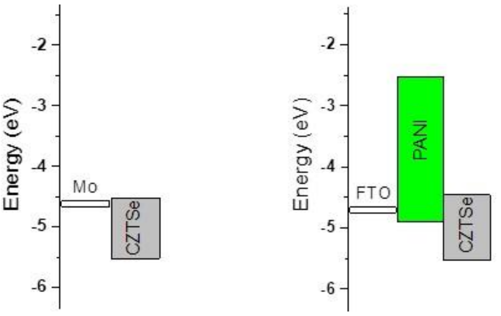

Fig.1. Energy diagrams of the studied structures. Energy levels of CZTSe [1] and PANI [2] match well for the hole transfer from the chalcogenide layer to the FTO electrode under illumination

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Tracking the Optical Mass Centroid of Single Electroactive Nanoparticles Reveals Electrochemically Inactive Zone

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Energy density is one of the most critical factors in the evaluation and optimization of electrode materials for ionic batteries because it determines the maximal work a battery can provide with a unit volume ($Wh \cdot m^{-3}$). While the theoretical energy density of a particular type of materials sets an upper limit by assuming complete and effective use of all the electroactive sites within the structure, the practical performance could be significantly compromised due to poor crystallinity and limited ion/electron conductivity. Inevitable microstructural defects, including cracks, grain boundaries and dangling bonds, could make a portion of the material inaccessible to electrons or ions, resulting in electrochemically inactive zones. These inactive zones not only reduced the effective energy density and the charging rate, but also could expand their territories during charge-discharge cycles, causing the capacity fading.

Here in, we employed 2D Gaussian fitting to track the migration of the optical mass centroid (OMC) of single Prussian blue (PB) nanocubes during electrochemical cycling. Any shift in the optical mass centroids (OMC) during charging, however, implied the partial transformation and therefore suggests the existence of inactive zones. PB was selected as a model material because individual PB crystals with nicely cubic shape can be obtained with a simple synthesis procedure, facilitating the interrogations on the relationship between electron accessibility and morphological crystallinity.

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Basic Bismuth Nitrate Sorbent Synthesised by Electrochemical Procedure: Characterization and Isothermal Studies of Adsorption of Reactive Orange 16

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Abstract

Electrochemical synthesis of basic bismuth nitrate (ECBBN) was done by galvanostatic electrodeposition from bismuth nitrate solution in 2 mol dm^{-3} nitric acid at constant current density of 150 mA cm^{-2}. Final product was obtained after thermal treatment at 200 ºC. Material was characterized by SEM-EDX, XRD, BET and FTIR methods, and its isoelectric point (pI) was also determined. Morphologically, it is composed from aggregates with different size and shape, which is formed from crystals which thickness varies between 200 and 800 nm. Some of them have nanometric dimensions with diameter from 30 to 50 nm. XRD analysis showed that synthesized material is trigonal $[Bi_6O_5(OH)_3](NO_3)_5{\cdot}2H_2O$ (space group P-3) with high crystallinity. Crystallite size of ECBBN determined by Williamson-Hall method is 11.3 ± 0.2 nm. According to the IUPAC classification the N_2 adsorption/desorption isotherm of ECBBN is type II, which is related to unrestricted monolayer-multilayer adsorption and nonporous or macroporous adsorbents. BET specific surface area of material is about 1 m^2 g^{-1}. The pI of the ECBBN is 2.12.

Significant quantities of synthetic dyes from industrial effluents are discharged into the environment and presents one of the major industrial pollutants and water contaminants[1]. Comparing to the other techniques of removal of pollutants, adsorption is considered to be highly efficient, simple and relatively inexpensive[2,3]. The synthesized ECBBN sorbent was applied for removal of textile dye Reactive Orange 16 (RO16) which is used as a model pollutant. The results show that ECBBN has very high sorption performance and low sorption equilibrium time (about a 1-2 minute).

The Langmuir, Freundlich, Redlich–Peterson and Brouers–Sotolongo adsorption isotherm models were used for investigation of adsorption equilibrium[4]. These isotherms were characterized by parameters, which values express affinity and surface properties of sorbents. Based on the fitting results and obtained determination coefficients, Langmuir, Redlich–Peterson and Brouers-Sotolongo (0.95, 0.94 and 0.99, respectively) models can be used to describe sorption of RO16 on ECBBN sorbent. The Freundlich model has significantly lower determination coefficient (0.72) than these three models. Maximum sorption capacity obtained for Langmuir model is in better agreement with experimental data in comparison with obtained value from Brouers-Sotolongo model. Thus the sorption equilibrium data were best interpreted by the Langmuir isotherm, and maximum sorption capacity is 473.07 mg g^{-1}. The Redlich–Peterson exponent β is close to 1, which means that Langmuir will be preferable isotherm in comparison with Freundlich. Brouers-Sotolongo exponent α is close to 1 and indicates that adsorption sites are energetically homogenous. Based on the applied isotherm models it can be inferred that the sorption on ECBBN has homogenous character, which confirms good agreement with the Langmuir type of isotherm. Dimensionless constant R_L derived from the Langmuir isotherm, for initial dye concentrations from 50 to 600 mg dm^{-3} decrease from 0.0219 to 0.0009. This means that the reaction is more favorable for high RO16 concentrations. ECBBN sorbent also showed high sorption capacity for removal RO16 from model solution of polluted water, which makes it a suitable means for the textile dyes removal from water.

Acknowledgements

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Electrochemical Degradation of Caffeic Acid Using Boron-Doped Diamond Electrode: Minimization of the Energy Consumption Using Modulated Current

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Coffee is one of the main global agribusiness products, however, the wet coffee processing industry is considered as being environmentally unfriendly due to the large volumes of water consumed and effluent generated. The resulting wastewater is rich in phenolic compounds, such as caffeic and chlorogenic acids, which can be toxic and refractory to biological treatment. In this context, we studied the electrooxidation of the caffeic acid (CA, 200 mg L^{-1}) in a flow reactor using boron doped diamond electrode (BDD). The effect of current density and flow velocity on the limiting current was firstly evaluated in order to propose an optimized process through the current modulation, *i.e.*, the applied current was diminished along the electrolysis according to the concentration of CA in order to maintain the process operating at current limit condition, thus maximizing the reaction rate and minimizing the specific energy consumption. The use of the modulated current approach compared with the galvanostatic electrooxidation reduced the energy consumption from 256 to 52.4 kWh kg^{-1} TOC due to the improvement of the mineralization efficiency from 17.9 to 77.1%. On the other hand, the time of electrolysis increased from 7.1 to 12 h. Finally, the modulated current technique was successfully applied for the degradation of a real effluent from coffee industry, revealing itself as a feasible alternative to treat these effluents.

Optimized Polyaniline-Derived Carbon Electrodes for Capacitive Deionization

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Capacitive deionization (CDI) emerged as new a water desalination technology in which ions are removed from brackish water by flowing between two polarized electrodes. Cations and anions move and are stored in the negatively and positively charged electric double layer (EDL), respectively. The electrode material is of paramount importance for CDI since it affects the salt adsorption capacity (SAC), conductivity, desalination kinetics, and energy consumption. Typically, the CDI electrodes are made of carbon-based materials, fulfilling requirements as high specific surface area (SSA), chemical stability, and conductivity. Here, we make a comprehensive study of the variables affecting the achievement of polyaniline activated carbons (PAC). A new mechanism is proposed to explain how the carbonization/activation conditions have influence on textural properties (SSA and pore volume) of PAC. We found that carbonization at temperatures ≤ 600 ºC are mandatory to provide more KOH-reactive carbon intermediates due to their turbostratic structure. After activation at 850 ºC, remarkable pore volume (2.30 cm^3/g) and SSA (~3600 m^2/g) was achieved, which has direct influence on promoting high electrode capacitance (213 F/g, in 0.2 M NaCl), and SAC (22.2 mg/g, in 600 mg/L NaCl, 1.2 V). This SAC is among the highest values reported for CDI desalination using carbon electrodes. This work enlightens the mechanism to achieve high performance activated carbons, and provides a promising electrode material for CDI desalination.

Studies on the influence of phosphate on the kinetics in a vanadium redox flow battery

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The vanadium redox flow battery (VFB) is a promising, stationary energy storage system, due to its durability and safety. A major research topic, however, is the improvement of the cell performance through enhanced vanadium kinetics. Up to now, research has mainly focused on electrode modifications, such as thermal treatment or the application of catalysts [1]. However, these electrode properties only affect the kinetics in the negative electrolyte. Therefore, possibilities for improving the kinetics in the positive electrolyte are of particular interest. In this work, the influence of phosphate additives, widely known as stabilizing agents, is investigated. Holland-Cunz et al. studied the use of phosphoric acid instead of sulfuric acid as base solvent for vanadium electrolyte and observed a significantly higher cell performance [2].

In order to study the detailed influence of phosphate on the kinetic activity of each vanadium species, we investigated different electrolyte solutions (negative and positive) with variable state of charge (SoC) and phosphate content. The experiments were carried out in a special test setup with flow cell, similar to the one used by Becker et al. [3], which ensures that only kinetic influences are measured and material transport effects can be neglected. Impedance spectra and polarization curves are recorded and the results are compared to verify the measurement method. The results show a significant influence on the kinetics of both electrolyte solutions. However, the effect on the negative side seems to be rather detrimental. The addition of phosphate based stabilization agents therefore might be problematic, and perhaps should be reconsidered. In contrast, the addition of ammonium dihydrogen phosphate improves the kinetics in the positive electrolyte significantly, as shown in figure 1. Up to a concentration of 0.4 mol·L^{-1} the measured current densities are increasing with the phosphate addition (for comparison: commercially available electrolyte already contains approx. 0.109 mol·L^{-1} phosphate). From this point on, a limit value seems to be reached, as the current density hardly changes with further increasing phosphate content. The same effect can be seen in the impedance spectra, where the size of the semicircles decreases with increasing phosphate content indicating a lower kinetic resistance. Hence, operation of a VFB with different phosphate content in negative and positive electrolyte could be an interesting option that will be investigated in future work.

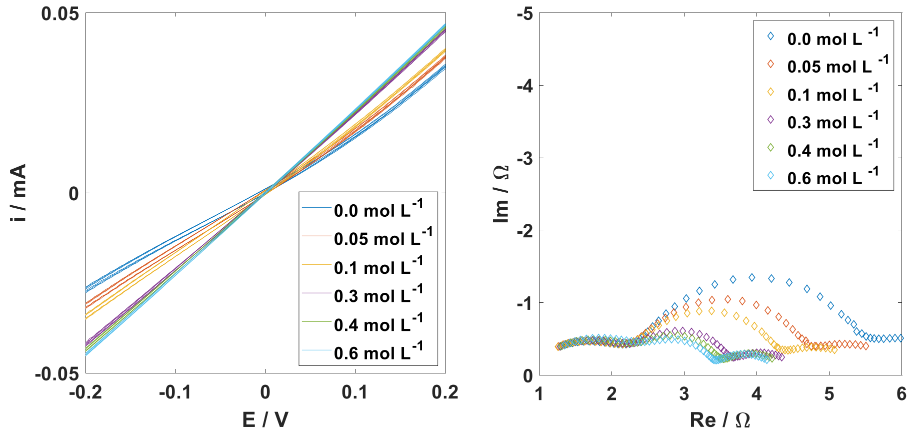

Figure 1: Polarization curve measurements (left) and impedance spectra (right) in the positive electrolyte (0.1 mol·L^{-1} Vanadium, 50 % SoC) with different content of ammonium dihydrogen phosphate.

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Highly selective electrochemical reduction of CO_2 to CO observed on commercially available brass electrodes modified by galvanic Zn replacement

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As countries across the globe have pledged to significantly reduce anthropogenic CO_2 emissions in order to limit the global temperature rise to less than 2° C, advanced technologies to convert CO_2 into valuable chemical feedstock products and fuels have become increasingly important. One proposed approach is the selective electrochemical reduction of CO_2, whereas its conversion to predominantly CO appears to be the most promising option. This is due to the already reported high faradaic efficiencies for CO compared to hydrocarbon products [1]. Ag and Au have been identified as the most active and selective catalysts for CO_2 conversion to CO due to the weak binding of the CO* intermediate to its surface [2, 3]. Consequently, surface-bound CO is desorbed already, before it can react any further.

In contrast to Ag and Au, Cu produces a variety of hydrocarbon species, in particular also ethylene, as it is able to catalyze the protonation of the CO* intermediate. Depending on particle size, oxidation state, morphology, local pH, and other variables not yet identified and understood completely [4], different products will be obtained at different overpotentials. Most detrimental to the catalytic efficiency, however, is the formation of hydrogen (HER) as a parasitic reaction competing with the CO_2 conversion into higher hydrocarbons.

In this paper, we present a study of commercially-available brass (Cu-Zn) foils. Galvanic replacement of the less noble Zn from the uppermost layers led to the growth of up to µm-sized Cu needles on the electrode surface. These were decorated with small Zn patches, which have deposited during further reaction as illustrated in Figure 1.

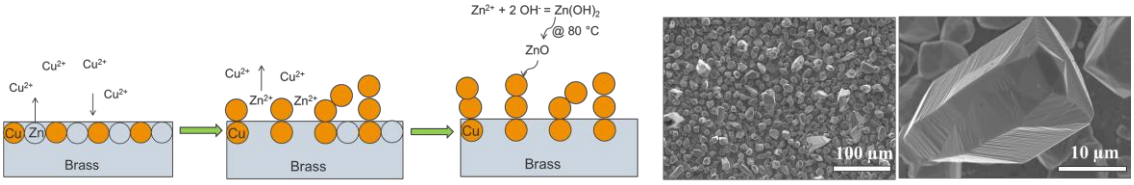

Fig. 1 Schematic illustration for the synthesis of CuZn catalyst and the SEM images of the resulting catalyst.

The influence of the electrode's morphology and composition (Zn content) on the product distribution and efficiency of CO_2 electroreduction is studied and compared to the pure Cu catalyst. The main objective here was to develop a cost effective and facile method to obtain structured Cu surfaces and to tune their product selectivity. It has been observed that modification of brass surfaces with galvanic replacement changed the product selectivity significantly. Surprisingly, high selectivities for the CO production have been found in comparison to pure Cu catalysts, which generally produce hydrocarbon products at the studied potentials [4]. The method is of significant interest, as commercial metal foils can be modified in a facile one step procedure and yield very robust catalytic performances over long-time measurements.

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Electrode modification with cobalt phthalocyanine via click chemistry, for application in electrocatalysis

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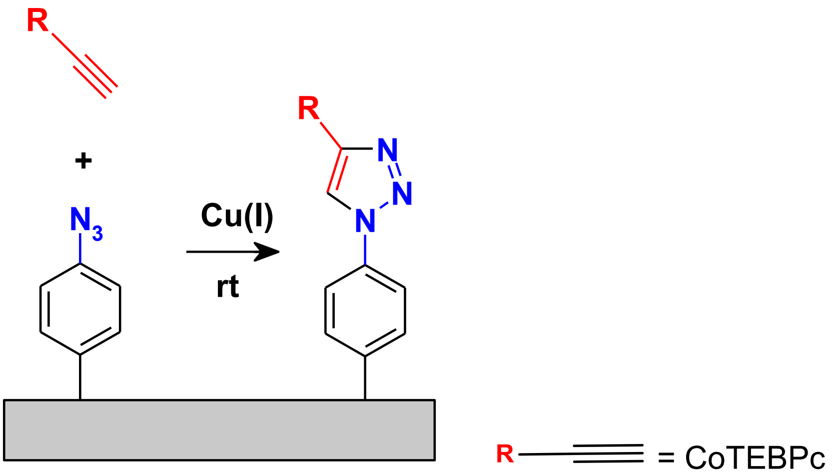
Electrode modification via click chemistry will be discussed as an effective method to attach an electrocatalyst on the electrode surface. The electrode was first grafted with azidobenzene diazonium salt rendering the GCE surface layered with azide groups terminated then, new synthesized cobalt tetrakis 4-((4-ethynylbenzyl) oxy) phthalocyanine (CoTEBPc)[1] was "clicked" to the grafted electrode (as shown on scheme 1). The reaction of azide group with alkyne group in presence of Cu (I) catalyst results in triazole linkages and it is named Sharpless click chemistry reaction[2]. Metalphthalocyanies have shown a good electrocatalytic behavior for detection of anylates[3] hence CoPc was used as an electrocatalyst for hydrazine oxidation. Hydrazine is an important indusial chemical however, it is reported as a harmful chemical when introduced to the environment[4] therefore it was used as analyte of interest in this work. The electrocatalyst developed shown high sensitivity, wide detection range at micromolar level of detection limit, which is a great improvement compared to other reported sensors for this analyte.



Scheme 1: Representation of grafting and click chemistry

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Simulation of Fe-Zn Sacrificial Corrosion under Dynamic Electrolyte Thickness Based on Real Time Monitoring Data in Singapore

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Atmospheric corrosion, as a complex problem, is an electrochemical process under thin electrolyte layers. One reason for complexity of atmospheric corrosion is variation in the electrolyte film thickness due to condensation and evaporation. Singapore is located one degree from the equator, as such, the number of hours of daylight is almost constant throughout the year and it has a tropical marine climate where nighttime relative humidity levels regularly exceed 95%.

The atmospheric corrosion rate of zinc at the west side of Singapore has been monitored for a period of one year using an electrical resistance monitoring system. Recordings were taken every 1 hour and analysis of the data revealed that significant corrosion rates only occur at specific hours during the day. The highest corrosion rates were nearly always found to occur from the dawn until close to the solar noon, corresponding to the period that the moisture on the zinc surface dries as the temperature increases. This finding allowed the drying rate of the moisture film to be estimated for input into a simulation model of the galvanic corrosion between an iron substrate covered with a damaged zinc plated layer. The model considers eight chemical species in the simulated electrolyte film, namely Na^+, Cl^-, Zn^{2+}, SO_2, CO_2, O_2, OH^-, H^+, along with their respective homogeneous chemical reactions in the electrolyte.

Based on the real corrosion rate monitoring data, the one-year corrosion was considered equivalent to sets of wet/dry cycles. However, for simplification, only one drying cycle was simulated for the time being. The simulation results showed that the maximum corrosion rate occurs at electrolyte thickness of 12 µm, which is a value quite close to the previous experimental research of Stratmann and Streckel [1-3]. Moreover, it was found that the mechanism of corrosion protection in the damaged region offer by the zinc coating is controlled by the variations in the dissolved oxygen concentration and the deposition of corrosion products. This results in the rate cathodic reaction on the exposed iron being at its highest in the middle of the scratched region and at its lowest near the zinc/iron interface. The models predictions for regional variations in the kinetics of the oxygen reduction reaction were confirmed by in-situ microprobe pH measurements.

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Electrochemical detection and determination of vancomycin using a novel water soluble metal organic framework

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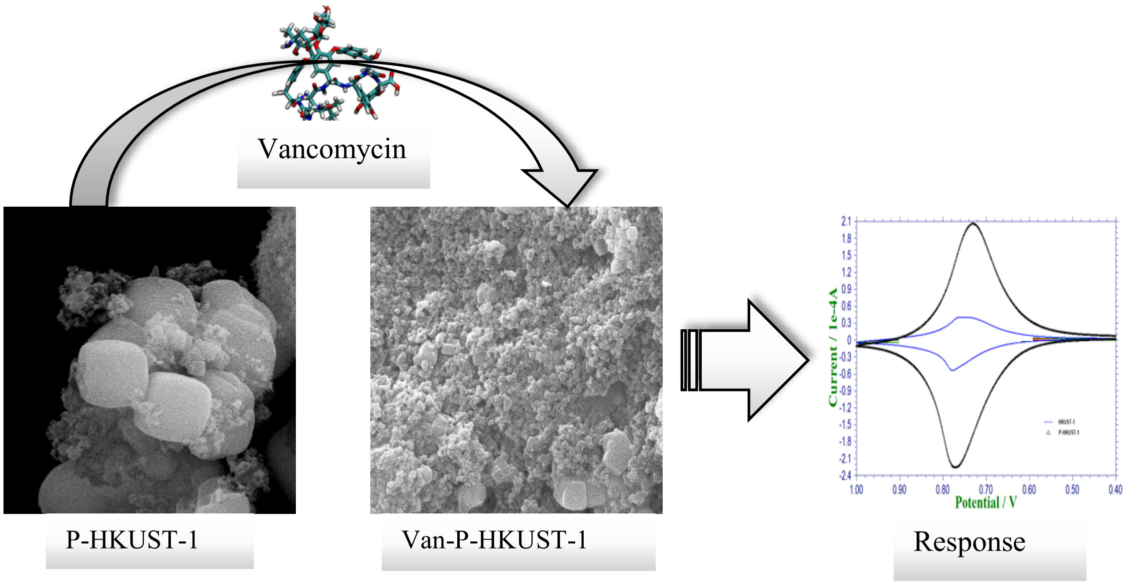
Vancomycin is a glycopeptide antibiotic and commonly administered drug for the treatment of various gram-positive severe bacterial infections. However, it has several side effects which can lead to unwanted infections and diseases, which makes it necessary to monitor the accuracy and specific dosage of vancomycin to the patients. This work reports a polyacrylic acid modified copper metal-organic framework (MOF) (HKUST-1) for highly specific and selective detection of vancomycin. The synthesized MOF exhibits enhanced water solubility and dispersibility as well as a better response towards vancomycin detection as compared to HKUST-1. The new MOF (P-HKUST-1) structure retains its crystalline properties which is confirmed via x-ray crystallography while providing enhanced electrocatalytic properties which was confirmed using cyclic voltammetry and electrical impedance spectroscopy. The Brunauer–Emmett–Teller (BET) surface area of the modified MOF obtained is larger than other methods that were previously employed for improving HKUST-1's solubility and conductivity. The structural and spectral characteristics of MOFs and their vancomycin complexes were carried out. Finally, the synthesized MOF was applied to carry out electrochemical detection and determination of vancomycin in water and spiked urine samples for practical applicability using cyclic voltammetry. A detection limit of 1 nM and a linear detection range from 1-500 nM was achieved with high specificity in the presence of various other analytes.

Graphical abstract



Novel flame Synthesis Of Iron Oxide Impregnated Carbon Nanotubes For Electrochemical Detection Of Antimalarial Drug: Proguanil

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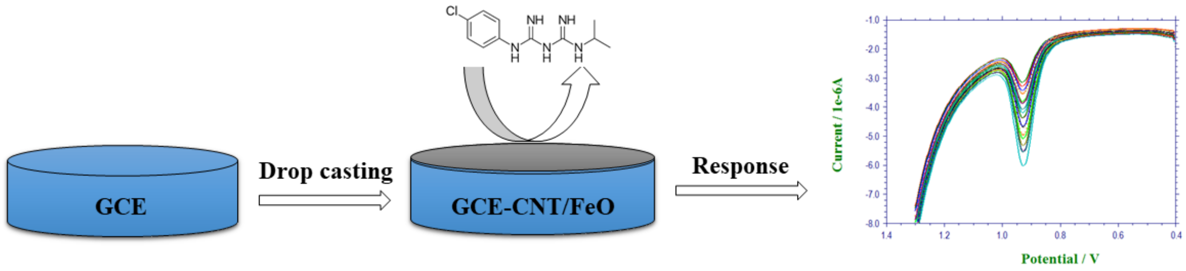
Quality control of antimalarial drugs in developing countries is of importance due to the high prevalence of counterfeit in commercially available drugs. This study proposes a sensitive electrochemical sensor for the detection of proguanil. Proguanil is an antimalarial drug that is used in combination therapy for the treatment of malaria due to *Plasmodium falciparum* and *Plasmodium vivax*. Iron oxide impregnated carbon nanotubes were synthesized and characterized using scanning electron microscopy, energy dispersive X-ray spectroscopy, transmission electron microscopy, X-ray diffraction spectroscopy, and Raman spectroscopy. The fabrication of the sensor was done by modifying a glassy carbon electrode with iron impregnated carbon nanotubes. Differential pulse voltammetry (DPV) and cyclic voltammetry (CV) were used to study the electrochemical oxidation of proguanil. Under optimum conditions, the sensor showed two linear response range of 1.3×10^{-6} - 3.2×10^{-6} and 3.4×10^{-6} - 18×10^{-6} with a detection limit of 3.45×10^{-8}. The selectivity of the sensor was investigated in the presences of organic and inorganic interfering agents. Furthermore spiked human urine sample and pharmaceutical formulation were used to evaluate the utility of the sensor.

Graphical abstract



3D and transparent photobioelectrodes based on photosystem I - analysis of performance factors

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Recent developments in photobioelectrochemistry demonstrate the feasibility of integration of well functional, complex biomolecules in hybrid electrode structures for bioenergetic and biosynthetic purposes [1,2]. 3D electrode materials have been shown to provide advantageous features since they can harbor a large amount of biomolecules while still allowing high currents to flow. One limitation of existing approaches is the limited transparency when higher thicknesses are prepared. Most of the common procedures start with a nanoparticular material such ITO nanoparticles. Here we show that preparation of 3D electrodes is feasible with a template approach starting from liquid precursors. We have chosen indium and tin precursors in order to prepare indium tin oxide electrodes (ITO) by a simple spin coating procedure followed by a backing step [3].

The prepared electrodes provide a high transparency and an open structure allowing the immobilization of photoactive supercomplexes such as photosystem I from *Th. elongatus* and other material. Several factors have been studied to evaluate parameters, which are important for the overall performance. Here the composition of the basic electrode material has been analyzed (tin content). Furthermore, the diameter of the polymeric beads during the preparation has been varied and thus, the pore structure in the ITO electrode. Finally the thickness of the 3D electrode has been varied from 3 to 17 µm by adjusting the number of spin coating steps during the deposition of the bead/precursor mixture. For the electrical connection of PSI with the electrode the small redox protein cytochrome *c* (cyt *c*) has been used [4,5].

The investigations show that both PSI and cyt *c* can be well integrated into the 3D electrode structure. The protein amount is increasing with the thickness of the prepared electrodes. Furthermore, it seems to be an optimum, when polymeric beads of 0,46 µm diameter are used during the template-based preparation process. ITO electrodes with 12 spin coating layers (about 13 µm thickness) still show a transmission of 30 %. When PSI and cyt *c* are integrated, the photocurrent densities of about 270 $\mu A/cm^2$ can be obtained in air-saturated buffer (oxygen is acting as final electron acceptor here). These photocurrent values seem to be transport limited since a stirring of the outer solution drastically changes the kinetics of the photocurrent decline during the illumination period since it facilitates oxygen supply.

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Preparation of ITO/TiO_2/nanomaterials electrodes and their applications in solar cells

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Titanium dioxide (TiO_2) is the most widely used material in photovoltaic cell (PVC) studies due to electrical properties, optical, chemical stability and photo-corrosion resistance, which makes it ideal for the development of PV [1]. Commonly TiO_2 is prepared by hydrothermal methods and are heated above 450° C and TiO_2 anatase form is obtained [2]. These methods use high temperatures and the processes last several hours to obtain electronically interconnected systems [3]. Additionally, the use of TiO_2 requires irradiation with UV light. Therefore, doping or modification of TiO_2 is an alternative that allows increasing the absorption of light towards the range of visible light. This could be completed by adding on its surface compounds such as metal nanoparticles (gold, nickel, iron, molybdenum) or nanomaterials such as carbon nanotubes or graphene. Doped TiO_2 are developed to improve the response to visible light for use in photovoltaic applications.

The aim of this work is to study the electrochemical preparation of TiO_2 modifying with nanomaterials such as graphene or metal nanoparticles. The preparation is performed by inducing the precipitation of TiO_2 from a titanium compound as a precursor, this by application of electrochemical techniques reducing the preparation time of the materials for use in photovoltaic cells.

In this work, TiO_2 is formed on ITO semiconductor glass electrode from $TiCl_3$ hydrolysis by repetitive cyclic voltammetry (RCV) (Figure 1) Subsequently, the surface is layered with graphene (G) or gold nanoparticles (AuNP). The preparation of graphene is from the pyrolysis of citric acid [4], which is deposited on the ITO/TiO_2 electrode by the droplet method evaporating the solvent. In the same way, AuNP was deposited on the ITO/TiO_2 electrode. Cyclic voltammetry and UV-visible showed the presence of TiO_2, TiO_2 with graphene or gold, on the surface of the ITO electrode. X-rays diffraction was used for characterized the surface electrode showed the TiO_2 anatase.

Finally, the photocurrent observed for a photovoltaic cell with AuNP (ITO/TiO_2/AuNP) was higher compared to TiO_2 and TiO_2/G (Figure 2).

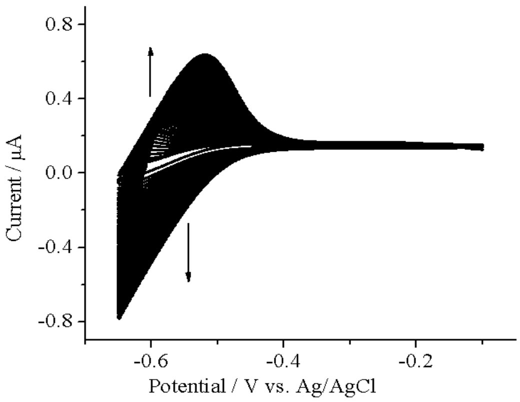

Figure 1. RCV for ITO/TiO_2 preparation.

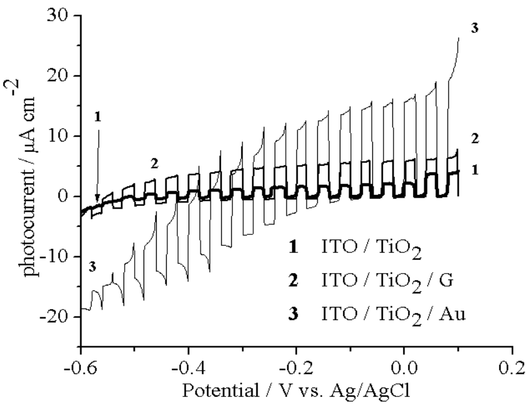

Figure 2. Comparison of photocurrent vs. potential for photovoltaic cells ITO/TiO_2, ITO/TiO_2/G, and ITO/TiO_2/AuNP.

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An electrocoagulation system for the removal of silica and reduction of alkalinity (carbonates): application to well waters and rejection water from reverse osmosis systems.

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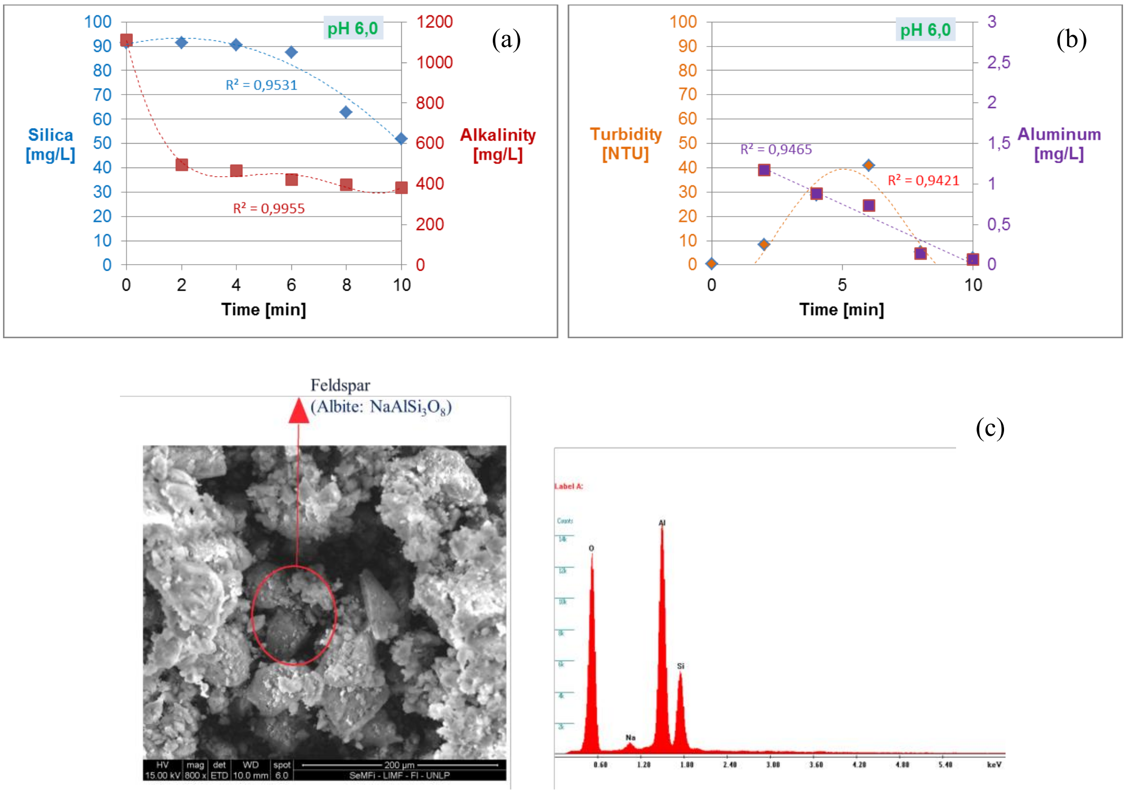
It is well-known that the presence of silica and carbonates deposits formed in water pipes in industrial plants severely affects their performance and useful life and also results in significant economic losses when the plant should be stopped for maintenance tasks.Because of this, water coming from wells is usually purified through an inverse osmosis (IO) procedure before entering into the refrigeration circuit. In this work we have studied how to improve the electrocoagulation technique for the treatment of water: i) before entering the IO stage in order to increase the efficiency and membranes life; ii) that is rejected during the IO stage, to recirculate it for increasing the efficiency of the circuit. The initial studies were performed in an electrochemical cell involving a two Al (1050) electrodes array under a constant solution stirring. Anode electrodissolution was produced by flowing a 1 A constant current. Initial data, obtained for pH values between 5.5 and 7.0, showed that depending on pH, the formation rate of flocs decreases markedly, diminishing significantly the concentration of silica and carbonates without an appreciable increase of either the turbidity or the amount of Al(III) ions in solution. Results suggest that the electrochemical reaction produces the formation of albite flocs that favors the precipitation process. Following the small scale results, a scale up system was designed that can process 120 L/h raw water. Currently a pilot plant for treating 3000 L/h raw water is under development.



(a, b) Data obtained from the electrocoagulation of rejected IO water; (c) SEM image of a floc produced at pH = 6.0 with EDAX spectrum obtained from the floc.

Design and fabrication of porous carbonaceous electrocatalysts for the oxygen reduction reaction

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With the ever-increasing fossil fuels crisis, modern life and society are badly in need of renewable energy resources. However, the development of a number of green energy technologies, including fuel cells, metal-air batteries, and chlor-alkali electrolysers, etc., have been severely hampered by the sluggish kinetics of ORR. Recently, porous nitrogen-doped carbon (N-C) materials, featuring with low cost, high activity, excellent selectivity, outstanding durability and environmental friendliness, have been born as promising alternatives to traditional expensive Pt-based ORR catalysts. For them, the pore structure plays a critical role in the catalytic process, in which micropores (< 2 nm) hold most active sites because of their superior surface. Meanwhile, although mesopores (> 2nm, including macropores) can provide a little of active sites, they mainly promote mass transport owing to their large size. However, the rational design principle of pore structure for activity maximization is still unclear. In our recent work, we investigate a series of N-doped carbon (N-C) catalysts with exclusively different micro-mesopore porosity for oxygen reduction reaction (ORR). Combining the experiment results and a pioneering mathematical model, we find that the best catalytic activity can only be attained when the micro-mesopore porosity achieves balance. These findings offer a definite criterion for pore structure construction in carbon-based ORR catalysts, which is of great meaning for plentiful energy technologies. [1-5]

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Polysulfone hydrogel nanocomposite alkaline phosphatase biosensor for the detection of Vanadium

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Abstract

Recently vanadium has been identified as the most effective natural treatments for diabetes. This unique trace mineral works to lower blood sugar by mimicking insulin and improving the cells' sensitivity to insulin. Vanadium compounds can be used to mitigate insufficient insulin response in diabetes mellitus. Studies on animals indicate that vanadyl sulfate and other vanadium compounds cannot entirely substitute for lack of insulin in type 1 diabetes. However, it can reduce reliance on exogenous insulin, or perhaps substitute for other oral hypoglycemic agents, in type 2 diabetes. The positive effects of vanadium can improve sensitivity to insulin in both Type 1 and Type 2 diabetes. Unfortunately, vanadium's effects are not all positive. It has been identified as carcinogenic by blocking the protein synthesis as well as oxidation of lipids, which is considered a primary step in the development of cardiovascular disease . Therefore, it is imperative to have a system in place that can be used as biomarker for early detection of vanadium in biological sample (in aqueous form). Several biosensors based on the immobilization of alkaline phosphatase (ALP) at different transducers have been reported. However, it is relatively uncommon to approach biosensor construction by direct immobilization of enzyme i.e. alkaline phosphatase (ALP) onto an electrode. In this work, a gold electrode covalently modified with novel polysulphone hydrogel (Au-HGL) was used as platform for the immobilization of ALP enzyme to produced Au-HGL/ALP biosensor. Step by step biosensor construction was evaluated by Raman spectroscopy and characterized by cyclic voltammetry (CV), and atomic force microscopy (AFM). The analytical performance of the biosensor was evaluated by square waves (SWV), electrochemical impedance spectroscopy (EIS) and amperometry. The biosensor displayed a linear response to the concentration of vanadium, in the range 0-30 μM which was modeled as Michaelis-Menten kinetics. The analytical performance displayed a limit of detection (LOD) and limit of quantification (LOQ) of 0.227 μM and 0.758 μM respectively. The biosensor was applied to Centrum® tablet for the detection of vanadium in pico molar range. Au-HGL/ALP biosensor exhibited high sensitivity to vanadium in aqueous medium with a good reproducibility (n = 4) and a relative standard deviation (RSD) of 8%.

Keywords: Alkaline phosphatase, hydrogel, polysulfone, vanadium biosensor, Raman, EIS, amperometry

Enhancing the electrocatalytic activity of cobalt phthalocyanines through coupling with nitrogen-doped graphene quantum dots

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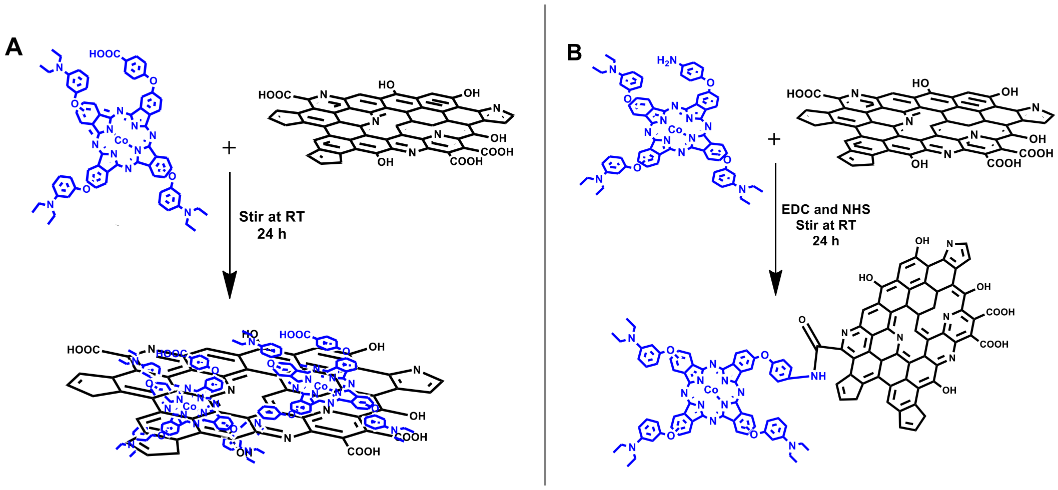
Unsubstituted phthalocyanines (Pcs), often commercially available, have aided in the exponential growth of Pcs in electrochemistry. These kinds of Pcs are often plagued by poor solubility as the Pc monomers are inclined to forming aggregates in solution. This however, can be remedied through the use of substituted Pcs with the asymmetrical Pcs being the most favourable as they enable controlled conjugate formation to/with other materials [**1-3**]. Furthermore, depending on the substituents selected, a push-pull effect can be observed. In this work, a series of asymmetrical cobalt Pcs (CoPcs) are coupled through covalent and non-covalent (π-π stacking) means (**Scheme 1**) with nitrogen-doped graphene quantum dots (NGQDs) for the electro-oxidation of hydrazine with the aim of improving the electrocatalytic activity of the CoPcs. NGQDs were selected instead of the pristine GQDs as their ability to function as electrocatalysts is further enhanced by the presence of pyridinic nitrogen atoms that lie within the graphene network [**4**].



Scheme 1: An illustration of how the π-π stacked conjugates (**A**) and the covalently linked conjugates (**B**) were prepared.

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Harvesting Electrochemical Energy from Oscillating Light Sources

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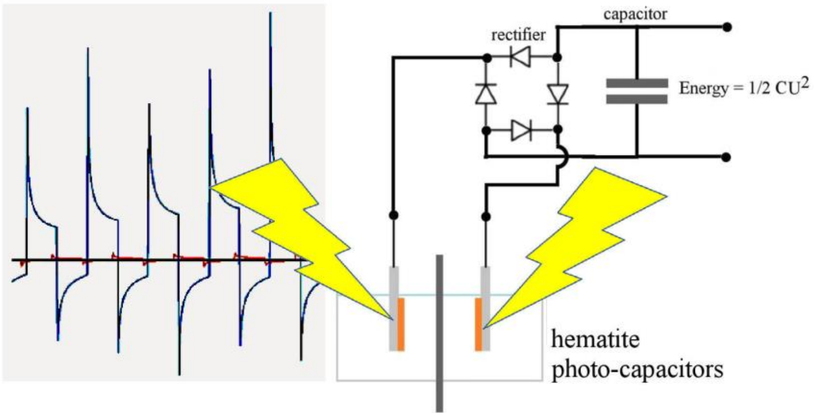
Photo-active electrochemical systems generally operate based on either (i) a steady state mode (e.g. light conversion directly to harvestable charge carriers) or (ii) a transient mode (e.g. capacitive charging up of interfaces). The latter charging component could be considered as an energy loss. However, during oscillations of the light intensity, an alternating "AC" current output can be generated and harvested. As a result, the charging or capacitive component can be employed to harvest energy from oscillating light sources. This approach takes inspiration from the principle of natural photosynthesis, which can provide energy even in the dark.

Transient or oscillating energy generation can be observed in different types of light energy harvesting systems. Organic quinone based dye systems [1] have been shown to generate strong transient alternating photocurrents. In addition, porous inorganic hematite films [2] have been demonstrated to generate AC photo-currents, which are readily rectified to charge a capacitor.



Finally, oscillating infrared radiation, when applied to pyroelectric structures [3], has been shown to result in energy generation and in a rectified current sufficiently strong to drive electrochemical reactions such as hydrogen evolution. This presentation will provide an overview and comparison of transient or AC-solar cell concepts in contrast to steady state concepts.

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Plasmonic Ag/Ag$_3$PO$_4$/MV/EG Photoanode for Photoelectrocatalytical Degradation of Diuretic Drug: A Case Study of Hydrochlorothiazide

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Pharmaceutical drugs are necessary for everyday life medication to treat different disease and as such they end been in the receiving water bodies. These emerging pollutants have been recognized as pollutants of emerging concern for the last 18 years [1]. Among these pharmaceuticals, hydrochlorothiazide (HCTZ) which is one of the most consumed drugs, has been considered for the fact that is omnipresent in most receiving waters. HCTZ falls under diuretic indispensable group of therapeutics used to treat hypertension, congestive heart insufficiency, renal tubular acidosis, diabetes insipidus, formation of kidney stones, and sometimes for hypercalciuria [2]. However, HCTZ does not completely metabolize and about 62.6% of the oral dose is eliminated by the kidneys unchanged in a period of 24 h [3]. Thus, it is most ubiquitous pollutant in the sewage and receiving water bodies. It is in this light, that a novel, robust, effective, efficient, and cost-effective methods of water treatment to combat the alarming water pollution caused by HCTZ, is worth investigating. Photoelectrocatalysis (PEC), a combination of heterogeneous photocatalysis and electrochemical oxidation, emerged as a novel hybrid process for efficient and effective treatment of water polluted by myriad of emerging pharmaceutical pollutants. In this process, the inherent challenges of photocatalysis and electrochemical oxidation are resolved, and both processes participate in generation of reactive oxygen species. For economic viability of PEC, visible light responsive semiconductor should be considered together with electrochemically active and available substrate material.

In this regard, plasmonic silver/silver phosphate/methyl viologen/exfoliated graphite (Ag/Ag$_3$PO$_4$/MV/EG) photoanode was constructed and employed in the photoelectrocatalytic degradation of HCTZ. The photoanode materials were synthesized and characterized using FESEM, EDS, TEM, XRD, XPS, FTIR, and UV-Vis DRS techniques to confirm their structural integrity and other physicochemical properties. The UV-Vis DRS results showed that the composite material exhibited a huge capacity to absorb visible light. After construction of photoanodes, CV, EIS, and LSV were used to characterize the anodes. As depicted from Fig. 1, the EIS results show that photoanode with 5% MV content demonstrated low recombination of photogenerated electron-hole pairs under visible light irradiation. This photoanode demonstrated high removal efficiency of 94% on HCTZ which might be attributed to the plasmonic Ag, MV as electron shuttle, visible light absorbing nature of Ag$_3$PO$_4$ and EG material for its electron transporting properties. The mineralization was tested with TOC, while HPLC was used for intermediates analysis. Among the intermediate, altizide was observed as a fragment of HCTZ. Therefore, this renders the photoanode potential for future applications.

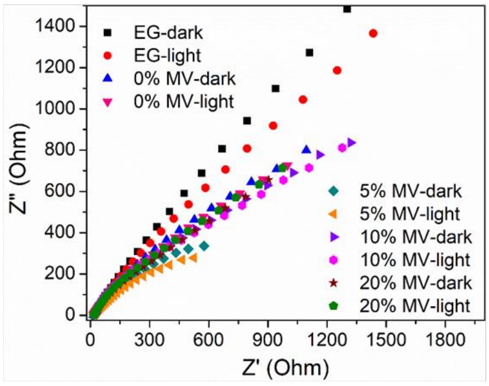

Fig. 1. Electrochemical impedance spectroscopic analysis of different anodes.

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Novel alkaline water electrolysis process with nickel-iron gas diffusion electrodes for oxygen evolution

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Hydrogen production by water electrolysis is one of the most promising energy storage technologies in the context of an increasing share of renewable energies. Alkaline water electrolysis (AEL) has recently gained renewed interest as it was shown that comparable performance to PEM electrolysis can be achieved with nickel-based electrodes using optimized electrodes and separators [1]. Remaining challenges in AEL are related to the electrode activity especially for the oxygen evolution reaction (OER) due to its slow kinetics, insufficient catalyst stability and ohmic losses resulting from gas bubbles detachment [2]. Moreover, the purity of the product gases at lower current density and under dynamic operation, which is mainly affected by the gas solubility in the mixed electrolyte cycles [3], may lead to electrolyzer shutdown for safety reasons. Therefore, our research focusses on the improvement of alkaline water electrolysis with special emphasis on new types of OER electrodes and novel process concepts.

Marini et al. [4] suggested to use two gas diffusion electrodes (GDE) for hydrogen and oxygen evolution separated by a flow of electrolyte. In the present work, we propose a novel AEL concept (Fig. 1) with a GDE as anode, a conventional electrode as cathode and a state-of-the-art Zirfon separator. In this configuration, the electrolyte is only circulated through the cathode compartment which greatly simplifies the process. Moreover, the gas purity during dynamic operation should be increased since dissolved hydrogen is no longer transferred to the anode side. In a first series of measurements, we employed GDE obtained by spraying a mixture of nickel particles and a PTFE suspension on a nickel net as current collector followed by hot pressing. Iron as an active electrocatalyst was introduced through addition of iron acetate to the spraying suspension which was subsequently decomposed during sintering. The electrodes were characterized with physico-chemical methods and subjected to electrochemical measurements in a lab-scale electrolysis cell at 353 K, atmospheric pressure and 32.5 wt.% KOH. Figure 2 shows the cell voltage for a GDE cell compared to a classical electrolysis cell with electrolyte flow in both half cells using an iron-coated nickel foam as anode. It can be seen that almost the same performance could be obtained up to a current density of 400 mA cm^{-2}.

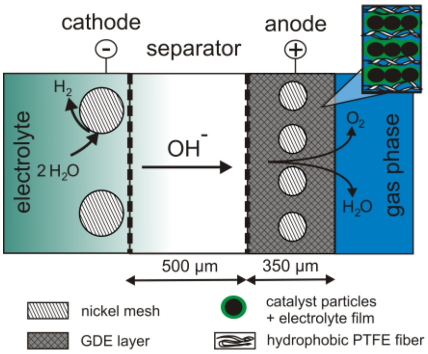

Figure 1: AEL process with anodic GDE

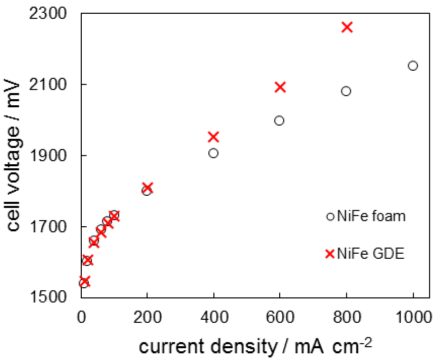

Figure 2: Polarization curve for GDE cell

These first results reveal that AEL with a GDE anode is a very promising new concept and we expect that even better results can be achieved by optimisation of the GDE pore system and through introduction of improved electrocatalysts.

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Improving PEM Fuel Cell Performance Using a Roll Press MPL on Metallic Gas Diffusion Layers

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Performance of fuel cells are highly dependent on the configuration of the membrane electrode assembly, above all the design of the gas diffusion layer and the microporous layer. Flooding within the gas diffusion layer, catalyst layer, and microporous layer pores present a constant challenge which limit the performance of a fuel cell. Metallic gas diffusion layers, coupled with microporous layers help to reduce the flooding phenomenon, which is seen in most high current density regions, as well as reducing contact resistance between the various layers. In this study, a thin film microporous layer was made with graphite flakes and carbon black by means of a roll press method. The thin film microporous layer measured the same thickness (20 µm) as that for carbon paste based microporous layers. The method of making thin film microporous is a novel method tailored for metallic gas diffusion layers. It is also ideal for roll to roll manufacturing and for up-scaling. The thin film microporous layer exhibited no cracking, uniform porosity, and infiltrated the holes of the metallic gas diffusion layer. With these characteristics, the thin film microporous layer displayed increased performance capable of 3 A/cm^2 when compared to metallic gas diffusion layers coated in carbon paste and carbon-fiber gas diffusion layers. High frequency resistance for the thin film microporous layer was also much lower than that of the other configurations to which it is compared, demonstrating improved high frequency resistance even at 2,2 A/cm^2. By adding the graphite flakes and using the roll press method, improvements to the pore shape, surface properties, wettability and morphology all attributed to the increase in fuel cell performance and lowering the contact resistances between the various layers.

Nanotechnology Assisted Electrochemical Biosensing Devices for Continuous Monitoring of Cytokines in Inflammatory Mice

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Cytokine are cell signalling molecules in our immune systems. The dynamic secretion of cytokines makes continuous monitoring of cytokines especially essential for the understanding of chemistry behind the biology of living organisms.[1] Structure-switching DNA molecular machine, recognised with the 2016 Nobel Prize for Chemistry, has demonstrated great success in the continuous monitoring of small molecules in blood serum.[2] Cytokine sensing is challenging due to their typically low abundances in physiological conditions. Nanomaterials fabricated interfaces demonstrated unique advantages in ultrasensitive sensing.[3] Graphene oxide (GO), with its exceptional physical and chemical properties and biocompatibility, holds a tremendous potential for sensing applications. In this study, GO, acting both as the electron transfer bridge and the signal reporter, was attached on the interface to develop an amperometric sensing device based on structure-switching aptamers for long-term detection of cytokines in a living organism. The device incorporates a single layer of GO acting as a signal amplifier on glassy carbon electrodes. The hairpin aptamers specific to interferon-γ (IFN-γ), which were loaded with redox probes, are covalently attached to GO to serve as bio-recognition moieties. IFN-γ was able to trigger the configuration change of aptamers while releasing the trapped redox probes to introduce the electrochemical signal. This *in vivo* device was capable to quantitatively and dynamically detect IFN-γ down to 1.3 pg mL^{-1} secreted by immune cells in cell culture medium with no baseline drift even at high concentration of other nonspecific proteins. The biocompatible devices were also implanted into subcutaneous tissue of enteritis mice, where they performed precise detection of IFN-γ over 48 hours without using physical barriers or active drift correction algorithms. Moreover, the device could be reused even after multiple rounds of regeneration of the sensing interface.

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Formation of Cr(VI) in cobalt containing Cr(III)-based treatment solution

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Chromate conversion coatings were formerly applied to zinc plated steel to enhance its corrosion resistance. Since Cr(VI) compounds were recognized as toxic and carcinogenic, the industrial usage of hexavalent chromium in treatment solution was substituted by a safer, yet effective, trivalent chromium. Due to health risks, the formation of Cr(VI) compounds in Cr(III)-based conversion coatings must be avoided.

The present work aims at enlightening the formation mechanism of hexavalent chromium in the Cr(III)-based conversion coatings, specifically obtained from treatment solution containing cobalt. It is shown that trivalent chromium compounds in the layer might be oxidized to hexavalent chromium by oxygen in the presence of water and under certain circumstances. The presence of Cr(VI) was detected by means of spectrophotometry and the dissolved chromium amount was measured with the aid of inductively coupled plasma optical emission spectroscopy (ICP-OES). Focused ion beam scanning electron microscopy was used to observe the morphology and structure of the films. The total amount of water in the layers was measured employing Karl Fischer Titration. The results indicate that the morphology of the film with a high density of micro-pores increases the probability of water entrapment. This leads to the oxidation of Cr(III) to Cr(VI) by oxygen in the presence of water at elevated temperatures.

Application of Bismuth Vanadate Based Photochemiresistor Sensor for Chemical Oxygen Demand Determination

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The development of electrochemical sensors for COD determination have received great attention in recent years. All these new sensors have been based on either electrocatalytic or photoelectrocatalytic [1] oxidation principles, but none photochemiresistor sensor for COD determination in aqueous solutions have been reported. Electrochemical impedance spectroscopy (EIS) was performed to measure the impedance of bismuth vanadate on FTO in presence of light. The impedance response of the sensor to variations of COD are shown in Fig. 1, and the Fig. 2 shown the equivalent circuit elements used to fit the corresponding spectra. It was found that after each successive addition of an aliquot of glucose, the resistance value decreases, seen also by the decrease in the diameter of the semicircle part of the complex plane impedance plot. The decrease in the resistance can be explained considering that increasing the amount of organic material, the amount of charge transferred between the $BiVO_4$ and glucose becomes higher, as well as the amount of photo-generated conduction band on film. This behavior is not observed when carrying out the same measurements in the absence of light.

The linear relationship between the real resistance and COD concentration in the range of 0.192 mg L^{-1} to 142.2 mg L^{-1} is represented by Equation:

$$R\ (\mathrm{k\Omega\ cm^2}) = 1.95 - 0.72 \pm 0.01 \log [\mathrm{COD\ (mg\ L^{-1})}] \qquad r = 0.9995$$

There is an excellent correlation between the charge transfer resistance and COD concentration in electrolyte solution, with good reproducibility, RSD = 4.1 % for 10 different sensors.

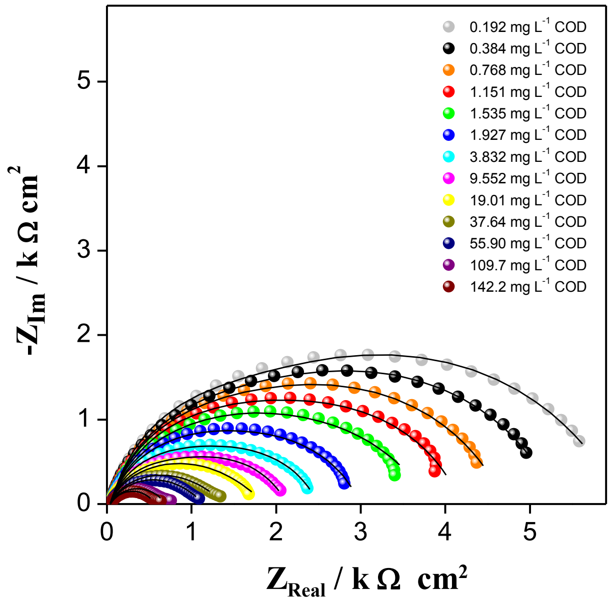

Fig. 1: Impedance spectra of the photochemiresistor sensor with different concentrations of COD in a solution of 0.1 mol L^{-1} $NaCO_3$. [COD] interval = 0.192 – 142.2 mg L^{-1}. Applied potential = 0.90 V (vs. SCE). t = 25°C.

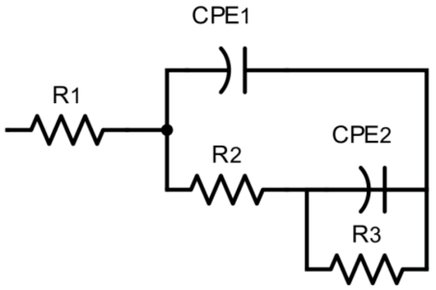

Fig. 2: Electrical equivalent circuit used to fit the complex plane impedance spectra in Fig. 1. R_1 = cell resistance; R_2 = charge transfer resistance at the $BiVO_4$/solution interface; CPE_1 = non-ideal capacitance of the $BiVO_4$/solution interface; R_3 = internal resistance of the film; CPE_2 = non-ideal capacitance of the porous surface.

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Structure and formation of trivalent chromium conversion coatings containing cobalt on zinc plated steel

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Chromate conversion coatings have been used for a long time to improve the corrosion resistance of zinc-electroplated steel parts. However, the industrial usage of Cr(VI) compounds has been strongly restricted by European directives due to their high toxicity. Therefore, Cr(VI)-based conversion coatings were replaced by Cr(III)-based coatings. Although the trivalent chromium conversion layers also serve as barriers, the corrosion protection of chromate conversion coatings without heat treatment is generally better.

It has been shown that the addition of transition metals such as Co(II), Ni(II), and Fe(II) incorporated into Cr(III)-based treatment solutions leads to a better corrosion protection. Not only is the corrosion resistance of the coatings improved in the presence of cobalt ions, but also the visual appearance of the layers seems to be somewhat better. Furthermore, the layers containing Co can be heated up to 150 °C, without loss of corrosion protection. However, the exact role of cobalt in Cr(III)-based treatment solution is not yet fully understood.

The present study intends to elucidate the effect of treatment solution composition on the formation and structure of Cr(III)-based conversion coatings containing cobalt on zinc plated substrates. Model solutions with two different complexing agents, viz. fluoride and oxalate, with and without cobalt were applied to zinc plated steel. Scanning electron microscopy and atomic force microscopy revealed a morphology with microstructural defects that can be improved to a more uniform and adherent structure by adding cobalt to the passivating bath. The elemental compositions of the layers were investigated by Auger electron spectroscopy (AES). Furthermore, the amounts of Cr and Co in the coatings were determined with inductively coupled plasma optical emission spectroscopy (ICP-OES). In good agreement with AES, cobalt was also detected in the layers via ICP-OES measurement. Additionally, the concentrations of Cr(III), Zn(II) and Co(II) species in the Cr(III) based conversion film in the pH range from 0 to 14 were calculated using a thermodynamic model. The aim was to better understand the mechanism of the film formation, together with the experimental results of AES and ICP-OES. Using accelerated corrosion tests, it could be confirmed that the formation of a dense layer is crucial for good corrosion protection.

Highly accurate Controlled Potential Coulometry: application to plutonium metrology

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Controlled-Potential Coulometry (CPC) is a method of choice for determining plutonium in solution because it is not related to chemical standards but only to physical parameters such as time and current which can be calibrated very accurately.

This analytical technique is based on the measurement of a quantity of electricity Q involved in an electrochemical transformation (during either oxidation of reduction) and is governed by Faraday's law which links the quantity of electricity involved in a reaction to the quantity of an element in solution:

$$m=Q\,M/(nF)$$

Where m is the mass of the element in g, M is the molar mass of the element (M=239.076 g/mol for our plutonium sample), n is the number of electrons exchanged during the electrochemical transformation (n=1 in the case of the Pu^{4+}/Pu^{3+} redox pair), and F is Faraday's constant (96485.34 C/mol).

The quantity of electricity is measured by the integration of the current flowing during the oxidation of Pu^{3+} into Pu^{4+} (Figure 1). For a selective reaction, it is necessary to control the potentials applied through a potentiostat and a three electrode set-up. The working electrode material and the medium are carefully chosen in order to minimize interferences. In the case of plutonium, a gold electrode, a pure plutonium nitrate solution and a 0.9 molar nitric acid electrolyte are recommended [1].

This method is called a "primary" method and is of great interest for metrology laboratories providing certified reference materials of plutonium, like the CETAMA. Indeed, it allows to attain high accuracy with a bias close to or below 0.1% on small sample quantities, typically a few milligrams of matter [2,3].

However, coulometry with a high degree of accuracy remains difficult to achieve because every step of the procedure, from sample preparation to signal integration, has to be carefully controlled and optimized.

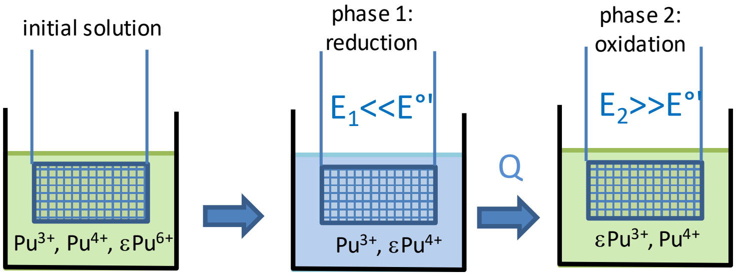

Figure 1: Scheme of the CPC protocol applied to Pu^{4+}/Pu^{3+} redox pair in aqueous nitric acid medium.

The present study describes the key points of the method and emphasizes uncertainty budget estimations through the Monte Carlo Method approach [4], which allows to better take into account the non-Gaussian probability density function of the measurement result.

This work allows to improve trueness and precision (in repeatability conditions) of the method for plutonium determination as well as adapt the procedure, through the appropriate choices of electrode and medium, to the determination of plutonium in presence of large amounts of uranium.

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Electrodeposition of silicon from sulfolane-based electrolyte: Influence of substrate

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Silicon is an important material, finding numerous applications in electronic industry, conversion of solar energy and electrochemical energy storage. Because of its high theoretical capacity of ca. 4 Ah/g [1], silicon is very attractive as alloying material for the anode in Lithium-Ion Batteries (LIB). However, current fabrication processes are expensive and complicated. Electrodeposition could be an alternative due to its simplicity and big advantage to adjust the properties of the silicon layer by varying the electrochemical parameters. Especially the substrate can have a big influence on both the electrochemistry and the composition of the resulting layer.

As highly stable, low volatile, non-flammable, and environmentally friendly solvent sulfolane is a promising candidate for silicon electrodeposition. Therefore, the aim of this study is to investigate the influence of the substrate on silicon deposition from sulfolane based electrolyte and in this way to determine the optimal experimental conditions for the process.

To this end, we have chosen Cu and Ni with the perspective to further apply these substrates as porous hosts for the deposited Si. Additionally, vitreous carbon (GC) as an inert substrate was used for comparison. The exact electrolyte composition was 0.5 M $SiCl_4$ and 0.1 M tetrabutylammonium chloride (TBACl) dissolved in sulfolane. The electrochemical reduction of Si was initially investigated by means of linear sweep voltammetry (LSV). Chronoamperometry, coupled with electrochemical quartz crystal microbalance (QCM) was used for the deposition of Si layers. The surface analysis of the obtained layers was accomplished by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS).

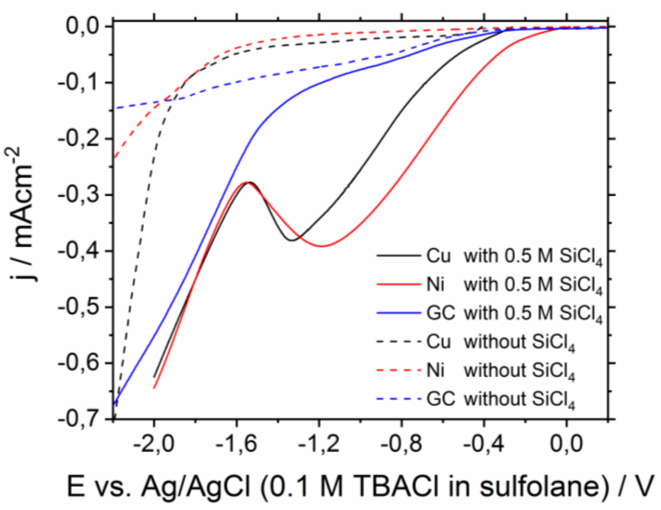

Fig. 1: Linear sweep voltamograms measured in sulfolane, containing 0.1 M TBACl and 0.5 M $SiCl_4$ (solid lines) and without $SiCl_4$ in the electrolyte (dashed lines), ν = 10 mV/s

The voltammetric data (Fig. 1) exhibit just one peak for copper (E = -1.3 V) and nickel (E = -1.2 V). Simultaneously performed QCM measurements did not show any corresponding frequency change. Hence, this redox process is not correlated with any bulk deposition, but could be related to a partial reduction of $SiCl_4$ to soluble species Si_xCl_{4-y}. At more cathodic potentials (E < -1.4 V) the resonance frequency of the QCM decreases, which corresponds to a mass increase at the electrode surface. Analysis of the QCM data for potentiostatic experiments give a M/z ratio of 8.1 g/mol (E = -1.5 V on Cu). With the assumption z = 4 for silicon reduction M_{QCM} = 32.3 g/mol, which is very close to the theoretical value M_{theo} = 28.1 g/mol. With higher overvoltage the damping increased, which is mainly attributed to the onset of electrolyte decomposition.

In contrast, there is no peak in the LSV for vitreous carbon. This could be due to the fact that this substrate is not able to stabilize intermediate compounds of $SiCl_4$. The absence of any bulk peak for all three substrates can be explained by an overlap with the electrolyte decomposition at more negative potentials.

XPS measurements did not detect any contamination from electrolyte decomposition in the silicon layers obtained at low overvoltages. Furthermore, they display the formation of metal silicides at the interface, which can enhance the adhesion of deposit.

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Hybrid capacitor based on a faradaic anthraquinone-grafted carbon electrode operating in low pH aqueous salt solution

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Internally hybridized capacitors can be realized by coupling an electrical double-layer (EDL) carbon electrode with a battery-like component undergoing faradaic redox reactions [1]. The latter can be for example a carbon electrode grafted with electroactive molecules, e.g., polycyclic quinones which in sulfuric acid medium exhibit highly reversible redox reactions involving two protons and two electrons [2, 3]. However, due to the implementation of sulfuric acid, the cell voltage is restricted to ca. 1 V as well as the usage of economically reasoned current collectors made of e.g., stainless steel is limited.

To circumvent the aforementioned disadvantages of sulphuric acid, as well as to provide stable operation of the grafted molecules acknowledged to be sensitive to a pH increase, we applied an acidic aqueous salt solution made from 1 mol L^{-1} $BeSO_4$ (pH = 2.1). Anthraquinone (AQ) moieties (0.1 eq. vs. carbon) have been grafted through the diazonium salts [2] on the surface of the SC2A carbon black (Cabot, S_{DFT} =1502 $m^2\ g^{-1}$, total pore volume = 1.05 $cm^3 \cdot g^{-1}$), giving rise to the SC2A@AQ material. The AQ mass loading in SC2A@AQ was ~15 wt% as determined by CV and TG analysis. The DFT specific surface area of SC2A@AQ was reduced to 191 $m^2\ g^{-1}$, and the total pore volume dropped to 0.46 $cm^3 \cdot g^{-1}$, while the pore size distribution revealed pores up to ca. 15 nm (Fig. 1a). Despite the large difference in S_{DFT} values of the materials, the EDL capacitance of SC2A and SC2A@AQ electrodes in 1 mol L^{-1} $BeSO_4$ were comparable (Fig 1b), which can be attributed to the enhanced wettability of the grafted material owing to the hydrophilicity of the quinone functionalities. In addition, SC2A@AQ demonstrated significant redox peaks resulting from the proton-coupled electron transfer on AQ species. The (-)SC2A@AQ||SC2A(+) hybrid capacitor in 1 mol L^{-1} $BeSO_4$ exhibited a quasi-linear GC/GD profile (Fig. 1c) and twice higher capacitance (51 Fg^{-1*}) compared to the symmetric (-)SC2A||SC2A(+) cell (24 F g^{-1*}). The hybrid capacitor demonstrated an excellent discharge (from 1.5 V) capacitance retention during cycling, with only 8% loss after 10,000 charge/discharge cycles.

* Capacitance expressed per total active mass of the two electrodes

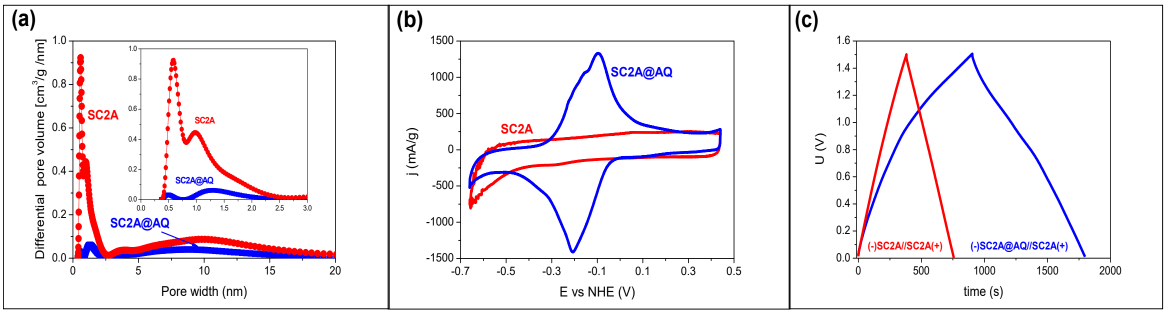

Figure 1: *(a) Pore size distribution of the SC2A and SC2A@AQ carbons; (b) cyclic voltammograms (v = 2 mV s^{-1}) of SC2A and SC2A@AQ electrodes and (c) galvanostatic charge/discharge (j = 200 mA g^{-1}) of symmetric and hybrid cells in 1 mol L^{-1} $BeSO_4$.*

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Electrochemical TERS under Reaction Conditions: Reactivity Mapping on the Nanoscale

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Local detection of reacting species during electrochemical reactions is crucial to establish rational design principles for future highly-efficient fuel cell materials. However, assessing topographic and chemical information simultaneously on the nanoscale level under electrochemical reaction conditions is challenging. Recently, we have suggested to employ electrochemical tip-enhanced Raman spectroscopy (EC-TERS) in the field of electrocatalysis as an important future nano-tool to complement established methodologies (*1*). EC-TERS is a combination of a conventional electrochemical scanning tunneling microscopy (EC-STM) setup and a Raman platform (*2*). The STM-tip is utilized as a nano-antenna that amplifies the otherwise weak Raman signals of few molecular adsorbates and the Raman enhancement originates from surface plasmons that create a strong localized near-field at the STM-tip apex (*3*).

Here, we map operando the electro-oxidation of nano-defects at Au(111) single crystal surfaces in contact with sulfuric acid, and correlate surface topography and electrochemical reactivity with a chemical feature sensitivity of 9.4 nm. Figure 1 shows an EC-STM image of such defective nanoscale structures on Au(111) and the simultaneously acquired EC-TERS map extracted by peak area integration of the gold oxide (AuOx) stretching at 560-580 cm^{-1}. We correlate the apparent height of the defect structures with the EC-TERS AuOx band intensity to quantify the local amount of Au defect oxide and find a linear trend up to 3 nm height difference before signal saturation. A shift in AuOx peak position from 572 to 560 cm^{-1} suggests the existence and nanometer spatial distribution of Au_2O and Au_2O_3 locally present on the nanoscale defect. Delivering such information, the prerequisites are fulfilled to advance the enormous potential of EC-TERS for nanoscale chemical reactivity mapping during electrochemical reactions. With further increase in both sensitivity and resolution, EC-TERS can provide extra-ordinary insights on a wealth of (electro)chemical reactions occurring at the nanoscale, possibly approaching the single active site in the future.

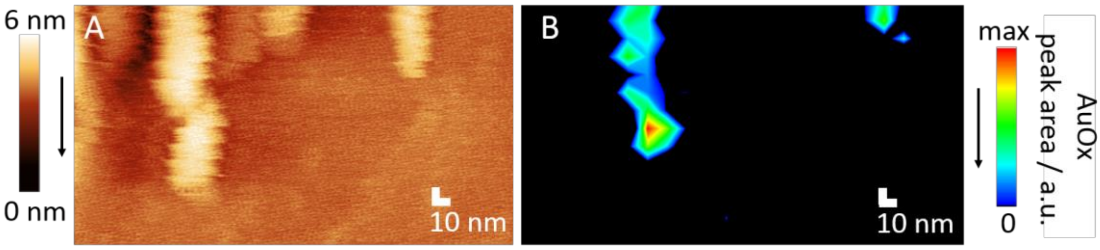

Figure 1 | EC-STM and EC-TERS reactivity mapping under reaction conditions. (A) EC-STM image recorded at 1.45 V vs. Pd-H during gold defect oxidation. The EC-STM image was recorded as scan-to-point image while simultaneously acquiring EC-TER spectra. (B) EC-TERS reactivity map simultaneously acquired with the EC-STM image of (A). The pixel size is 9.4 nm with a spectral acquisition time of 1 s.

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Electrochemical Determination of Arsenic using Silver Nanoparticles.

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Contamination of groundwater and food with arsenic is a problem in many countries around the world. Indeed, the presence and the exposure to this metalloid in food and in water cause a serious public health problem. The response that one can bring is to develop a simple, sensible and accurate analytical method for its detection in environment. With this in mind, we have exploited the feature of nanoscale materials to develop an electrochemical sensor able to detect and quantify arsenic in water.

In the present work, silver colloid was produced by chemical reduction of silver salt (silver nitrate) using citrates in aqueous solution. UV-Vis spectrophotometry indicated the formation of nanoparticles. The surface plasmon resonance peak in absorption spectra of the silver colloidal solution showed an absorption maximum at 435 nm. The dynamic light scattering and zeta potential measurements showed that the size and the zeta potential of the synthesized nanoparticles were about 98 nm and – 50 mV respectively. The nanoparticles have been used to modify the gold electrode for use as a potential electrochemical sensor for the analysis of arsenic in aqueous solution. The cyclic voltammogram recorded using gold electrode modified with silver nanoparticles depicted a well-defined reduction peak of arsenic compared to bare gold electrode. The enhancement of the signal is essentially due to the large surface area attributed to silver nanoparticles. Linear sweep voltammetry has been used to optimize the analytical conditions of arsenic in aqueous solution: it came out that the detection of arsenic in 0.1 M HNO_3 was optimal while the electrode was conditioned at – 0.6 V during 300 s. Under these optimum conditions, a calibration curve was plotted in the concentration range of 0.05 mM to 0.2 m M and the detection limit was estimated at 1.38×10^{-8} M, calculated from a ratio signal / noise 3.

The analytical performance of this modified electrode is good and comparable with electrodes with less complicated structural features. However, the presence of copper and chloride significantly affected the detection system. The developed sensor in this work has shown its ability to determine a high amount of arsenic concentration (5.9 mM) in a small river crossing the city of Yaounde.

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Electrochemical SERS to Mesure Redox Potential of Methylene Blue Bound to Bovine Serum Albumin.

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Proteins play a crucial role in the life process and they contain many chemical functions that can bind with a wide range of ligands including heavy metals, surfactants and drugs. Among various biomolecules, serum albumin is the most abundant protein in many mammalians (52 – 60 % of the total protein plasma). As function, serum albumin maintains the osmotic pressure and pH of the blood and transports a variety of compounds such as drugs and nutrients, mostly through the formation of noncovalent complexes at specific biding sites.

The study of the interactions between proteins and drugs is important since these interactions have consequences for the absorption, distribution, metabolism, excretion, stability and toxicity of drugs. In the literature it is shown that the binding process between bovine serum albumin and methylene blue is spontaneous and the specific electrostatic interactions play a major role is the binding. The present work is essentially focused on determination of the redox potential of methylene blue bound on BSA.

We have prepared a mixture of methylene blue 0.2 mg/mL and BSA 0.2 mg/mL in phosphate buffer 0.01 M containing KNO_3 0.1 M pH 7.0. A volume of this mixture (*approx*. 150 µL) was placed in a specially designed spectroelectrochemical Raman cell. The working electrode was a sphere segment void (SSV) nanostructure made of gold. On scanning the potential from – 100 mV to – 700 mV and back, the SERS spectra change drastically. Even though there is BSA in the solution, the electrochemical transformation and the SER spectra of methylene blue can still be observed. From the changes in the peak height of the feature at 1625 cm^{-1}, assigned to C=N ring stretching, as a function of applied potential and fitting of this experimental data, the mid peak potential for the methylene blue/leuco bound to BSA is found to be – 384 ± 5 mV *vs.* Ag/AgCl. This value is more negative than the value obtained when methylene blue is bound to dsDNA (– 322 ± 8 mV *vs.* Ag/AgCl 1 M NaCl, pH 7.2).

This result can be a starting point for designing and understanding drug delivery process using BSA.

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Functionalized Carbon Nanostructure Platform for Efficient Electrochemical Removal of Heavy Metal from Aqueous System

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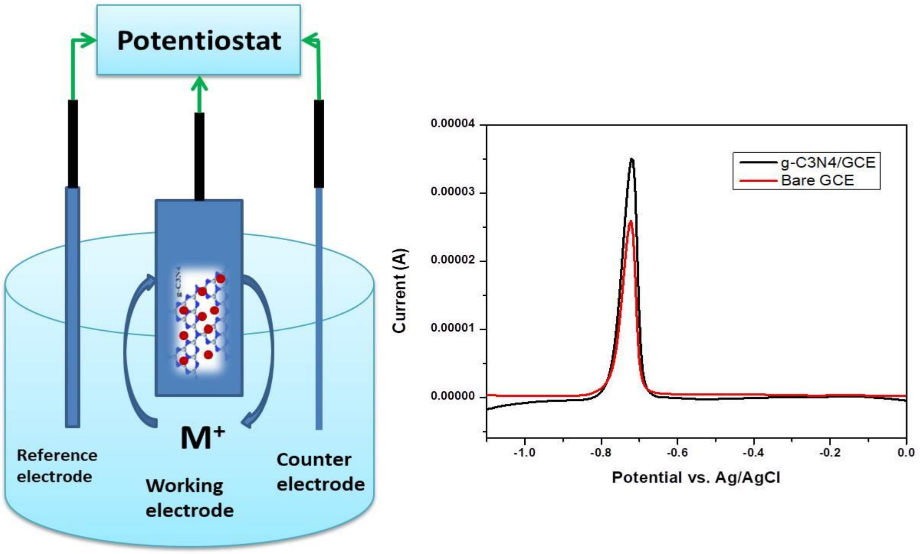
Recently, electrochemical adsorption through pre-concentration of heavy metals on the modified electrodes has been employed as a potential method for removal of heavy metals from aqueous solutions. With this perspective, a novel electrochemical separation system has been developed based on functionalized carbon nanostructures for removal of heavy metals including radionuclide from wastewater. Various carbon nanostructures were compared for their electrochemical adsorption capacity with respect to heavy metal pollutants encountered in waste water. While multi-walled carbon nanotubes and reduced graphene oxide have been explored immensely for sensing, graphitic carbon nitride is still new in the scenario. It was found to show impressive potential for heavy metal decontamination in the present study. Further, it was functionalized with an ion exchange molecule to explore the synergistic effect. This novel structure is proposed to enhance the conductivity of ion exchange molecule for efficient and speedy heavy metal decontamination with aprreciable reusability. Besides being considerably stable, it also allows electrochemical regeneration of the hybrid for subsequent use. The electrochemical adsorption/desorption system using carbon nanostructure supported ion exchange hybrid is a promising strategy for heavy metal decontamination from waste water.



Scheme for electrochemical removal of heavy metal

Voltammetric determination of caffeine in real sample based on the cork-graphite electrochemical sensor

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Caffeine (3,7-dihydro-1,3,7-trimethyl-1H-purine-2,6-dione) or 1-3-7-trimethylantine is a natural alkaloid belonging to N-methyl derivatives of xanthine. This compound is found in food such as coffee, carbonated soft drinks, tea, cocoa beans, chocolate, furthermore in various kinds of beverages. Caffeine has important physiological effects, such as stimulation of the central nervous system, diuresis and gastric acid secretion. However, in high concentration to be a risk species for cardiovascular diseases and also cause hyperactivity. For this reason, different electrochemical sensor has been developed based on the various modified electrodes. In this context, cork consists in the outer bark of the cork oak tree, known botanically as *Quercus Suber L.*. Then, cork powder has been demonstrated promising resources with potential application on adsorption technologies. Cork is composed by organic carbon material (68%±8 of lignocellulosic materials, where theses materials tend to have a much higher content of cellulose, whose main components are suberin (45%) and lignin (21%) and nitrogen content (0.30%±0.09). Majority compounds is suberin and consists of a polyester structure composed of long chain fatty acids, hydroxy fatty and phenolic acids, linked by ester groups. Considering the described, in this study we report the electrochemical behaviour of caffeine and the development and optimization of simple, rapid and low-cost electroanalytical methods using a cork-graphite electrode sensor for determination of caffeine in real samples. The results were compared to high performance liquid chromatography (HPLC) to confirm that this electrochemical sensor is an efficient and cheap technology. Cork-graphite electrode was performed using cork and graphite in a mass ratio of about 10, 50 and 70%. Surface morphology and electrochemical properties was characterized, and after that electrochemical sensor was tested for the determination of caffeine in real samples. Three-electrode cell consisted of an Ag/AgCl (3.0 M KCl) reference electrode, a platinum counter electrode and a synthesized working electrode, with an area of 0.0045 cm^2. Experiments were carried out at room temperature (25±1ºC). Calibrations were analyzed by ordinary linear least-square regression and the relevant results (slopes and intercepts) was obtained with their confidence interval, P=95%. Calibration curves for detection of caffeine (2.5 – 1000 µ caffeine) were obtained using H_2SO_4 0.5 M as supporting electrolyte. Cork-graphite electrode in a mass ratio of 70% exhibits a stable and better sensitive response to caffeine in real samples (drug and beverages). Linear relationship of current peak and caffeine concentration was achieved up to 1000 µM, with a limit of detection of about 2.94 µM.

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ALD Pt Nanoparticles decorated Anodic TiO_2 Nanotube Layers for the Electrocatalytic Oxidation of Methanol

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During the last 15 years, self-organized, anodic TiO2 nanotube layers have attracted significant scientific and technological interest due to the wide range of applications, such as (photo-) catalysis, hydrogen evolution or biomedical uses [1,2]. The synthesis of these 1D TiO2 nanotube structures with high surface are is realized by a conventional electrochemical anodization of Ti substrates, usually in fluoride containing electrolytes.

To increase the catalytic performance of the TiO_2 nanotube layers, the layers can be decorated with noble metal nanoparticles, e.g. Pt [3] or Au [4]. Among the various techniques to coat and decorate TiO_2 nanotube layers homogeneously with secondary materials, atomic layer deposition (ALD) is the only technique able to do it uniformly in the whole volume [5-7]. While metal oxides deposited via ALD usually result in (ultra-) thin films, noble metals are typically deposited as nanoparticles, which is advantageous for catalytic applications.

In this presentation, the homogenous decoration of TiO_2 nanotube layers of various thickness and aspect ratios with Pt nanoparticles is shown [3]. The Pt nanoparticle size was adjusted by using different ALD cycle numbers. The resulting ALD Pt nanoparticle decorated TiO2 nanotube layers showed a superior electrocatalytic performance for the methanol oxidation compared to various reference substrates: Pt-decorated graphite sheets and TiO_2 flat layers (on annealed Ti foils) and a commercial Pt/C catalyst.

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Facile fabrication of WO$_3$ film on FTO glass and its application in photoelectrocatalysis

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WO$_3$ is considered as one of the most attractive materials in photoelectrocatalysis for its stability in acidic condition, nontoxic and low price. Uniform WO$_3$ nanosheetlike film as working electrodes were fabricated on FTO glass by a water bath method and subsequent annealing process. The WO$_3$ film was characterized by scanning electron microscope (SEM), X-ray diffraction (XRD). The property of photoelectrocatalysis is measured by linear sweep voltammetry and cycle voltammetry. The SEM results showed that WO$_3$ film is composed of nanosheets vertically growing on the surface of FTO glass. The thickness of the nanosheets are nearly 100 nm and the side length of them are nearly 1.5 um. The XRD figure shows H$_2$WO$_4$ films is the product after water bath, and it turns into WO$_3$ after annealing. Both samples show a great crystalline. By Linear Sweep Voltammetry (LSV), the ability of photoelectrocatalysis can be speculated by the photocurrent intensity. The sample shows an increasing with photocurrent at the bias of 0.3 V vs Ag/AgCl and it means the voltage added can obviously increasing the separation of photoexcited electrons and holes. Fig. 1 D) is the CV curves of WO$_3$ film in different scan rates ranging from 5 mV to 50 mV in a voltage window of -0.5 V to 0.8 V. It shows the sample is stable in this lager potential window.

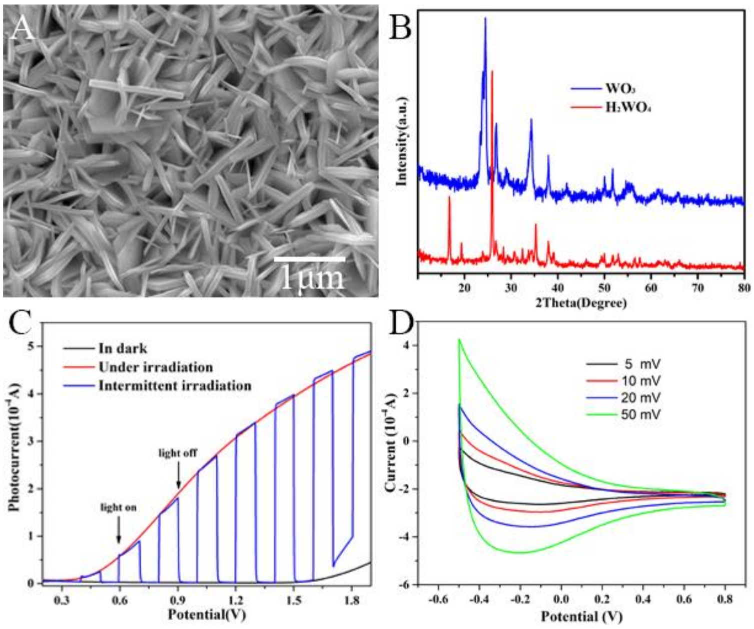

Figure.1 A) SEM image of WO$_3$ film. B) XRD patterns of WO$_3$ film and H$_2$WO$_4$ film. C) LSV curves of WO$_3$ film in dark and under irradiation. D) CV curves of WO$_3$ film in different scan rates.

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Polyaniline nanocomposite based electrochemical sensor for detection of organosulfur compounds in fuels

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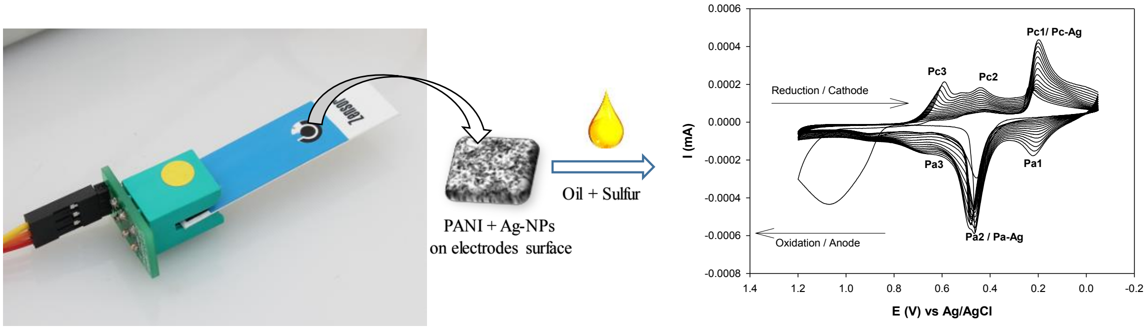
Combustion of organosulfur compounds in fuel results in the emission of sulfur oxides (SO_x), causing various environmental and health hazards, thus, mandating more stringent regulations ≤10 ppmS [1-2]. Quantification of ultralow sulfur containing compounds (SCCs) from fuels requires sampling from consignments, transportation and adequate storage of sample in such a way that it possesses the essential characteristics of the bulk. The samples are then taken to laboratories for analysis using chromatographic techniques such as GC-AED, GC-SCD and GC-MS [3-4]. Such analyses could lead to analyte loss and long turnaround time. Hence, the need to develop real time sulfur detection techniques such as electrochemical sensor for detection of SCCs in fuels. Herein, cyclic voltammetry was employed for the modification of glassy carbon electrode through electro-polymerization with polyaniline (PAni) and electrodeposition of Ag-NPs and Au-NPs. The PAni/AgNPs hybrid conducting electrochemical sensor presented a limit of detection of 7.2 µg/mL for sulfur in fuel. The incorporated PANI/Ag material on the electrode surface was characterized *via* spectroscopic (EDX, XRD, and FT-IR) and microscopic techniques (TEM and SEM). The modified GC/PANI/Ag electrode was used to quantify SCCs in samples and model fuel. Density functional theory studies indicated that hydrogen bonding as well as π–π interactions between the interacting molecules may take place. The science presented herein, demonstrated the potential to develop a cheaper and efficient technique for quantifying sulfur levels in fuel.



Electrode

Electrical Signal (Voltammogram)

Figure 1: Electrode modified through electro-polymerization of PANI/Ag NPs for the detection of SCCs in Fuel (Oil).

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Chemically activating MoS_2 via spontaneous atomic palladium interfacial doping towards efficient hydrogen evolution

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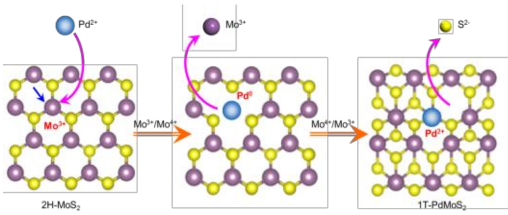
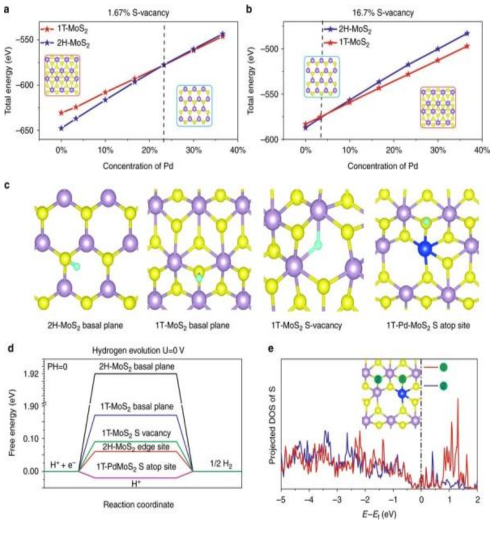
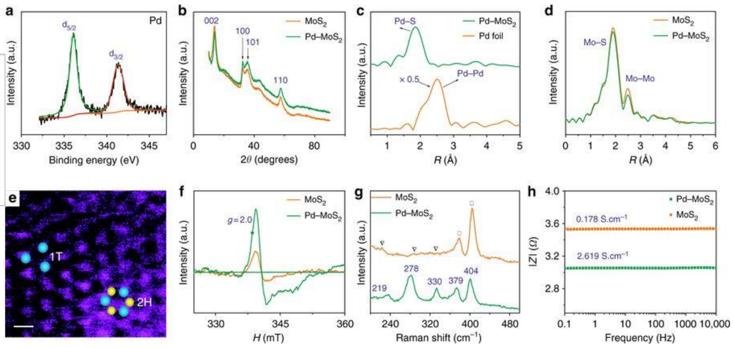
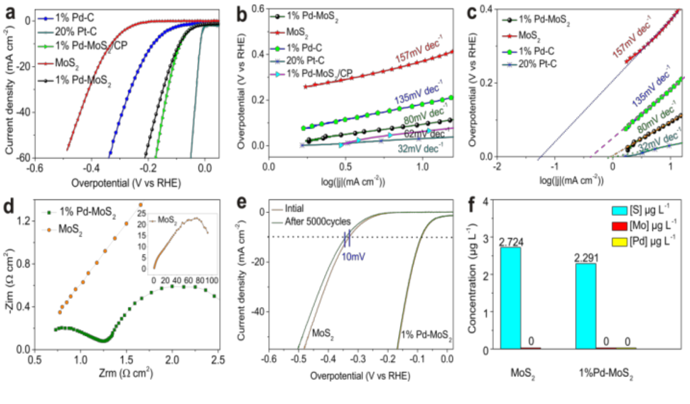
Lacking strategies to simultaneously address the intrinsic activity, site density, electrical transport, and stability problems of chalcogels is restricting their application in catalytic hydrogen production. Herein, we resolve these challenges concurrently through chemically activating the molybdenum disulfide (MoS_2) surface basal plane by doping with a low content of atomic palladium using a spontaneous interfacial redox technique. Palladium substitution occurs at the molybdenum site, simultaneously introducing sulfur vacancy and converting the 2H into the stabilized 1T structure. Theoretical calculations demonstrate the sulfur atoms next to the palladium sites exhibit low hydrogen adsorption energy at –0.02 eV. The final MoS_2 doped with only 1wt% of palladium demonstrates exchange current density of 805 μA cm^{-2} and 78 mV overpotential at 10 mA cm^{-2}, accompanied by a good stability. The combined advantages of our surface activating technique open the possibility of manipulating the catalytic performance of MoS_2 to rival platinum.[1]









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Increased Understanding of non-PGM Catalysts for PEMFC Cathodes

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Electrochemical devices, and PEMFCs in particular, are under intense development for a cleaner and more efficient use of energy, including the use of renewable electricity for transportation. Due to the much slower kinetics of the ORR than those of the hydrogen oxidation reaction on platinum surfaces, 80-90 % of Pt in H_2-fuelled PEMFCs is currently positioned at the cathode. Ideally, highly active and durable PGM-free cathode catalysts could replace Pt-based cathodes in PEMFCs designed for all types of markets.[1] Alternatively, PGM-free cathodes not meeting the stringent durability and power performance targets of the automotive industry may be competitive for other applications (e.g. backup power, mobile applications, CHP…). In project CRESCENDO, dedicated to "Critical Raw material ElectrocatalystS replacement ENabling Designed pOst-2020 PEMFC", we are progressing research and development of non-PGM fuel cell catalysts, and developing methodologies and diagnostic methods for the characterisation of their active site density and turnover frequency as well as approaches for the stabilisation of operation of non-PGM cathode catalysts. Importantly, the reasons why current non-PGM cathode catalyst layers lead to high losses, besides kinetic losses, have been analysed and the learning is being used to rationally re-design the composition and configuration of the catalyst layer. This poster will describe the synthesis routes under consideration and characterisation of catalytic activity towards the oxygen reduction reaction, as determined using rotating disk and floating electrode methods, and in an operating fuel cell. Measured activities will be related to the key descriptors of site density and turnover frequency. Progress made in advancing fuel cell performance towards the final targets by catalyst layer redesign will also be described.

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A Novel Graphene Oxide-Wrapped Pyramidal Sulfur Cathode with Ultra-High Sulfur Content for Lithium–Sulfur Battery

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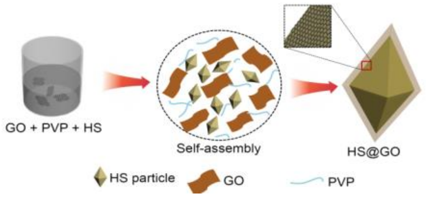
The overwhelming merits of the sulfur cathode in terms of high gravimetric energy density (2500 Wh kg^{-1}) and high theoretical capacity (1675 mAh g^{-1}) of sulfur have created a huge enthusiasm among the academic and industrial community. The numerous drawbacks hindering the practical take-off of the lithium–sulfur (Li–S) technology require significant breakthrough in designing novel sulfur host. Herein, pyramidal sulfur wrapped with graphene oxide (HS@GO) composites cathode with sulfur content up to 92% is obtained via an improved room-temperature bottom-up approach with the aid of polyvinylpyrrolidone (PVP). Material characterization reveals the uniform coating of each individual sulfur particle by a thin wall of graphene oxide and residual PVP. Owing to the particles internal cavity, robustness of the protective GO layer and the interfacial chemical interaction with sulfur, the diffusion of polysulfides is largely avoided. As a result, the HS@GO cathode manifest a high initial reversible capacity of 1301 mA h g-1 at 0.2 C, outstanding capacity retention of 86.4 % at 1 C after 115 cycles and long cycle life of 250 cycles at 2 C. The present work provides an affordable and sustainable approach of confining sulfur at high content which is essential for high-energy density Li–S battery.



Scheme 1. Fabrication process of the HS@GO composites

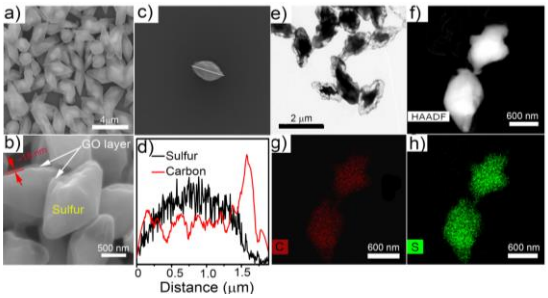


Fig. 1 SEM images of the sulfur particles (a) before and (b) after coating with GO, (c-d) EDX map line scanning profile of HS@GO; (e) TEM image and (f-h) HAADF-STEM-EDS maps of (c) C and (d) S elements.

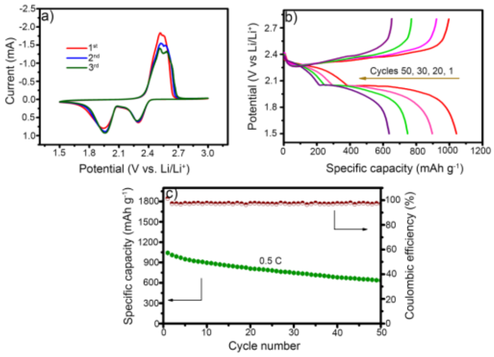


Fig.2 (a) CV curves; (b) voltage vs. capacity profiles at different cycle numbers; (c) cycling performance at 0.5 C of HS@GO composites.

Metal Air Battery
using Expanded Natural Graphite Sheet as a Cathode

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Metal air battery is superior to lithium secondary ion battery because of none danger of ignition and possibility of keeping for a long time. Though it has many problems for development of secondary battery, we think that it is promising device for primary battery for backup power supply and emergency one. In this paper, metal air battery using expanded natural graphite sheet as a cathode and galvanized plate as an anode has been investigated for a power units at the emergency.

Expanded natural graphite sheets have been using for gasket and heat radiation materials because of high thermal conductivity, high electric conductivity, physical and chemical stability, workability and so on. They can be easily get the large size with the wide of 1.3m and long of more than 100m.

The cathode and the anode of the battery were expanded natural graphite sheets and galvanized plate with thickness of 0.4 mm, respectively. The electrolyte was used 10 % sodium chloride water solution absorbed to the filter paper of the thickness of 0.7mm. The cell size was square of 25cm^2. The standard properties of the primary battery, such as discharge capacity, voltage and internal resistance, were measured. We investigated the relationships between the thickness and density of the expanded natural graphite sheets and the battery properties.

The discharge power increased in increasing the thickness and decreasing the density of the expanded natural graphite sheets. Figure 1 shows the discharge properties of the metal air batteries using standard and optimized graphite sheets as cathodes. Standard graphite sheet is the mass production for gasket. Its thickness and density is 0.4mm and 1.0g/cm^3, respectively. The optimized graphite sheet for metal air battery has the thickness of 0.8mm and density of 0.5g/cm^3. The discharge power increased to 8mW/cm^3 from 5mW/cm^3. This value was more than that of metal air battery having the Bincho charcoal as the cathode which have been used science teaching materials for a long time. We studied the series connection for metal air batteries with our original structure shown in Fig. 2. This cell can be obtained the oxygen for activate material from the side of the extended natural graphite sheets. Figure 3 shows DC voltage of the metal air batteries dependence on the number of battery cells connected in series. The DC voltage proportionally and theoretically increase in increasing the number of battery cells. We found that the metal air battery with our original structure is good working which indicate that the oxygen as an activate material for the cathode can be enough obtained from side of the expanded natural graphite sheet. Figure 4 shows a light-emitting (a) and smart phone (B) charging by our metal air battery having an original series connection structure.

We hope that this battery can be used a lot of applications, such as the backup power supply and emergency battery and so on, because DC 12 V output can be obtained in 15 cells connected in series.

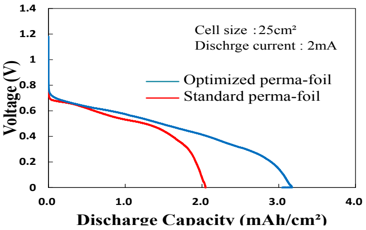

Fig.1. Discharge characteristics of the metal-air battery at red solid line for standard graphite sheet and blue solid line for optimized one. (cell size : 25cm^2)

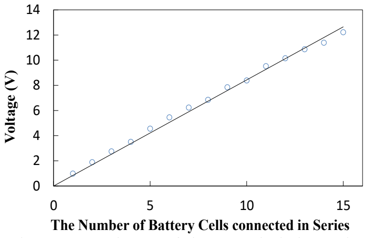

Fig.3 DC voltage of the metal air batteries on the number of battery cells connected in series.

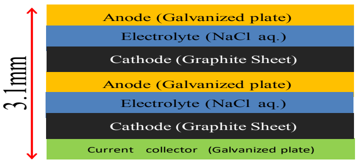

Fig.2 Original series connection of our air metal battery.

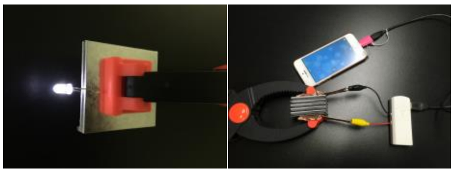

Fig.4 Light-emitting (a) and smart phone (B) charging by our metal air battery having an original series connection structure

Effect of Low Oxygen Annealing on Photoelectrochemical Water Splitting Properties of α-Fe_2O_3 Prepared by Anodization

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Photoelectrochemical (PEC) water splitting is a promising method for the conversion of solar energy into chemical energy stored in the form of hydrogen. Hematite (α-Fe_2O_3) is the one of the most attractive material for photoanodes due to its favorable band gap (1.9-2.2 eV), chemical stability in electrolyte, abundance and low cost. However, the photoelectrochemical performance is limited by several factors such as very short excited state lifetime (<10 ps), short hole diffusion length (2-4 nm), poor surface oxygen evolution reaction kinetics and poor electrical conductivity ($10^{-6}\ \Omega^{-1}\ cm^{-1}$) [1]. In order to enhance the PEC performance of α-Fe_2O_3 photoanodes, wide variety of studies have been reported. Among these approaches, nanostructuring of α-Fe_2O_3 photoanodes is one of the important factors for improving the photogenerated carrier collection [2]. On the other hand, it has been reported that anodization of Fe substrate can fabricate self-organized nanotube structure, and α-Fe_2O_3 prepared by anodization indicate good PEC performance [3]. Therefore, the application of α-Fe_2O_3 nanostructured by anodization as photoanode is expected to yield improved PEC properties. In this work, PEC water splitting properties of nanostructured α-Fe_2O_3 on the FTO glass prepared by anodization and annealing were investigated in order to further improve the PEC performance. As a result, it was found that annealing in a low oxygen ambient leads to nanostructured α-Fe_2O_3 with excellent PEC water splitting performance.

The scanning electron microscopy (SEM) images of α-Fe_2O_3 annealed at 600 °C in 0.03% O_2-Ar and 750 °C in air show a clear difference in morphology (Figure 1). The α-Fe_2O_3 annealed at 750 °C in air (750-Air) consists of nanoparticles with diameter of 60-120 nm, whereas that annealing at 600 °C in low oxygen ambient (600-LO) shows nanoporous structure. The photocurrent of 600-LO shows a value of approximately 1.1 mA/cm^2 at 1.5 V vs. RHE, which is 1.8 times higher than that of 750-Air (approx. 0.6 mA/cm^2) (Figure 2). In addition, it was reported that PEC performance of α-Fe_2O_3 on FTO glass is greatly improved by annealing at 750 °C or higher [4], and the results of our air annealing (600-Air, 750-Air) are consistent with that. However, it is shown that low oxygen annealing can activate α-Fe_2O_3 at a lower temperature of 600 °C. From X-ray photoelectron spectroscopy (XPS) measurements, it was suggested that oxygen vacancies were formed in 600-LO, and conductivity measurements showed that 600-LO had a quite low electrical resistance. Furthermore, intensity modulated photocurrent spectroscopy (IMPS) measurements showed that the generation of the electron-hole pairs were improved as well as the rate constants of recombination and charge transfer. From the above results, it is considered that the combination of anodization and low oxygen annealing is an effective method for obtaining excellent PEC water splitting performance of α-Fe_2O_3.

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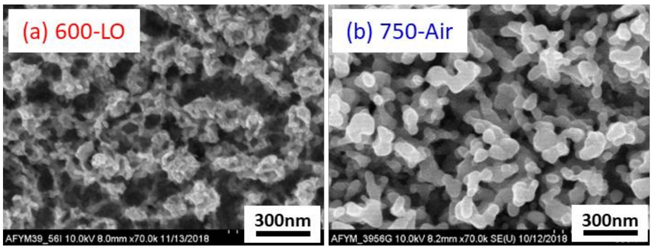

Figure 1. SEM images of α-Fe_2O_3 on the FTO glass after annealing at (a) 600 °C in 0.03% O_2-Ar and (b) 750°C in air.

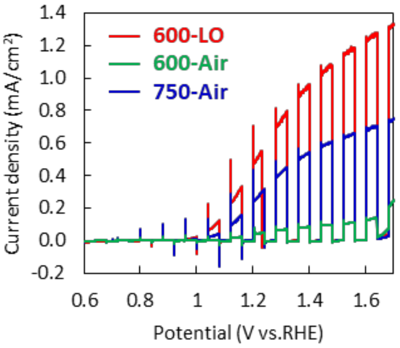

Figure 2. *J-V* curves with chopped light of α-Fe_2O_3 in 1.0 M KOH.

Ionic Liquids in Experiments for School and Schülerlabor

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Ionic Liquids (ILs) are a fascinating class of liquid materials with a unique combination of properties that are otherwise unknown to molecular fluids. Meanwhile sustainable ("Green Chemistry") applications have been established (or are being established) in large-scale chemical processes as well as in the fields of solubilization of biopolymers, in machine technology (good lubricity combined with low compressibility), … , and as electrolytes in electrochemical devices. We are active in the latter field [1, 2]. At the same time, basic physico-chemical research on this class of materials has made tremendous progress in recent years, we ourselves are delivering scientific contributions [3]. In our application-oriented fundamental research we are particularly interested in transport properties of Ils [4-6] which are of great importance for electrochemical energy storage and conversion devices.

However, Ionic Liquids are unknown to most teachers in the field from their own university studies, as their importance has only been revealed by research over the last 10 years. Therefore, based on our scientific expertise and with our Schülerlabor [7] NanoBioLab as test ground, we have developed new school experiments with Ils which we are successively publishing in journals of chemistry-specific didactics [8] and which we have recently summarized in a monograph [9]. It is, in a sense, a down-scaling of scientific achievements, in three respects: from specialist content knowledge to a comprehensible technical level, from high-tech apparatus to simple equipment, and from research laboratories´ budgets to the limited possibilities of schools. The simple yet meaningful and revealing experiments can be carried out by advanced school students or undergraduate chemistry university students, or they can be presented as demonstration experiments in lectures. They are designed to show the diverse benefits of ILs in a variety of fields to the student and at the same time strengthen their evaluation skills for sustainable technologies. Each of the eight experimental chapters includes recipes to synthesize and to recycle the respective Ionic Liquids, for reasons of cost savings.

Here at this conference we present in detail the electrochemistry-related school experiments of this book and show how supercapacitors, lithium-ion batteries and dye-sensitized solar cells can be built and operated with Ils as electrolytes and how lignocellulose can be processed with Ils and the resulting lignin can be electrochemically cleaved with an Ionic Liquid as solvent and simultaneously as electrolyte.

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Enhanced Electrochemiluminescent Brightness and Stability of Porphyrins by Supramolecular Pinning and Pinching for Sensitive Zinc Detection

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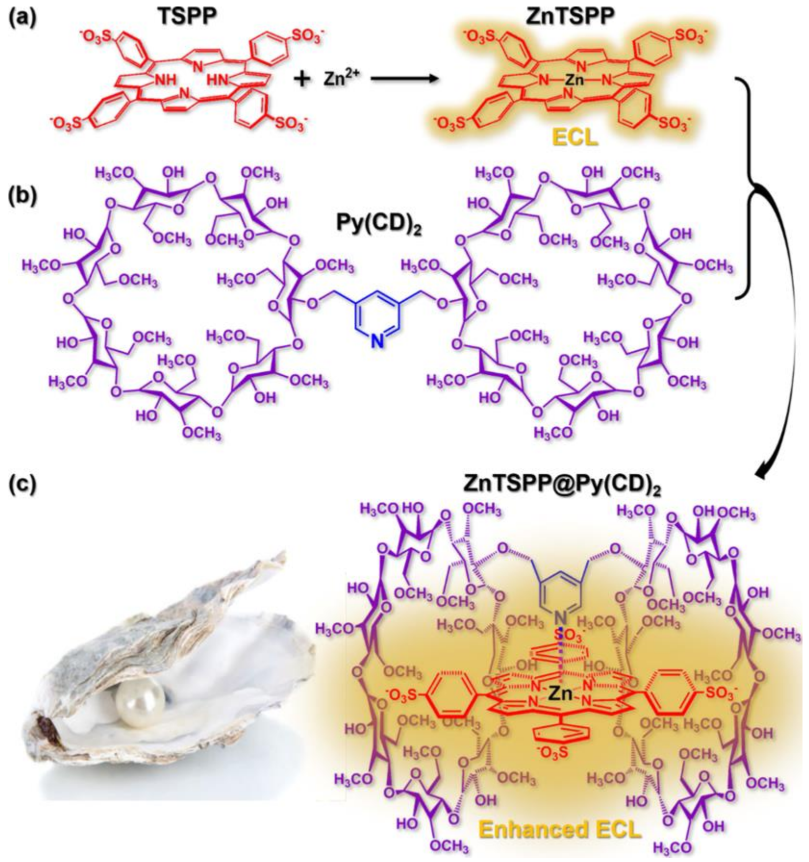
Ultrasensitive electrochemiluminescence (ECL) detection can benefit substantially from the rational configuration of emitter−enhancer stereochemistry. Here, using zinc(II) *meso*-tetra(4-sulfonatophenyl) porphine (ZnTSPP) as a model, we demonstrate that both ECL intensity and photostability of this emitter are significantly improved when trapped in a synthetic ECL-inactive enhancer, pyridyl-bridged β-cyclodextrin dimer (Py(CD)$_2$). Through NMR characterization, we confirmed that ZnTSPP forms a clam-like inclusion complex by pinning and pinching forces from the biocompatible container Py(CD)$_2$ (**Scheme 1**). Up to three-fold increase in ECL brightness of ZnTSPP was witnessed when encapsulated in β-CD. Absorption and emission spectroscopies revealed that the extended excitation lifetime and the restricted mobility of the guest both dedicated to the observed improvement in signal transduction within the host molecule. Such bioinspired entrapment also brought about a marked outperformance in ECL stability. With the help of a newly found coreactant H_2O_2, the hollow and black TSPP@Py(CD)$_2$ was recruited to compose a Zn^{2+}-selective probe capable of sensitive and accurate zinc detection. The reported amplification in E−CL conversion and photophysical properties makes this compact supramolecular assembly and the like a new viable pattern for general enhancement in ECL analytical applications.



Scheme 1. Schematic illustration of the ECL activation on TSPP by Zn^{2+} ligation **(a)**, the structure of the synthetic Py(CD)$_2$ **(b)**, and the enhanced ECL of the supramolecular complex ZnTSPP@Py(CD)$_2$ in which β-CD shell pinches TSPP in and pyridyl *N* pins Zn^{2+} down, a reminiscent of a pearl in a clam **(c)**.

Co-immunocapture and Electrochemical Quantitation of Total and Phosphorylated Amyloid-β40 Monomers

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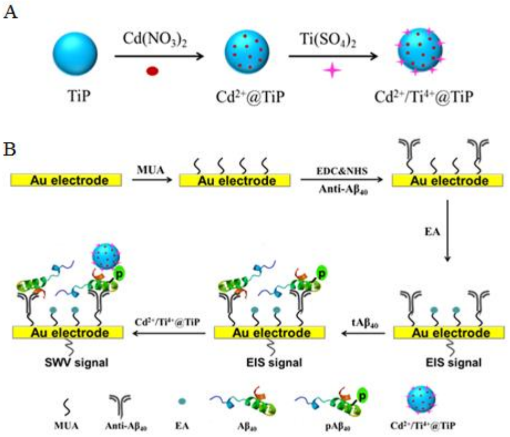
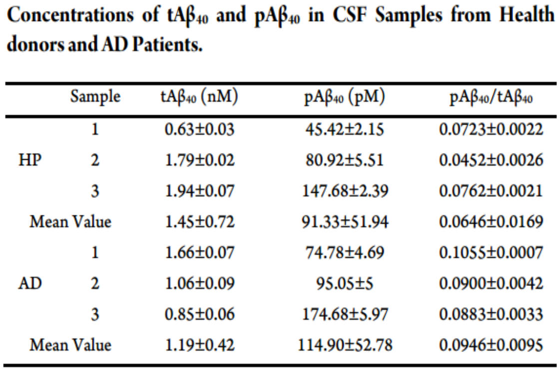
Phosphorylated proteins play important roles in the pathogenesis of Alzheimer's disease (AD). The most abundant constituent in AD's brain deposit is the amyloid-β_{40} peptide ($A\beta_{40}$). Based on it, the degree of phosphorylated $A\beta_{40}$ in body fluids (e.g., cerebrospinal fluid, CSF), which is defined by the ratio of phosphorylated $A\beta_{40}$ to total $A\beta_{40}$ ($pA\beta_{40}/tA\beta_{40}$), is anticipated to be an index for early diagnosis of AD. The major challenge in $pA\beta_{40}/tA\beta_{40}$ detection is the large concentration difference between two $A\beta_{40}$ forms in the real samples, which usually requires multi-channel equipment and complicated detection process. In this paper, we revealed the unexpected close affinities of the anti-$A\beta_{40}$ antibody to $A\beta_{40}$ (40.2 nM^{-1}) and to $pA\beta_{40}$ (42.3 nM^{-1}). Based on it, a convenient co-immunocapture and electrochemical quantitation of $tA\beta_{40}$ and $pA\beta_{40}$ was achieved on an anti-$A\beta_{40}$ antibody immobilized Au electrode (anti-$A\beta_{40}$/Au). Once $A\beta_{40}$ and $pA\beta_{40}$ were synchronously captured on the anti-$A\beta_{40}$/Au electrode, the $tA\beta_{40}$ levels in CSF samples were quantified with electrochemical impedance spectroscopy. With the signal amplification from Cd^{2+}/Ti^{4+}-functionalized titanium phosphate nanospheres (Cd^{2+}/Ti^{4+}@TiP) which was selective conjugated to $pA\beta_{40}$, concentrations of low abundant $pA\beta_{40}$ as low as 1 fM were readily measured by square wave voltammetry. Our results reveal that despite the concentrations of $pA\beta_{40}$ and $tA\beta_{40}$ fluctuate in each individual case, the concentration ratios of $pA\beta_{40}/tA\beta_{40}$ in CSF samples from AD patients are significant larger than those from healthy donors. It demonstrates that the degree of phosphorylated $A\beta_{40}$ is hopeful to be an effective index for evaluating the AD progress and improving the accuracy of clinic AD diagnosis.





Concentrations of $tA\beta_{40}$ and $pA\beta_{40}$ in CSF Samples from Health donors and AD Patients.

	Sample	$tA\beta_{40}$ (nM)	$pA\beta_{40}$ (pM)	$pA\beta_{40}/tA\beta_{40}$
HP	1	0.63±0.03	45.42±2.15	0.0723±0.0022
	2	1.79±0.02	80.92±5.51	0.0452±0.0026
	3	1.94±0.07	147.68±2.39	0.0762±0.0021
Mean Value		1.45±0.72	91.33±51.94	0.0646±0.0169
AD	1	1.66±0.07	74.78±4.69	0.1055±0.0007
	2	1.06±0.09	95.05±5	0.0900±0.0042
	3	0.85±0.06	174.68±5.97	0.0883±0.0033
Mean Value		1.19±0.42	114.90±52.78	0.0946±0.0095

The Effect of Au in Shape-controlled Pt based Nanoparticles as Anodic Catalysts for Low-temperature Fuel Cells

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Fuel cells are regarded as high-efficiency promising alternative power sources that could offer pollution free energy. Even though hydrogen oxidation in polymer electrolyte membrane fuel cell leads to zero emission of harmful gasses, small organic molecules (SOM) are also investigated as fuels due to the issues with hydrogen availability, cost of production and safety hazards. Formic acid is one of the most investigated SOMs for this use. At state of the art platinum nanocatalysts formic acid oxidation reaction (FAOR) proceeds through a dual path mechanism, involving a formation of a catalytic poison, CO that is formed in the indirect reaction pathway. In order to address this problem, Pt/C nanocubic catalysts were synthesized by a water-in-oil microemulsion method, with the addition of the optimal amount of a capping agent to induce the change of nanoparticle shape.[1,2] Pt nanocubes, that have a higher contribution of (100) oriented planes than common cube-octahedron nanoparticles, have exhibited higher stability under fuel cell operating conditions in acidic media, and better resistivity towards CO poisoning due to a higher share of weakly adsorbed CO. This contributed to their improved catalytic performance in FAOR. Further catalytic enhancement is achieved by synthesizing shape controlled bimetallic PtAu nanoparticles under the same conditions.[3] Presence of Au during simultaneous precursor reduction affects the kinetic of the particle growth, causing the formation of tetrahedron-like shaped nanoparticles. The ensemble effect of Au on Pt further improves catalyst activity over four times, and ordered shape contributes to particle stability. This was corroborated by Electrochemical and High Resolution Transmission Electron Microscopy characterization (HRTEM) with Energy Dispersive X-ray Spectroscopy (EDXS), and also by X-Ray Diffraction (XRD) and X-Ray Photoelectron Spectroscopy (XPS).

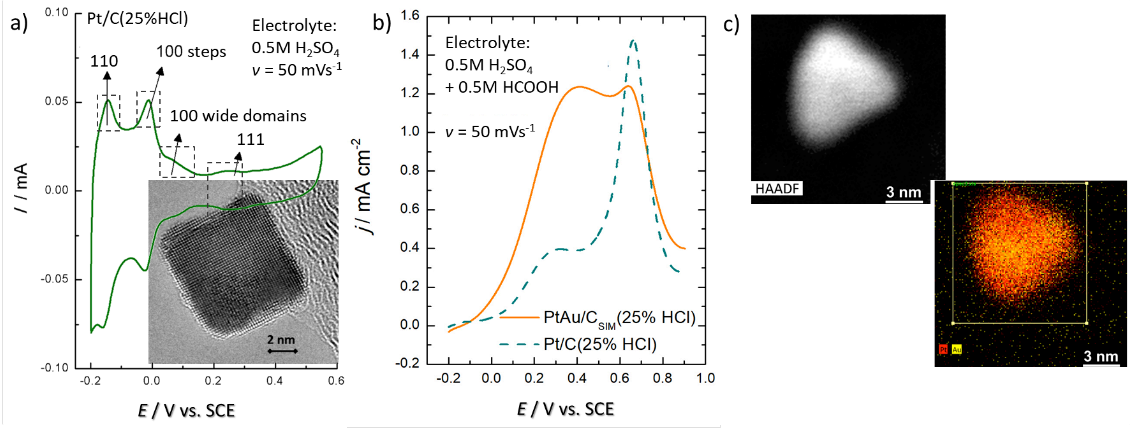

Fig 1. a) Short range CV recorded at Pt nanocubic catalyst in supporting electrolyte with HRTEM micrograph in inset,[1] b) FAOR potentiodynamic curves in anodic direction recorded at Pt nanocubes and PtAu nanotetrahedrons, c) HAADF TEM image of PtAu nanoparticle with corresponding EDXS map

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