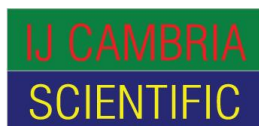


Butler Meeting

BOOK OF ABSTRACTS

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ABERDEEN

The 2018 RSC Butler Meeting has been made possible by the generous support of our sponsors:



Welcome to the Royal Society of Chemistry Scotland and North of England Regional Electrochemistry Symposium, 2018! The following contains safety information, abstracts and a running order for the symposium. This meeting would not be happening without the hugely generous support of our sponsors, so please do visit them in the exhibition area and show your gratitude for keeping the Butler meetings free to attend. Many thanks also to my students (Jonathan Mwanda, Onagie Ayemoba, Marco Papasizza and Chris Wildi) for their helping in organising this meeting. I hope you enjoy Butler2018.

Angel

Meeting Information

Registration will be in the foyer area just before lecture theatre Meston 1 of the Meston Building. Talks will be held in lecture theatre Meston 1. **Breaks, lunches** and the **poster sessions** will also take place in this foyer area. We would be grateful if poster exhibitors could put up their posters as soon as they can in order to allow people more time to read them during breaks.

Fire and Security information

In case of a fire alarm please leave in an orderly fashion and assemble at the Academic Square enclosed by Meston Building, Fraser Noble Building and the Library. In case of emergency on campus, please dial 01224 273939 (int. ext. 3939).

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Local Information

The King's College Campus of the University of Aberdeen (AB24 3UE) is located in Old Aberdeen, approximately 1.5 miles from the city centre. It can be accessed from the airport by bus (Stagecoach 727, alight at Kittybrewster, Burnett Place) or by taxi (£10-15). From Aberdeen train station the campus can be reached by bus (First buses Number 20, 23, 60 and 68), by taxi (£5-10), or on foot (allow 35-40 minutes).



2018 RSC Butler Symposium

25th April, Department of Chemistry

School of Natural and Computing Sciences

University of Aberdeen

Programme

- 10:00 Registration and coffee
- 10:45 Welcome / safety notes
- 10:50 – 11:10 Li Tianyue – *University of Edinburgh*
Lead-free Pseudo-three dimensional Iodobismuthate Materials as Light Absorbers for Hybrid Solar Cells
- 11:10 – 11:30 Michael Shipman – *University of Glasgow*
A re-evaluation of Sn(II) phthalocyanine as a catalyst for the electrosynthesis of ammonia
- 11:30 – 11:50 Zhen Yao – *University of St Andrews*
Electrodeposition of Cu-Pd onto a Pyridine-terminated Self-assembled Monolayer
- 11:50 – 12:10 Jonathan Amolo Mwanda – *University of Aberdeen*
Electrochemical Metallization of Cyanide-Modified Pt (111) electrodes with Copper, Silver and Palladium
- 12:10 – 12:30 Mohammed Shbeh – *University of Sheffield*
Modification of Titanium Foams for Biomedical Applications

- 12:30 – 13:30 Lunch and posters
- 13:30 – 13:50 Marco Papasizza – *University of Aberdeen*
In situ monitoring with ATR-SEIRAS of CO₂ electroreduction on Au in a RTIL / water mixture
- 13:50 – 14:10 Liam Plunkett – *Newcastle University*
Investigation into Non-Aqueous Aluminium Battery Materials for Enhanced Power and Capacity
- 14:10 – 14:30 Edmund Leary – *University of Liverpool*
Bias-driven conductance increase with length in porphyrin tapes
- 14:30 – 14:50 Tabbi Wilberforce – *University of the West of Scotland*
Effect of humidification of reactive gases on the performance of a proton exchange membrane fuel cell
- 14:50 – 15:15 Coffee and posters
- 15:15 – 16:00 **Keynote lecture** – Prof. Richard Nichols, *University of Liverpool*
Charge Transfer at the Single Molecule Level with Metal and Semiconductor Electrodes
- 16:00 – 16:15 Prizes and close

KEYNOTE LECTURE

Charge Transfer at the Single Molecule Level with Metal and Semiconductor Electrodes

Richard J. Nichols^{a*}, Edmund Leary^a, Nicola Kay^a, Samantha Catarelli^a, Andrea Vezzoli^a, Richard J. Brooke^b, Nicolò Ferri^a, Simon J. Higgins^a, Walther Schwarzacher^b and Jens Ulstrup^c

a) Department of Chemistry, University of Liverpool, Crown Street, Liverpool L69 7ZD, UK

b) H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK

c) DTU, Lyngby, Denmark.

***Department of Chemistry, University of Liverpool, Crown Street, Liverpool L69 7ZD, UK**

Abstract: We have exploited STM based methods for making single molecule measurements on a wide variety of molecular targets from short molecular bridges, to redox active organometallic molecular wires and for complex supramolecular assemblies. Such measurements have been made as two-terminal determinations and also under electrochemical potential control with electrolytes varying from aqueous solutions to ionic liquids. Recently we have extended such measurements to semiconductor electrodes. In this lecture I will start by discussing charge transfer through single molecules at electrochemical interfaces and in particular discuss how the electrochemical environment can influence charge transfer. I will then focus on recent results with semiconductor contacts. In a recent publication in Nano Letters [1] we have shown that it is possible to make measurements of single molecules connected at one end to gallium arsenide and at the other end to a gold scanning tunnelling microscope tip. Using this methodology we can record current-voltage response of semiconductor – molecule – metal devices and measure the electrical conductance of single molecules in such junctions. As well as showing that it is possible to form single molecule devices contacted to the semiconductor gallium arsenide we have also recently demonstrated that such single molecule devices show a strong photocurrent response.[2] The photo-current response in these molecular junctions can be controlled through the choice of the semiconductor and its doping density, the molecular bridge and also the light intensity and wavelength. To conclude potential future applications in single-molecule semiconductor (photo-) electrochemistry will be discussed.

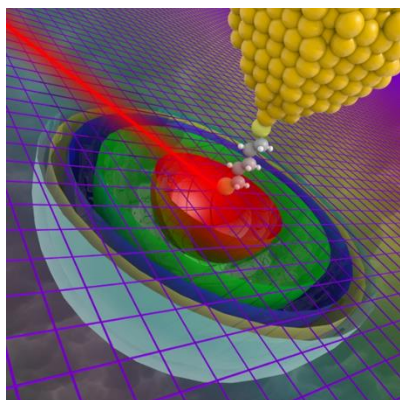


Fig. 1 Image of GaAs-molecule-gold junction from Reference [2], American Chemical Society.

References

- [1] Vezzoli, A.; Brooke, R. J.; Ferri, N.; Higgins, S. J.; Schwarzacher, W.; Nichols, R. J. *Nano Lett.* **2017**, 17 (2), 1109–1115.
- [2] Vezzoli, A.; Brooke, R. J.; Higgins, S. J.; Schwarzacher, W.; Nichols, R. J. *Nano Lett.* **2017**, acs.nanolett.7b02762.

ORAL CONTRIBUTIONS

Lead-free Pseudo-three dimensional Iodobismuthate Materials as Light Absorbers for Hybrid Solar Cells

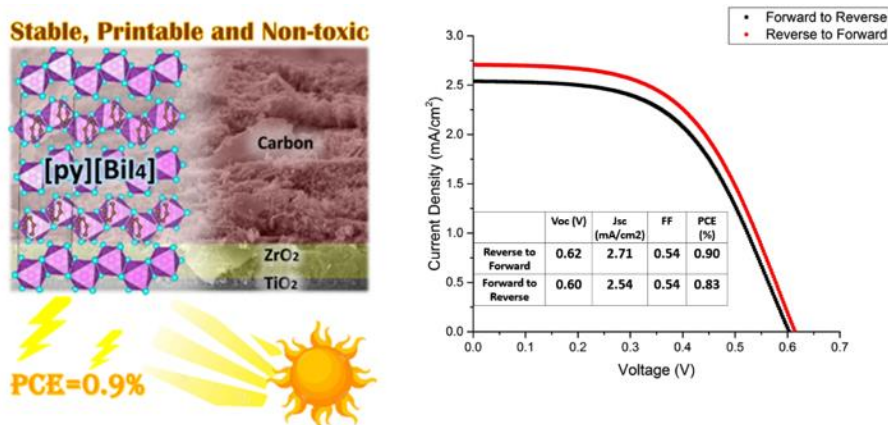
Tianyue Li,¹ Qifei Wang,² Gary S. Nichol,¹ Carole A. Morrison,¹ Hongwei Han,² Yue Hu,² and Neil Robertson^{1*}

¹School of Chemistry and EaStCHEM, University of Edinburgh, King's Buildings, David Brewster Road, Edinburgh, Scotland EH9 3FJ, UK. Email: Tianyue.li@ed.ac.uk; Neil.Robertson@ed.ac.uk

²Michael Grätzel Center for Mesoscopic Solar Cells, Wuhan National Laboratory for Optoelectronics, School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan, Hubei, 430074, People's Republic of China.

Abstract: The outstanding efficiency of organic-inorganic lead-halide perovskites solar cells has led to a new era of solar energy research.¹ One of the potential limitations however is the use of toxic Pb in the absorber, and studies into main-group halides are therefore emerging. In this work, $[\text{C}_5\text{H}_6\text{N}][\text{BiI}_4]$ (PYB) and $[\text{C}_3\text{H}_5\text{N}_2\text{S}][\text{BiI}_4]$ (ATB) with 1D structures have been studied and compared with other 0D Bi-iodide materials. Their structures have been investigated by single crystal X-ray diffraction showing $[\text{BiI}_4]^-$ anionic chains built by edge-sharing $[\text{BiI}_6]^{3-}$ octahedra in both materials. Short I...I, I...C contacts and hydrogen bonding of PYB and ATB give rise to three-dimensional intermolecular interactions. All the compounds are semiconductors, with band gaps lower than 2.0 eV, and the contribution from the organic moieties to the conduction band minimum has been derived by density functional theory calculations. Solid-state optical and electrochemical studies performed on powders and thin films were carried out, and their stabilities under ambient environment have been demonstrated. PYB and ATB were used as light absorbers in fully-printable mesoscopic solar cells giving functioning cells with efficiencies up to 0.9%, showing a promising new approach towards the development of lead-free third-generation photovoltaic materials.²

Fig. 1 Cross-sectional SEM image of the mesoscopic triple-layer solar cell architecture (left) and J-V curve of champion cell (right).



References

1. M. Green and A. Ho-Baillie, *ACS Energy Lett.*, 2017, **2**(4), 822-830
2. T. Li, Y. Hu, C. Morrison, W. Wu, H. Han and N. Robertson, *Sustain. Energy Fuels*, 2017, **1**, 308-316

A re-evaluation of Sn(II) phthalocyanine as a catalyst for the electrosynthesis of ammonia

Michael A. Shipman, Mark D. Symes

School of Chemistry, University of Glasgow, Glasgow, G12 8QQ, United Kingdom .
m.shipman.1@research.gla.ac.uk

Abstract:

The electrosynthesis of ammonia from nitrogen and water is a topic of considerable interest in the quest for sustainable and decentralized ammonia production.¹ Tin(II) phthalocyanine complexes have been proposed as electrocatalysts for nitrogen reduction to ammonia in aqueous solutions, with Faradaic yields approaching 2% having been reported. Herein, however, we show that such complexes are not electrocatalysts for this transformation, with the amount of ammonia detected being essentially the same under Nitrogen and under Argon. Instead, we suggest that apparent ammonia generation could arise either through contaminants in the as-prepared tin(II) phthalocyanine complexes, or by the electro-decomposition of these complexes under cathodic bias.²

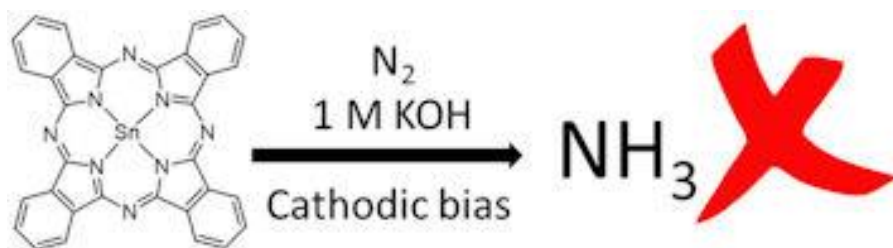


Fig. 1 Simplified Mechanism for the proposed ammonia synthesis route.

References

- 1 M.A. Shipman, M.D. Symes, *Catalysis Today*, 2017, **286**, 57-68.
- 2 M.A. Shipman, M.D. Symes, *Electrochimica Acta* 2017, **258**, 618-622

Electrodeposition of Cu-Pd onto a Pyridine-terminated Self-assembled Monolayer

Zhen Yao, Manfred Buck

EaStCHEM School of Chemistry, University of St Andrews, North Haugh, St Andrews, Fife, KY16 9ST, UK
zy9@st-andrews.ac.uk

Abstract:

Self-assembled monolayers (SAMs) on metal substrates have diverse applications ranging from molecular sensors to molecular electronics. There have been efforts to expand the versatility of these SAMs via generation of a metal/organic interface on top of a SAM¹ as these metal-SAM-metal systems are of interest to molecule based electronics. Experiments²⁻⁴ have identified a highly practical two-step procedure to deposit Pd on top of a pyridine-terminated SAM where metal clusters are generated via complexation and electrochemical reduction. This scheme, compared to conventional SAM templated deposition⁵, is not limited by defects in the SAM but harnesses molecular properties, thus providing better control over nucleation and growth from which new opportunities for producing metal structures with ultra-small dimensions arise.

Here we present an exploration of the two-step deposition scheme towards the generation of ultra-small metal structures. Nucleation and growth of Cu-Pd nanoparticles via complexation and electrochemical reduction are investigated by cyclic voltammetry (CV), chronoamperometry, scanning tunnelling microscopy (STM) and atomic force microscopy (AFM). By optimising conditions, metal layers less than 2 nm thick can be generated. Furthermore, patterned layers can be generated using STM and AFM with dimensions ranging from the micrometre to the sub-10 nm range.

References

- 1 H. Haick and D. Cahen, *Prog. Surf. Sci.*, 2008, **83**, 217–261.
- 2 C. Silien, D. Lahaye, M. Caffio, R. Schaub, N. R. Champness and M. Buck, *Langmuir*, 2011, **27**, 2567–2574.
- 3 T. Baunach, V. Ivanovo, D. M. Kolb, H. G. Boyen, P. Ziemann, M. Büttner and P. Oelhafen, *Adv. Mater.*, 2004, **16**, 2024–2028.
- 4 V. Ivanova, T. Baunach and D. M. Kolb, *Electrochim. Acta*, 2005, **50**, 4283–4288.
- 5 Z. She, A. DiFalco, G. Hähner, and M. Buck, *Beilstein J. Nanotechnol.*, 2012, **3**, 101-113.

Electrochemical Metallization of Cyanide-Modified Pt (111) electrodes with Copper, Silver and Palladium

Jonathan A. Mwanda and Angel Cuesta

Department of Chemistry, University of Aberdeen

AB24 3UE, Aberdeen Scotland, UK

r01jam15@abdn.ac.uk

Abstract: The demand to increase electronic power densities has led to extensive research into the use of molecules as conductors as a means to attain the ultimate miniaturization of electric components. Development of robust contacts across small groups of molecules will most likely be required for future applications of molecular electronics. One viable method to establish this kind of contacts is to sandwich small areas of a molecular monolayer between a metal substrate and electrodeposited 2-dimensional metallic nanoislands. Metal cations have been shown to attach to the surface of cyanide-modified Pt (111) electrodes via non-covalent interactions between the negative end of the cyanide dipole and their positive charge¹. In the case of Cu²⁺, the interaction is irreversible, and reduction yields Cu bidimensional nanoislands on the cyanide adlayer in a Pt/CN/Cu ‘sandwich’ configuration². We have attempted the metallization of cyanide-modified Pt (111) electrodes with palladium, copper and silver using the same sequence of irreversible adsorption followed by electrochemical reduction. Cyclic voltammetry in both sulfuric acid and perchloric acid solutions shows that also in these cases the attachment of Pd²⁺ and Ag⁺ via non-covalent interactions is irreversible, but a gradual change in the cyclic voltammograms upon cycling suggests a slow migration of palladium and silver underneath the cyanide adlayer, in direct contact with the Pt (111) substrate. In-situ STM imaging shows the epitaxial deposition of small palladium bidimensional islands that are stable within the potential region positive of the hydrogen evolution region. Excursion to the hydrogen evolution potential region provokes the growth of the palladium islands, which increases with continuous potential cycling, as does the voltammetric profile. In the case of silver, displacement of cyanide and direct deposition of silver on the platinum substrate was also observed by in-situ STM. Repeated cycling led to the formation of Ag/Pt surface alloy accompanied with dissolution at more positive potentials with each repeated potential cycling.

In-situ STM imaging of Cu deposition on the cyanide modified platinum (111) clearly shows the formation of bidimensional islands that grow via an Ostwald ripening process². Comparison of the results with Pd²⁺ and Ag⁺ with those obtained with Cu provides further support to our previous conclusions² that the cyanide adlayer on Pt (111) can be successfully metallized with bidimensional Cu nanoislands.

References

1. Escudero-Escribano, M. *et al. ChemPhysChem.* 2011, **12**, 2230–2234.
2. Escudero-Escribano, M., Wildi, C., Mwanda, J. A. & Cuesta, A. J. *Solid State Electrochem.* 2016, **20**, 1087-1094.
3. J. A. Mwanda and A. Cuesta, manuscript submitted for publication.

Modification of Titanium Foams for Biomedical Applications

Mohammed Shbeh¹, Aleksey Yerokhin², Russell Goodall¹

¹Department of Materials Science and Engineering, University of Sheffield, Sir Robert Hadfield Building, Mappin Street, Sheffield S1 3JD, UK ; r.goodall@sheffield.ac.uk; mmmshbeh1@sheffield.ac.uk,

²School of Materials, University of Manchester ; Aleksey.yerokhin@manchester.ac.uk

Abstract: Every year, hundreds of thousands of people in the UK endure tooth loss. This problem is becoming more serious than ever, especially with increased life expectancy and poor nutrition. Titanium dental implants are currently a popular choice for replacing missing teeth. However, there are several issues associated with them, such as the high cost and the stress shielding phenomenon as well as the bio-inertness of Ti (where bio active behaviour would be preferred. Solving the aforementioned issues can be approached by developing novel Ti implants using cost effective manufacturing techniques with porous bioinspired structure that replicate the natural structure of the bone for better mechanical fixation and a biologically active surface for improved chemical integration. Hence, the usage of cyclic voltammetry in PEO treatment of porous Ti parts with different amount of porosity produced by Metal Injection Moulding (MIM) and MIM in combination with a space holder was investigated. It was found that porous samples with higher porosity and open pores develop much thicker surface layers that penetrate through the inner structure of the samples forming a network of surface and subsurface coatings. The results are of potential benefit in producing surface engineered porous samples for biomedical applications which do not only address the stress shielding problem, but also improve the chemical integration [1].

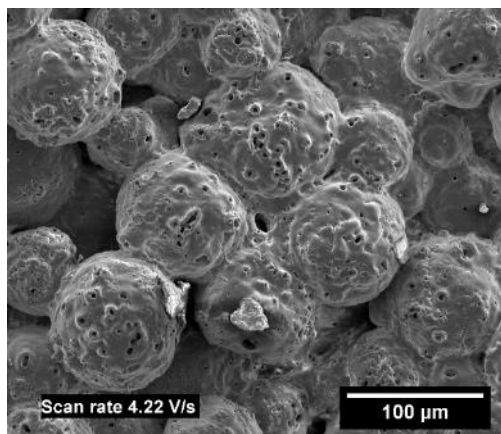


Fig. 1 SEM micrograph of relatively dense sample treated at a scan rate of 4.22 V s^{-1} [1]

References

1. Shbeh, M., A. Yerokhin, and R. Goodall, *Cyclic Voltammetry Study of PEO Processing of Porous Ti and Resulting Coatings*. Applied Surface Science, 2018.

In situ monitoring with ATR-SEIRAS of CO₂ electroreduction on Au in a RTIL / water mixture

Marco Papasizza, Angel Cuesta

Department of Chemistry, School of Natural and Computing Sciences, University of Aberdeen,
AB24 3UE Aberdeen, Scotland, UK.

m.papasizza@abdn.ac.uk

Abstract: The electrochemical reduction of CO₂ to CO in ionic liquids and ionic-liquid / water mixtures has received considerable attention due to recent claims of extraordinarily high energy efficiencies. We report here a study of CO₂ electroreduction on Au in a [EMIM]BF₄ / H₂O mixture (18% mol / mol) combining cyclic voltammetry and surface-enhanced infrared absorption spectroscopy in the attenuated total reflection mode (ATR-SEIRAS). The onset of the reduction current in the CV coincides with a decrease of the interfacial CO₂ concentration, but the appearance of adsorbed CO (CO_{ad}) is slightly delayed, as CO must probably first reach a minimum concentration at the interface. Comparisons with spectra collected in the absence of CO₂ and in CO-saturated electrolyte reveal that the structure of the double layer at negative potentials is different when CO₂ is present (probably due to the formation of CO_{ad}) and allow us to assign the main band in the spectra to CO adsorbed linearly on Au (CO_L), with a smaller band corresponding to bridge-bonded CO (CO_B). The CO bands show a large inhomogeneous broadening and are considerably broader than those typically observed in aqueous electrolytes. While both CO_L and CO_B can be observed in the CO adlayer generated by the electroreduction of CO₂, only a single, even broader band, at a frequency characteristic of CO_L is seen in CO-saturated solutions. We attribute this to the lower coverage of the adlayer formed upon reduction of CO₂, which leads to a lower degree of dipole-dipole coupling. Upon reversing the direction of the sweep in the CV, the intensity of the CO bands continues increasing for as long as a reduction current flows, but starts decreasing at more positive potentials due to CO desorption from the surface.

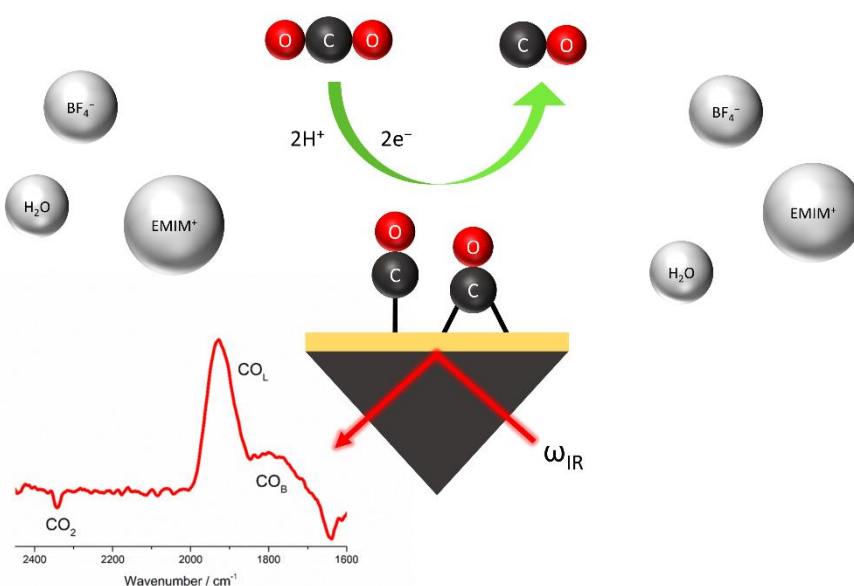


Fig. 1 Monitoring Au-catalysed CO₂ reduction to adsorbed CO with ATR-SEIRAS.

Investigation into Non-Aqueous Aluminium Battery Materials for Enhanced Power and Capacity

Liam Plunkett

Newcastle University l.plunkett@ncl.ac.uk

Abstract: Batteries are used in modern electronic devices yet the length of time the battery lasts is still an issue in today's society; phones needing to be recharged at least once a day. Research into better performance, namely better capacity and power, are large areas of interest. Lithium ion batteries are predominantly used due to their large capacity though cost is an issue as more and more batteries are needed.

Aluminium has a higher theoretical energy density than lithium, the current leading battery material, of 1060 Whkg⁻¹ compared to 406 Whkg⁻¹ respectively¹. This means that more energy can be withdrawn from an aluminium battery than out of a lithium battery of the same weight and design. Aluminium is also inherently safer than lithium due to the absence of dendrite formation which leads to short circuiting and potential ignition of the battery². Aluminium is at least 30 times cheaper than lithium which will make for a cheaper battery for future commercial use.

Investigation of cathode materials as well as various non-aqueous electrolytes with the aim of increasing the power output and capacity in aluminium ion batteries. Looking at the intercalation of aluminium ions into different cathode materials and the energies associated with the electrodes.

References

- 1 M. P. Paranthaman, G. M. Brown, X. Sun, J. Nanda, A. Manthiram, A. Manivannan, (2010) '*A Transformational, High Energy Density Secondary Aluminium Ion Battery*'
- 2 Alias, N.; Mohamad, A. A., (2015) '*Advances of aqueous rechargeable lithium-ion battery: A review*'

Bias-driven conductance increase with length in porphyrin tapes

Edmund Leary^{#,†}, Ian Grace[§], Sara Sangtarash[§] Bart Limberg,[‡] Katsutoshi Swada,[‡] Louisa J. Esdaile,[‡] M. Teresa González,^{||} Gabino Rubio-Bollinger,[⊥] Nicolás Agrait,^{||,⊥} Simon J. Higgins[‡], Colin J Lambert[§], Harry Anderson[‡] and Richard J. Nichols^{#,‡}

[†]Department of Chemistry, Donnan and Robert Robinson Laboratories, University of Liverpool, Liverpool L69 7ZD, U.K.

[#]Surface Science Research Centre and Department of Chemistry, University of Liverpool, Oxford Street, Liverpool L69 3BX, UK

[‡]Department of Chemistry, Chemistry Research Laboratory, Oxford University, Oxford OX1 3TA, U.K.

[§]Department of Physics, Lancaster University, Lancaster, U.K.

^{||}Instituto Madrileño de Estudios Avanzados (IMDEA), Calle Faraday 9, Campus Universitario de Cantoblanco, 28049 Madrid, Spain.

[⊥]Departamento de Física de la Materia Condensada, and Instituto “Nicolás Cabrera”, Universidad Autónoma de Madrid, E-28049, Madrid, Spain

Abstract: One of the main goals of molecular electronics is to design molecules which can transport charge efficiently over several nanometres and which could act as interconnects in molecule-based circuitry. Normally molecular wires become less conductive as they become longer.¹ Here I will discuss some recent experimental results for a series of fused porphyrins showing that the conductance actually increases substantially with length at a bias of 0.7 V. We achieve conductance values of 0.02 G_0 over distances of 4 nm, which is the same as 1,4-benzenedithiol,² but over six times the distance. This behaviour can be attributed to the rapid decrease of the HOMO-LUMO gap with length due to the high inter-ring coupling of fused porphyrins.

References

- 1 Huang, C., Rudnev, A. V., Hong, W. & Wandlowski, T. Break junction under electrochemical gating: testbed for single-molecule electronics. *Chem. Soc. Rev.* **44**, 889–901 (2015).
- 2 Leary, E. *et al.* The Role of Oligomeric Gold-Thiolate Units in Single Molecule Junctions of Thiol-Anchored Molecules. *J. Phys. Chem. C* (2018).

Effect of humidification of reactive gases on the performance of a proton exchange membrane fuel cell

Tabbi Wilberforce, F.N Nisar, O. Emmanuel, O. Ijaodola, A. Alanzi, A. Al Makky, A.G. Olabi

University of the West of Scotland, Institute of Engineering and Energy Technology

Abstract:

The University of the West of Scotland (UWS), Institute of Engineering and Energy Technologies (IET), is currently embarking on series of innovative strategies to improve the performance of a Proton Exchange Membrane (PEM) fuel cell both numerically and experimentally. The work validated the best humidification conditions to improve the performance of the fuel cell at optimum operating conditions and the best flow direction (cross/counter flow) to improve the fuel cell performance was critically investigated. Each humidification condition was carefully discussed to ascertain the impact it will have on the water management of the fuel cell to reduce the possibility of flooding. The results obtained was compared with experimental results obtained in the University of West of Scotland and that in literature to determine the deviation between the simulation results and the experimental results. The simulated results were in perfect agreement with the experimental results, hence validating the results obtained in ANSYS Fluent. The work concluded that using humidified hydrogen with 100%RH oxygen gave the best performance of the fuel cell but was not economically viable as using 100%RH air gave almost the same performance with a slight difference hence since air is readily available, it was the best recommended reactive gas for the cathode region. The reasons behind the low performance in the other humidification conditions were also discussed and clearly analyzed.

Key words: Humidification, PEM fuel cell, Polarization curve, ANSYS

References

- [1]. Tabbi Wilberforce, A. Alaswad, A. Palumbo, A. G. Olabi, Advances in stationary and portable fuel cell applications, International Journal of Hydrogen Energy 41(37) March 2016.
- [2] T. Wilberforce, Z. El-Hassan, F.N. Khatib, A. Al Makyy, A. Baroutaji, J. G. Carton and A. G. Olabi, Modelling and Simulation of Proton Exchange Membrane Fuel cell with Serpentine bipolar plate using MATLAB, International journal of hydrogen, 2017. DOI: 10.1016/j.ijhydene.2017.06.091.
- [3] Tabbi Wilberforce, Zaki, El-Hassan, F.N. Khatib, A. Al Makyy, A. Baroutaji, J. G. Carton and A. G. Olabi. Developments of electric cars and fuel cell hydrogen electric cars. DOI: 10.1016/j.ijhydene.2017.07.054.
- [4] T. Wilberforce, A. Al Makky, A. Baroutaji, R. Sambhi, A.G. Olabi, Computational Fluid Dynamic Simulation and modelling (CFX) of Flow Plate in PEM fuel cell using Aluminum Open Pore Cellular Foam Material, Power and Energy Conference (TPEC), IEEE, Texas. 2017. DOI: 10.1109/TPEC.2017.7868285.
- [5] T. Wilberforce, A. Al Makky, A. Baroutaji, R. Sambhi and A.G Olabi, Optimization of bipolar plate through computational fluid dynamics simulation and modelling using nickle open pore cellular foam material, International conference on renewable energies and power quality (ICREPQ'17), ISSN 2171-038X, No 15 April 2017.
- [6] Tabbi Wilberforce, F. N. Khatib, Ahmed Al Makky, A. Baroutaji, A.G. Olabi Characterisation Of Proton Exchange Membrane Fuel Cell Through Design Of Experiment (DOE). Proceedings of SEEP2017, 27-30 June 2017, Bled, Slovenia

POSTERS

Using an Ultrasonic Input to Enhance Ammonium Persulfate Electrosynthesis

Alexander G Wallace, Patrick McHugh, Mark D Symes

A2-06a/b, Joseph Black Building, University of Glasgow

a.wallace.3@research.gla.ac.uk

Abstract: Electrochemical conversion of ammonium sulfate to ammonium persulfate was coupled with an ultrasonic input. It was found that ammonium persulfate Faradaic yields increased as a result, and chronopotentiometry showed ultrasonic inputs lowered the overpotential of the process. Experiments were also performed that decoupled enhanced mass transport and increased temperature from cavitation effects. It was also shown that some Caro's acid and hydrogen peroxide were made in side reactions but that the major product was persulfate.

Conditions	Product Yield (μmol)	Error (μmol)	Faradaic Efficiency (%)	Error (%)
Still	10.5	1.22	22.5	2.6
Heating	13.8	1.60	29.5	3.4
Stirring	16.6	1.59	34.9	3.4
Heating and Stirring	17.5	1.86	37.6	4.0
Sonication	25.3	1.51	54.4	3.2

Table 1. Table showing the product yields and Faradaic efficiencies observed for chronopotentiometric electrolysis of 3.6 M ammonium persulfate solutions.

Probing Ion Mobility in Li-Stuffed Garnets Using Multinuclear Solid-State NMR.

Abby R. Haworth,¹ Ivan Trussov,² Peter R. Slater,² and Karen E. Johnston¹

¹ Department of Chemistry, Durham University, Durham, DH1 3LE, UK

² School of Chemistry, University of Birmingham, Birmingham, B15 2TT, UK

abby.r.haworth@durham.ac.uk

Abstract: Li-ion batteries have become increasingly popular for use in portable electronic devices. However, their use of organic carbonate liquid electrolytes makes them potentially unsafe. As a result, research efforts have focused on the development of all-solid-state batteries, *i.e.*, those composed of solely solid components. Lithium-stuffed garnets are just one class of materials with the potential to be solid electrolyte materials in the future.

$\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($\text{M} = \text{Nb}, \text{Ta}$) is one example of a Li-stuffed garnet currently of interest due to its Li-ion conduction capabilities. Although the conductivity is relatively low at room temperature, the material is compatible with lithium metal anodes and the structure can be doped to increase the conductivity, *e.g.*, the substitution of La with Ba, Ca, Sr, or K.¹⁻³ Despite a number of metals having been successfully doped into these materials, sodium doping has yet to be investigated.

Samples in the series $\text{Li}_{5+2x}\text{La}_{3-x}\text{Na}_x\text{M}_2\text{O}_{12}$ ($x = 0 - 1$, $\text{M} = \text{Nb}, \text{Ta}$) have been prepared via traditional solid-state methods. Rietveld refinement of the X-ray diffraction data supports the incorporation of Na into the structure and onto the La site, with a decrease in the unit cell parameters, as expected. Electrical impedance spectroscopy measurements completed for compositions $x = 0, 0.2, 0.4$, and 0.6 indicate a decrease in the ionic conductivity as the Na content is increased. This is likely due to Na-Li disordering on the Li site. The compositions $x = 0.2$ and 0.4 have been studied via multinuclear solid-state NMR spectroscopy and first-principles density functional theory (DFT) calculations to determine the position of Na within the structure and to understand the effects of structural substitutions on the associated physical properties. We will present our ^{23}Na and ^7Li multiple-quantum magic-angle spinning (MQMAS) NMR data which suggest Na is substituting onto multiple sites within the garnet structure. ^{23}Na exchange spectroscopy (EXSY) experiments have also been performed, in conjunction with variable-temperature ^6Li NMR studies, to investigate ion mobility within the structure, the results of which will be presented. We will also present our preliminary ^{93}Nb , ^{17}O , and static ^{139}La NMR data, discussing any structural conclusions that can be drawn. Combining this with quantum-chemical calculations will enable us to accurately model and characterise any Na/Li disorder and understand the mechanisms for ion conductivity in $\text{Li}_{5+2x}\text{La}_{3-x}\text{Na}_x\text{M}_2\text{O}_{12}$.

References

1. V. Thangadurai and W. Weppner, *Adv. Funct. Mater.*, 2005, **15**, 107-112.
2. J. Percival, D. Apperley and P. R. Slater, *Solid State Chem.*, 2008, **179**, 1693-1696.
3. V. Thangadurai and W. Weppner, *J. Solid State Chem.*, 2006, **179**, 974-984.

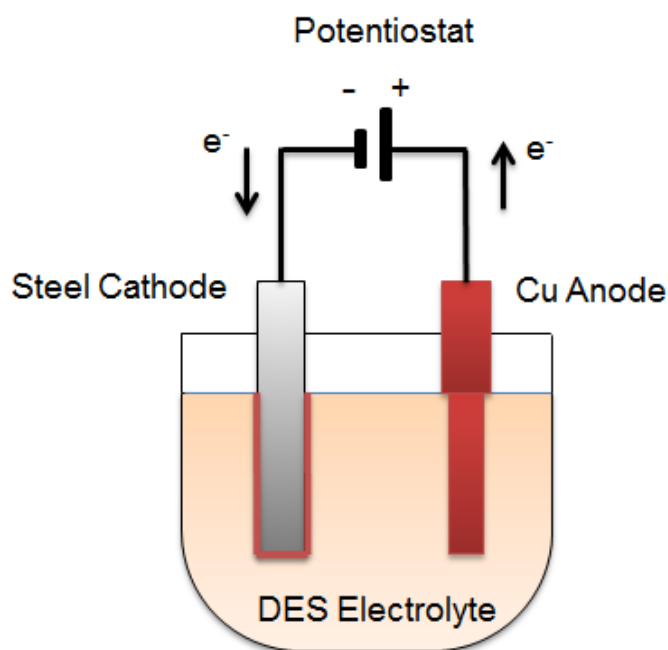
Electrodeposition of Copper from Deep Eutectic Solvents (DES) by Using Pulse Current

Xiaomeng Su, Dr. Todd Green, Prof. Sudipta Roy

Xiaomeng.su@strath.ac.uk

Abstract: Cu electrodeposition is of great significance in various industries, such as electronics, sensors and aerospace. Electroplating is the main production process for the deposition of metallic Cu films. Traditionally the process was performed using aqueous solutions due to their convenience and low cost. However, such electrolytes suffer a number of drawbacks including poor deposit quality for some metals and pose serious environmental concerns, for example, when cyanide or chromium (VI) electrolytes are used. In addition, other metals with very negative reduction potentials, like aluminum and magnesium, cannot be plated from the aqueous solutions. Deep eutectic solvents, which are a type of room temperature molten salts, serve as the alternative and can overcome many of the limitations of aqueous solution.

The nature of the applied deposition current is another important factor. The application of direct current (DC) is the conventional method for plating metals. However, the deposit quality and metal properties are inadequate in many cases. One way of improving the deposits is by using additives, but these need to be monitored carefully to maintain performance. However, these issues can often be solved by applying pulse current (PC) without the use of additives. This research investigates the combined effects of using deep eutectic solvents and pulsed current deposition. The aim is to explore how they affect the morphology and microstructure of the metal deposit, with comparisons of the results to those obtained using aqueous solutions and direct current plating.



Evaluation of the Conduction Band Edge Positions of Stannates with Perovskite Structure Using Photoelectrochemical Methods

Iêda Maria Garcia dos Santos^{1,2}, Luzia Maria de Castro Honório², Amer Hakki¹, Donald Macphee¹

¹University of Aberdeen, Meston Building, Meston Walk, AB24 3UE, Aberdeen, Scotland, UK

²NEP/LACOM, Universidade Federal da Paraíba, João Pessoa/PB, Brazil. E-mail: ieda.dossantos@abdn.ac.uk

Abstract: Researches reporting the use of stannates with perovskite structure as photocatalyst have been growing in the last years^{1,2}. In spite of this, few papers have focused in the evaluation of the energy edge positions. For instance, Zhang¹ and Alamar² used a semi-empirical method to calculate the conduction band edge potential (E_c), while experimental measurements have been reported for La-doped SrSnO_3 ³ and BaSnO_3 ^{4,5}. In the present work, ASnO_3 ($A = \text{Ca}^{2+}$, Sr^{2+} and Ba^{2+}) powders were prepared by the Pechini method and SrSnO_3 was deposited on commercial ZrO_2 ($\text{SrSnO}_3/\text{ZrO}_2$) using the same method. Evaluation of the band edge positions was done in agreement to the photoelectrochemical methods described by Beranek⁶ (open circuit measurement - E_{oc} ; and determination of the photocurrent onset) and to the Butler⁷ method. Similar band edge potentials were found using the photocurrent onset measurement and the Butler method – the flat band potentials were around -0.5 V (vs NHE) for all of the stannates and for SrSnO_3 deposited on ZrO_2 (Fig 1a). These data are similar to the theoretical values calculated by Alamar et al.², especially for BaSnO_3 , who obtained $E_c = -0.89$ eV for SrSnO_3 and $E_c = -0.59$ eV for BaSnO_3 . E_{oc} measurements (Fig 1b) indicated very different values for the flat band potentials: 0.01 V for BaSnO_3 , 0.55 V for SrSnO_3 and 0.56 V for CaSnO_3 . A decrease of the flat band position to 0.35 V was observed for $\text{SrSnO}_3/\text{ZrO}_2$. Open circuit measurements also indicated that BaSnO_3 was less sensitive to UV irradiation than the other stannates with less than 0.01 V of variation, while SrSnO_3 and CaSnO_3 had a very similar variation (0.27 V).

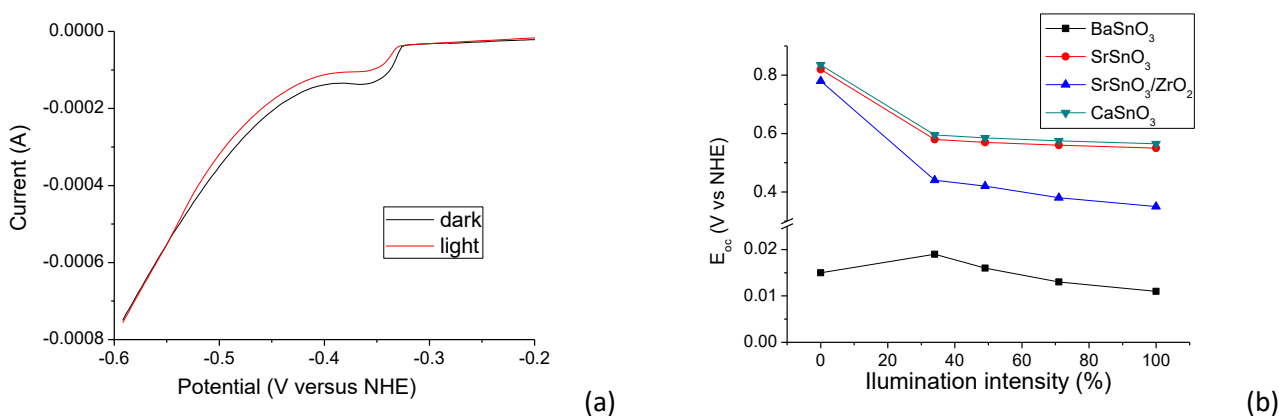


Fig. 1 Evaluation of the conduction band edge positions of ASnO_3 . (a) Photocurrent onset of the sample $\text{SrSnO}_3/\text{ZrO}_2$; (b) Open circuit measurements

References

- 1 W. Zhang, J. Tang and J. Ye, *J. Mater. Res.* 2007, **22**, 1859-1871.
- 2 T. Alamar, I. I. Slowing and J. Anderegg, *ChemSusChem*. 2017, **10**, 3387-3401.
- 3 B. Hadjarab, A. Bouguelia and M. Trari, *J. Phys. Chem. Solids*. 2007, **68**, 1491-1499
- 4 N. Zidi, S. Omeiri, B. Hadjarab, A. Bouguelia, A. Akroun and M. Trari, *Physica B*. 2010, **405**, 3355-3359
- 5 B. Hadjarab, M. Trari and M. Kebir, *Mater. Sci. Semicond. Process.* 2015, **29**, 283-287
- 6 R. Beranek, *Adv. Phys Chem.* 2011, 786759
- 7 M. A. Butler, *J. Appl. Phys.* 1977, **48**, 1914-1920

To Gel, or Not to Gel, That is the Question: A Novel Method to Screen Supramolecular Hydrogels is the answer.

Emily R. Cross, Dave J. Adams

School of Chemistry, University of Glasgow, Glasgow, G12 8QQ e.cross.1@researcher.gla.ac.uk

Abstract: Multicomponent supramolecular systems have the potential to be used as exciting new functional materials.¹ Development of these materials is hindered by the inability to fully understand and control the assembly process.¹ Some of the important factors affecting the final properties of the hydrogels include: pK_a , fiber length and hydrophobicity. Current methods used to probe the systems are usually time consuming, expensive or inaccurately represent our system.² Here, we present an efficient, inexpensive and accurate electrochemical screening method to analyse the pK_a and, morphological changes over time. Moreover this method can predict whether a system will successfully gel or not.

Low molecular weight gelators form free-flowing liquids at high pH with viscosities comparable to water. However, other dipeptide solutions form worm-like micelles at the same pH which are significantly more viscous.³

Here, we stabilize the gelators at high pH with redox-active cations which leads to the immobilization of the gelator. When the pH is then lowered to below the pK_a of the gelator, we observe an exchange of cations and protons.

We present a novel quantitative screening method to identify whether a gelator will form a hydrogel or crystal (**Fig.1**). Finally, using a combination of cyclic voltammetry, Multiple pulse amperometry, rheology, pH evolution, and SEM-EDX to probe the assembly process (**Fig. 2**).

References:

1. J. Raeburn et al., *Chem. Commun.*, 2015, **51**, 5170-5180
2. R. Weiss, *Gels*, 2018, **4**, 25
3. L. Chen, et al., *Langmuir.*, 2010, **26**, 5232-5242

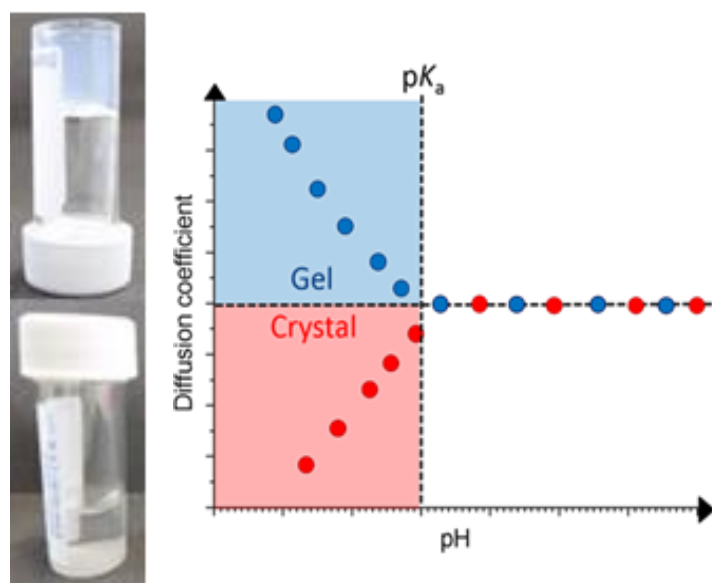


Fig. 1 Schematic graph showing the trends in diffusion coefficient based on gelator morphology.

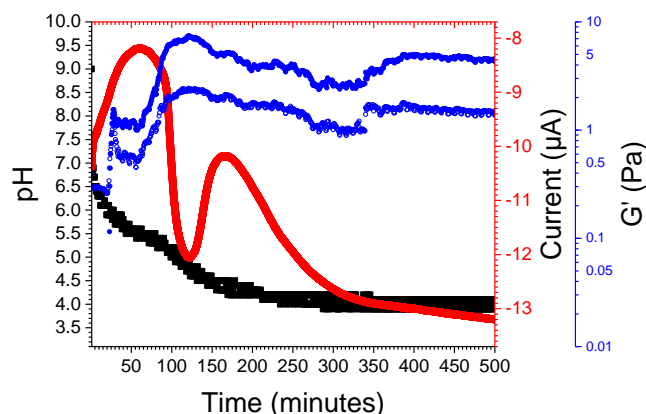


Fig. 2 Graph to show the evolution pH (Black), current (Red), Storage modulus (Blue ●), Loss modulus (Blue ○) of a gelator molecule assembling with a pH trigger.

Electrochemical Assessment of the Psychoactivity of New Illicit Substances

Kelly Brown*, Pamela Allan, Lynn Dennany

WestCHEM. Department of Pure and Applied Chemistry, Technology and Innovation Centre, University of Strathclyde, 99 George Street, Glasgow, G1 1RD.

*kelly.brown.100@strath.ac.uk

Abstract:

The UK government introduced the Psychoactive Substances Act 2016 (PSA) to tackle the increased use of new psychoactive substances (NPS). NPS are typically designed to mimic the effect of controlled substances, but through the use of different chemical structures were initially out with legislative control. The introduction of the PSA saw for the first-time drug legislation based upon drug effect rather than chemical structure.^{1, 2} Traditional techniques used within forensic drug analysis and toxicology, although considered the gold standard for identification and quantification of substances, are not suitable for determining drug effect. It has therefore become a requirement for forensic practitioners to develop new strategies to address the requirements of the new legislation.

Our current research hopes to offer an alternative method for the assessment of drug psychoactivity through the employment of electrochemistry. Based on the principle of recognition-event detection, electrochemistry will be employed to monitor the change in current response as a result of the interactions between substances and their specified receptors. Through the modification of electrode surfaces with receptors linked to psychoactivity in the human body, such as the CB₁ receptor, we aim to build a predictive model for assessing the psychoactivity of unknown substances. The model will be initially built using known psychoactive substances and employing cyclic voltammetry and differential pulse voltammetry to monitor the electrochemical changes at the modified electrode surfaces. Interference effects will be investigated, with a focus on the cutting agents commonly observed in forensic samples, which may have psychoactive effects themselves. The potential to allow for multiplexed detection will also be examined with the hope to develop a multiplexed array capable of detecting a range of psychoactive substances. The successful development of this electrochemical sensor would offer a simple technique and rapid assessment method, which could be directly applied to street samples.

References

1. S. Beharry and S. Gibbons, *Forensic Sci. Int.*, 2016, **267**, 25-34.
2. H. Office, New Psychoactive Substances (NPS) resource pack, <https://www.gov.uk/government/publications/new-psychoactive-substances-nps-resource-pack>, (accessed 12th October, 2017).

The influence of protein concentration on the corrosion behaviour of CoCrMo biomedical grade alloys.

Righdan Namus, and Prof. Mark Rainforth

The University of Sheffield, Mappin Street, Sheffield, S1 3JD

rmnamus1@sheffield.ac.uk

Abstract: CoCrMo alloys have been widely used in metal-on-metal (MoM) hip replacements. On the one hand, they have exhibited excellent long-term survival rates, but recently high failure rates have been observed, associated with adverse local tissue reactions. It is still a puzzle why CoCrMo alloys sometimes work very well, while at the other times the wear rate is unacceptably high. The protein concentration of the synovial fluid is reported to increase significantly for patients who have rheumatoid arthritis. This could weaken the protective oxide layer of these implants increasing the potential of local break down of the oxide layer or even having scratched surface. In both cases, part of the surface is bare metal exposed to protein, while, the surrounding area is polarised. The current work aims to investigate the influence of protein adsorption on the corrosion properties of CoCrMo biomedical grade alloys proposing different surface and media conditions. Fully and partially scratched surfaces have been simulated by applying different potentials at static conditions. Electrochemical Impedance Spectroscopy EIS, and Scanning Electron Microscopy SEM have been employed to characterise the surfaces.

Na₆V₁₀O₂₈ Supercapacitor Electrodes

Kate Phipps,^{a, d} R. John Errington,^a Keith Scott,^b Walter G. Klemperer,^c Ulrich Stimming^a and Jochen Friedl^a

^a School of Chemistry, Newcastle University, NE1 7RU, UK

^b School of Chemical Engineering and Advanced Materials, Newcastle University, NE1 7RU, UK

^c Department of Chemistry, University of Illinois, Urbana, IL 61801, USA

^d k.phipps@newcastle.ac.uk

Polyoxometalates (POMs) are promising electrode materials for supercapacitors.¹ The sodium salt of the decavanadate ion, [V₁₀O₂₈]⁶⁻, (Fig. 1) has been tested previously as an electrode material for supercapacitors by Chen et. al.² In this study Na₆V₁₀O₂₈ (V₁₀) electrodes have been investigated for supercapacitor applications in an attempt to reproduce results previously achieved by Chen et. al., determine the factors affecting capacitor performance and understand details of the associated redox chemistry.² The V₁₀ POM electrodes were tested electrochemically by cyclic voltammetry (CV) and chronopotentiometry (CP), and specific capacitance (C_{sp}) was calculated from these measurements. The Na₆V₁₀O₂₈ was prepared following two different procedures.^{2, 3} Various precipitation strategies were coupled with grinding and sonication in order to obtain small crystals and assess the effect of crystallite size on capacitance. Crystal phase and morphology were investigated by powder XRD and SEM respectively.

The highest capacitance achieved in this study was 126 F/g, which is lower than the value of 354 F/g achieved by Chen et. al.² The capacitance achieved by the current study was for electrodes produced using drop casting to deposit the dilute slurry on to a carbon fiber paper current collector. The investigation of the effect of crystal size on capacitance revealed that smaller crystals do not yield higher capacitance (Fig. 2).

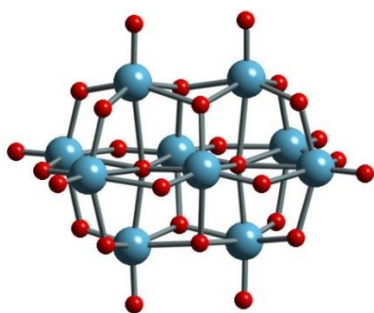


Fig. 1 Ball and stick representation of [V₁₀O₂₈]⁶⁻

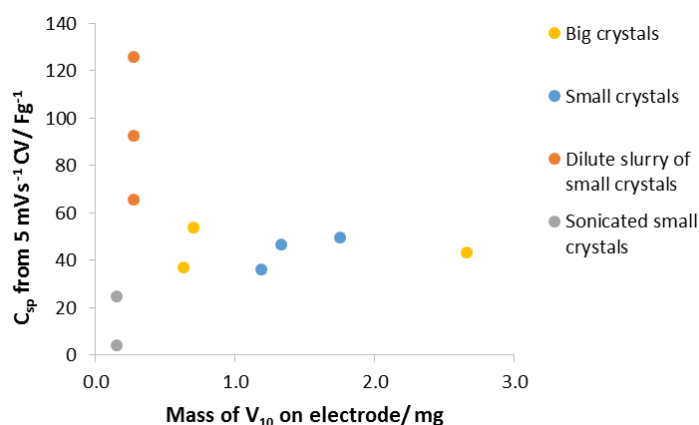


Fig. 2 A plot of mass of V₁₀ on electrode vs. specific capacitance, calculated from 5 mV/s CVs

References

1. A. Yamada and J. B. Goodenough, *J. Electrochem. Soc.*, 1998, **3**, 737
2. H-Y. Chen, G. Wee, R. Al-Oweini, J. Friedl, K. S. Tan, Y. Wang, C. L. Wong, U. Kortz, U. Stimming and M. Srinivasan, *ChemPhysChem*, 2014, **15**, 2162
3. G. K. Johnson and R. K. Murmann, *Inorg. Synth.*, 1979, **19**, 142

Electronic structure engineering of ZnS for achieving efficient photoelectrochemical performance

Fran Kurnia¹ and Judy N. Hart^{2,3}

¹Centre for Nanostructured Media, School of Mathematics and Physics, Queen's University Belfast, University Road, Belfast BT7 1NN, United Kingdom. Email: f.kurnia@qub.ac.uk

²School of Materials Science and Engineering, UNSW Sydney, NSW 2052, Australia.

³Integrated Materials Design Centre, UNSW Sydney, NSW 2052, Australia.

Abstract: Zinc sulphide (ZnS) is a promising material for use in photoelectrochemical applications due to its direct band gap and high conduction band energy.¹ However, the wide band gap of ZnS (3.6 eV) makes it only active under ultraviolet (UV) irradiation which is only 5% of the total solar spectrum.² In order to improve its efficiency, the electronic structure of ZnS should be adjusted such that it can absorb photons in the visible-light region of the solar spectrum. Doping is known to be an effective method for modifying the electronic structure of semiconductors.³ Here, we present the results of electronic structure calculations of anion-, cation- and co-doped ZnS from density functional theory. We discuss the band gap, crystal reconstruction and formation energy, which are all important in determining the photoelectrochemical activity under visible-light irradiation. The results could provide useful hints to improve the photoelectrochemical efficiency of ZnS under visible-light irradiation.

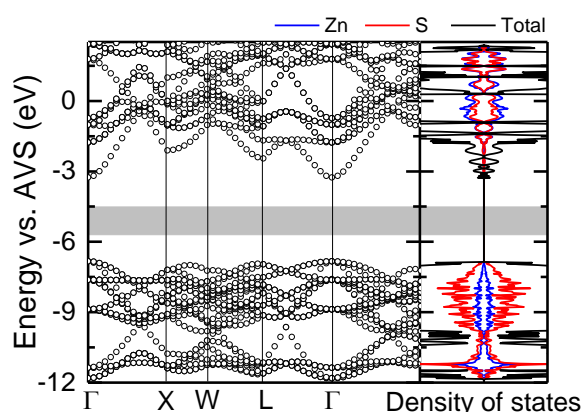


Fig. 1 Electronic band structure and density of states of pure ZnS showing the direct band gap of about 3.6 eV.

References

- 1 J. F. Reber and K. Meier, *J. Phys. Chem.* 1984, **88**, 5903-5913.
- 2 S. J. A. Moniz, S. A. Shevlin, D. J. Martin, Z.-X. Guo and J. Tang, *Energy & Environmental Sci.* 2015, **8**, 731-759.
- 3 F. Kurnia and J. N. Hart, *Chemphyschem* 2015, **16**, 2397-2402.