two 2014

NEWSLETTER

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SPECIAL ISSUE ELECTROCHEM 2014

Serving Electrochemical Science, Technology and Engineering within the catchment of

The Royal Society of Chemistry

and

The Society of Chemical Industry

SCI Where science meets business
an environment to advance knowledge exchange

RSC | Advancing the Chemical Sciences

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Contents

Editorial

It is a pleasure to release the Electrochemistry Newsletter special issue dedicated to the ***Electrochem 2014*** conference, which was held 7th to 9th September 2014 at Loughborough University. This meeting included symposia on a range of topics in electrochemistry with 4 plenary lectures (including the Faraday Medallist lecture), 15 keynote lectures, 82 oral presentations and 58 poster presentations. In this special issue the programme and abstracts are documented. A special symposium on fundamental electrochemistry was dedicated to the celebration of Professor W. John Albery's work and influence in electrochemistry. As one of the highlights during this symposium, the first W. J. Albery lecture was presented by Dr. Tim Albrecht from Imperial College London. A big thank you to Prof. Upul Wijayantha and his local organising team for an enjoyable meeting with excellent organisation.

Next year the **Electrochen 2015** will be organised by Ritu Kataky at Durham (email Ritu.Kataky@durham.ac.uk). The main theme of this meeting will be "Molecular Materials in Electrochemistry" with a special symposium on "Soft Matter". Other symposia will be on Nanoelectrochemistry, Electroanalysis and Electrochemical Measurements, Electrochemistry at Soft Interfaces, Fundamental Electrochemistry, Energy Production and Storage, Electrochemical Processes and Materials, and the Corrosion Symposium. Award lectures will include the presentation associated with the 2015 Electrochemistry Group Faraday Medal. In the run-up to this event there will be local one-day conferences with student presentations selected for sponsored oral contributions to ***Electrochem 2015***.

ELECTROCHEM 2015 CONFERENCE

"MOLECULAR MATERIALS IN ELECTROCHEMISTRY"

DURHAM UNIVERSITY

SUNDAY 13TH - TUESDAY 15TH SEPTEMBER 2015

A MEETING OF SCIENCE AND INDUSTRY

RSC Advancing the Chemical Sciences · SCI · Durham University · Newcastle University

If you wish to notify the editor with your view on the material or the content of any item in this issue, or if you wish to contribute to the newsletter, please write to the Editor-in-Chief (Frank Marken, Department of Chemistry, University of Bath) at:

f.marken@bath.ac.uk

Missed a copy? You can catch up on all the news *via* our webspace hosted by the Royal Society of Chemistry at the following URL.

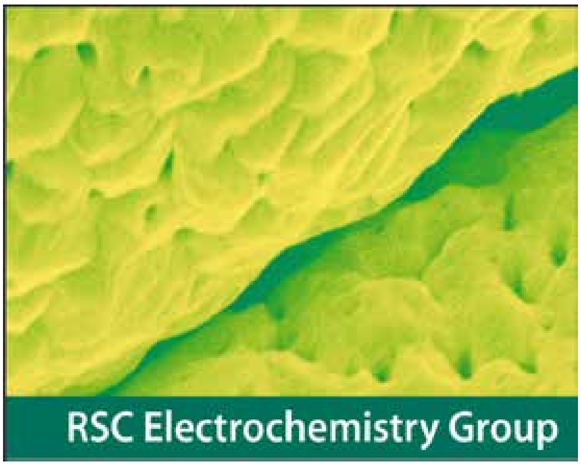
http://www.rsc.org/Membership/Networking/InterestGroups/Electrochemistry/news.asp

Call for Nominations....

RSC Electrochemistry Group

The RSC Electrochemistry Group Committee membership changes regularly and in 2015, during the Electrochem 2015 event, the following positions will have to become vacant.

- **Academic Representative**
  for up to a three year duration
- **Industry Representative**
  for up to a three year duration



Please send nomination to the current RSC Electrochemistry Group Secretary,

Prof. Upul Wijayantha (email: **U.Wijayantha@lboro.ac.uk**),

before the Electrochem 2015 event or ***participate*** directly at the AGM September 2015 at Durham University. In the event of more than one candidate standing for either of these positions, an election will be held during the group AGM.

ELECTROCHEM

2014

LOUGHBOROUGH UNIVERSITY, 7TH TO 9TH SEPTEMBER 2014

Royal Society of Chemistry

ISE

SCI
where science meets business

UK&I Semiconductor Photochemistry Network

Loughborough University

Welcome

It is our pleasure to welcome you to Loughborough University for the 20th meeting of the ELECTROCHEM conference series. Over the past 20 years, ELECTROCHEM has grown to be a major international conference, attracting many distinguished colleagues from all over the world.

Coincidentally, this year also marks the 50th anniversary of the beginning of electrochemistry research at Loughborough, when Professor Noel Hampson and his co-workers published their first peer-reviewed article. Since then electrochemists at Loughborough University have significantly contributed to the advancements made in fundamental and applied research in this field. As one of the top 20 research-led universities in the UK, Loughborough is renowned for the relevance of its work, driven by society's need for solutions to real-life issues. Today, Loughborough University contributes at the very highest levels to new knowledge and understanding, helping business and industry to compete more effectively, shaping public policy and, ultimately, helping to improve the quality of people's lives.

We are pleased to present a diverse programme at this year's conference reflecting the interdisciplinary nature of electrochemistry, including 4 plenary lectures, 15 keynote lectures, 82 oral presentations and 58 poster presentations distributed into 7 symposia:

1) Electrochemistry of Advanced Materials and Nanomaterials
2) Energy Harvesting and Conversion
3) Fundamental Electrochemistry
4) Electroanalysis and Sensors
5) Coordination/ organometallic Electrochemistry
6) Energy Storage
7) Electrochemical Aspects of Fuel Cells

This year's meeting is organised in close collaboration with the Electrochemistry and Electroanalytical Sensing Systems Groups of the Royal Society of Chemistry (RSC) and the Electrochemical Technology Group of the Society of Chemical Industry (SCI).
We are grateful to them and all the contributors, convenors, sponsors, collaborators, supporters and participants for all their time and resources that they have expended to make ELECTROCHEM 2014 a success. Without their corporation and support over a period of nearly two years of planning, we could not have prepared this excellent conference programme.

Dr Upul Wijayantha *(Chair, Organising Committee)*
Reader in Physical Chemistry
Department of Chemistry
Loughborough University

Prof Roger Mortimer
Professor of Physical Chemistry
Department of Chemistry
Loughborough University

Naomi Purvis
Events
Manager
Imago @ Loughborough
Ltd

Andrew McInnes PhD
Researcher
Department of
Chemistry
Loughborough
University

CAMPUS KEY

Residential Buildings

Department Buildings

Facility Buildings

Indoor Sports Facilities

LUSEP

University Boundaries

Dining Room

Café

Bar

Shop

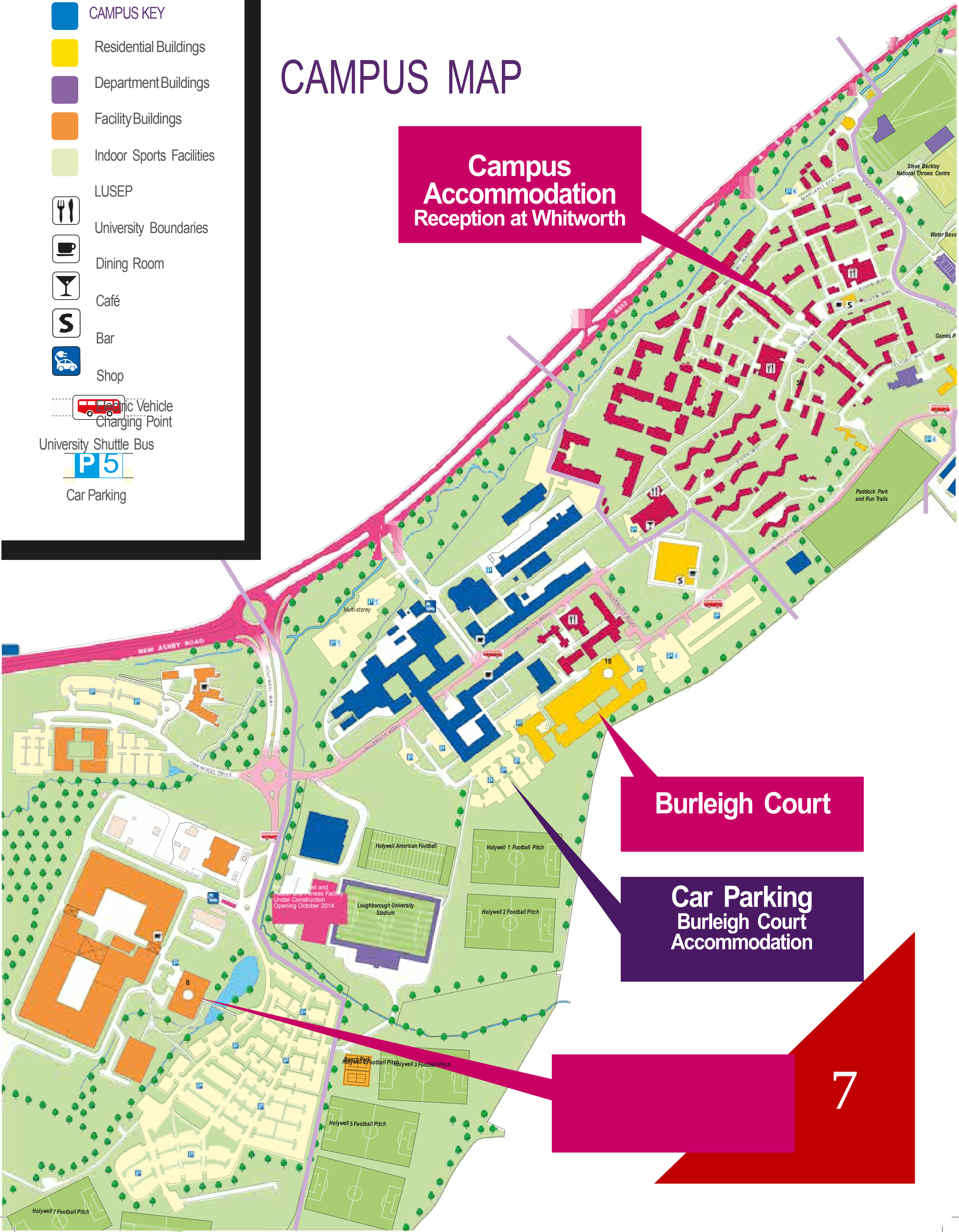
Electric Vehicle Charging Point

University Shuttle Bus

P5

Car Parking

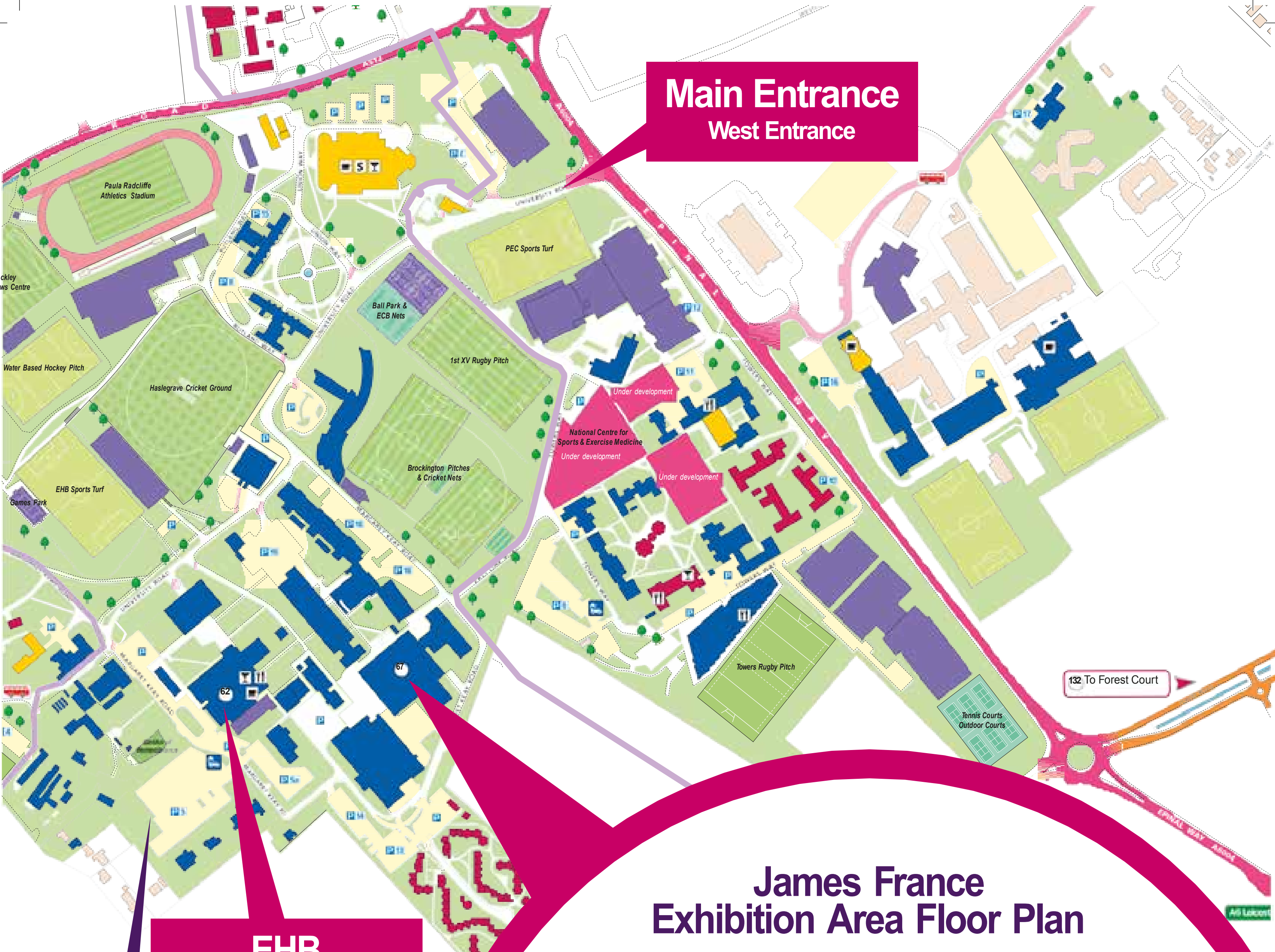
CAMPUS MAP



Campus Accommodation
Reception at Whitworth

Burleigh Court

Car Parking
Burleigh Court Accommodation

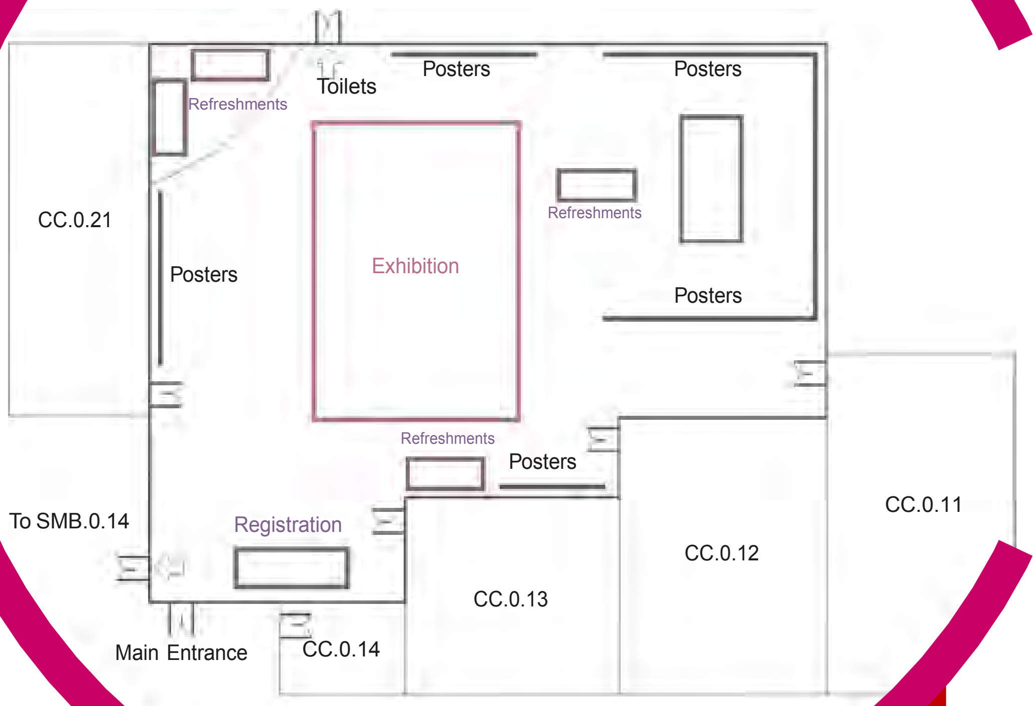


Main Entrance
West Entrance

EHB
Linford Restaurant
Bar open Sunday
(3.00pm - 11.00pm)

Car Parking
Campus Accommodation

James France Exhibition Area Floor Plan



Sponsors:
The organisers would like to thank the following organisations for their support through sponsorships in Electrochem 2014

INTERNATIONAL SOCIETY OF ELECTROCHEMISTRY
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AMERICAN ELEMENTS

World Scientific
Connecting Great Minds

WILEY

ROYAL SOCIETY OF CHEMISTRY

Maney Publishing
Research • Knowledge • Innovation

PCCP

Analytical Methods

CAMBRIDGE
UNIVERSITY PRESS

ELSEVIER

Springer

Exhibitors:

The following companies will be found the main exhibition area in the James France Building:

ACS Applied Materials & Interfaces is for the interdisciplinary community of chemists, engineers, physicists and biologists focusing on how newly-discovered materials and interfacial processes can be developed and used for specific applications. The journal publishes full length articles and letters from researchers in academia and industry in addition to featuring comments and forums dedicated to advancing applied materials research.

Pine Research Instrumentation manufactures a full line of affordable, durable and reliable electrochemical research equipment. Pine offers benchtop bipotentiostat/galvanostat instruments as well as portable USB potentiostat systems, all of which are controlled using our powerful AfterMath software package. We offer unique quartz electrochemical cells for photoelectrochemistry and spectroelectrochemistry, and we are the world leader in rotating disk, ring-disk, and cylinder electrode instrumentation. Our line of compact voltammetry cells, featuring screen-printed patterned electrodes, provides a quick and easy way to perform routine electrochemical measurements.

Alvatek supplies high performance research tools for Electrochemistry, Corrosion, Fuel Cell and Battery applications . We offer a wide range of potentiostats, impedance analyzers and fuel cell research equipment as well as complementary accessories such as cells and electrodes. Our philosophy is simply to offer high performance, competitive products backed up by first class Customer Service and Support.

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Blue Scientific's directors are applying big corporate best practices to running a professional European distribution company. Products are market leading and in Surface and Material science, including Solartron and Princeton Applied Research for Potentiostats and EIS. Other products include; Bruker microCT, Anasys AFM-IR, Jacomex glove boxes and Hysitron nano-indenters.

IJ Cambria Scientific was launched in 1999 and introduced, the advanced but highly cost effective CH Instruments, Inc series of instruments and accessories for electrochemistry, to the UK, Ireland and rest of EU. For each instrument series, various models exist to suit different needs and budgets. In addition we also offer the ALS JPN Ltd range of accessories, for spectroelectrochemistry and many other techniques. See: www.ijcambria.com

Aqualogy offer a unique range of integrated water solutions focussed on maximising efficiency in operations. With over 10,000 experts worldwide, the continuous research and development into pioneering technologies ensures Aqualogy deliver a diverse and innovative approach to water management for industrial, commercial and utilities customers.

EC-Lab Ltd distributes the electrochemical products from Bio-logic SAS. in the UK & Ireland. These range from single channel to multichannel potentiostats - with the option of impedance on any channel, scanning probe techniques like SECM, LEIS and SDS. A full range of accessories includes RRDE, EQCM, spectro-electrochemistry, electrodes, cells and other consumables are available. Application areas include renewable energy sources like batteries & super-capacitors, sensors, general electro-chemistry, corrosion and materials.

ec-lab

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Whistonbrook Technologies Limited designs and manufactures custom and prototype electrochemical equipment that meets your exact requirements. We can supply you with a range of custom electrochemical instrumentation to help you with your research projects, or prototype and trial equipment to help you transfer your technology to commercialization. Custom equipment is not expensive and can be less costly than purchasing an electrochemical workstation.

Photon Institute, LLC (**www.fotonowy.pl**), is a manufacturer of laboratory instruments for photoelectrochemistry.

Our main product groups involve light sources, spectrometers, Kelvin probes and other measurement electronics like lock-in amplifiers, PMT power supplies, data acquisition and communication modules.

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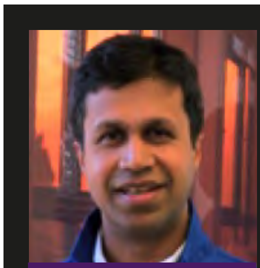
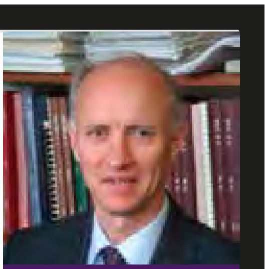
THE ORGANISING COMMITTEE



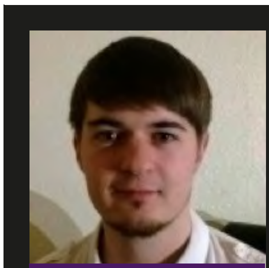
Dr Upul Wijayantha
Committee Chair

Upul worked on semiconductor photoelectrochemistry for his doctorate with Professor Laurie Peter (University of Bath). He then spent 4 years in industry developing solar water splitting devices. In 2007 he moved to the Department of Chemistry at Loughborough University to set up the Energy Research Laboratory (RCUK Fellow). He was promoted to a Senior Lecturer in 2010 and then to a Personal Readership in 2012. He was a member of RSC Downland Section Trust Committee between 2003-2006 and is the current secretary of RSC Electrochemistry Group.

Roger studied heterogeneous catalysis for his doctorate with Dr Michael Spiro at Imperial College. He then held various positions in CalTech, University of Exeter, Anglia Ruskin University and Sheffield Hallam University. This was followed by his appointment as a Lecturer in Physical Chemistry at Loughborough University in 1989. He was promoted to Senior Lecturer in 1999, to Reader in 2001, and to a Personal Chair in Physical Chemistry in 2006. He was a member of RSC Electrochemistry Group committee between 1997-2001, and he successfully organised the 'Electrochem 2001' conference at Loughborough University.



Professor Roger Mortimer

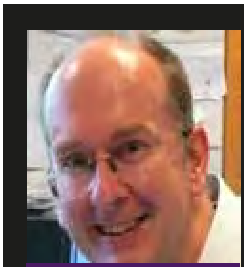


Andrew McInnes

Andrew completed his MChem at Loughborough University, with first class honours, in 2013. Currently he conducts his doctoral study on photoelectrochemical water splitting and nanoscale clusters with Dr Upul Wijayantha (Department of Chemistry, Loughborough University) and Professor Richard Palmer (School of Physics and Astronomy, University of Birmingham). Andrew is attached to the 'Doctoral Training Centre in Hydrogen, Fuel Cells and their Applications'.

Ray studied for his doctorate at Loughborough University with Prof. Noel Hampson, working on nickel-cadmium and lead-acid electrochemical battery systems and subsequently with Dr Phil Mitchell on the development of solid polymer electrolyte fuel cells and redox flow cells. Ray is currently the Senior Technical Officer for the School of Science and Director of Laboratories in the Chemistry Department.

Dr Ray Barton



Professor Frank Marken

Frank was appointed to a Senior Lecturer position at the University of Bath in September 2004. He has since been promoted to Reader in 2008 and to Professor in 2011. In 2009 Frank Marken was awarded the Theophilus Redwood lectureship by the Analytical Division of the RSC. He was the secretary (elect) of RSC Electrochemistry Group between 2006-2011 and he is the current Newsletter editor of the group. Frank successfully organised the 'Electrochem 2011' conference at the University of Bath.

Symposia Key and Lecture Venues

Symposium	Convenors
Electrochemistry of Advanced Materials and Nanomaterials	Roger Mortimer, Karl Ryder, Emma Smith, Sudipta Roy
Energy Harvesting and Conversion	Carlos Ponce-de-Leon, David Fermin, Mike Lyons, Darren Walsh
Fundamental Electrochemistry	Robert Dryfe and Frank Marken
Electroanalysis and Sensors	John Hart, Peter Fielden, Yannis Ieropoulos
Coordination/ Organometallic Electrochemistry	Frantisek Hartl, Neil Robertson
Energy Storage	George Chen, Laurence Hardwick, Peter Hall
Electrochemical Aspects of Fuel Cells	Neil Rees, Toby Reisch, Trevor Davies, Vivien Chapman, Dan Brett

Presenters are listed in the programme below, with page numbers referring to their respective abstracts.

Programme

Sun 7th

15:00	**Optional Sunday Afternoon Sporting Activity** - *Cricket - Brockington Pitch and Graham Dilley Pavillion*
17:00	**Registration, Welcome Reception and Informal Poster session** - *James France Exhibition Area*
19:00	**Dinner for those staying in University Accommodation**
20:30	**Evening Drinks** - *EHB Bar (Open from 15:00pm till late)*

Mon 8th

08:00	**Registration -** *James France Exhibition Area*									
08:50	**Welcome -** Upul Wijayantha and Bob Allison (Vice Chancellor of Loughborough University) *(CC011)*									
09:10	**Plenary Lecture** - Masatoshi Osawa (Faraday Medallist) *(CC011)*									
10:10	**Refreshments, Posters and Exhibition** - *James France Exhibition Area*									
	Room - CC011		***Room - SMB014***		***Room - CC012***		***Room - CC021***		***Room - CC013***	
10:55	Robert Hillman	pg. 21	Birparjit Sarkar	pg. 93	Alan Bond	pg. 63	Damien Arrigan	pg. 77	Muhammad Mazhar	pg. 47
11:15							Gareth Keeley	pg. 78	Christopher Wood	pg. 48
11:35	Adriana Santos-Ribeiro	pg. 22	Neil Robertson	pg. 94	Daniela Plana	pg. 64	Sunyhik Ahn	pg. 79	Kieren Bradley	pg. 49
11:55	Naray Pewnim	pg. 23	Qiang Zeng	pg. 95	Natasa Vasiljevic	pg. 65	Ronan Baron	pg. 80	I.M. Dharmada	pg. 50
12:15	David Weston	pg. 24	Masa-aki Haga	pg. 96	Rudiger Mueller	pg. 66	Alan O'Riordan	pg. 81	Alexander J. Cowan	pg. 51
12:35	Ben Horrocks	pg. 25			Maria Calleja	pg. 67	Nicola Kay	pg. 82	Kelly Morrison	pg. 52
12:55	**Lunch, Posters and Exhibition** - *James France Exhibition Area*									
13:55	**Plenary Lecture** - Tim Albrecht *(CC011)*									
15:00	Peter Richardson	pg. 26	Wesley Browne	pg. 97	Steve Fletcher	pg. 68	Damion Corrigan	pg. 83	Julie Stephenson	pg. 53
15:20	Sarah Horswell	pg. 27					H. Djelad	pg. 84	Veronica Celorrio	pg. 54
15:40	Andrew Wain	pg. 28	Muhammad Khan	pg. 98	Robert Johnson	pg. 69	Kevin Honeychurch	pg. 85	Ulrich Hintermair	pg. 55
16:00	**Refreshments, Posters and Exhibition** - *James France Exhibition Area*									
16:30	Andrew Cobley	pg. 29	Mark Symes	pg. 99	Michael Hitchman	pg. 70	Andrew Gross	pg. 86	Erdem Irtem	pg. 56
16:50					Frank Marken	pg. 71	Reshma Sultana	pg. 87	Isabella Poetzelberger	pg. 57
17:10	Ignacio Tudela	pg. 30	Konrad Szacilowski	pg. 100	Mike Lyons	pg. 72	Stanislav Hason	pg. 88	Barak Aaronson	pg. 58
17:30	Andrew Ballantyne	pg. 31			Jo Humphrey	pg. 73	Rawa Abdallah	pg. 89	Paul Brack	pg. 59
17:50	**Close**									
19:30	**Conference Gala Dinner** - *Holywell Park Conference Centre*									

Tues 9th

09:00	**Plenary Lecture** - Peter Bruce (Barker Medallist) *(CC011)*								
10:00	**Refreshments, Posters and Exhibition** - *James France Exhibition Area*								
	Room - CC011		***Room - SMB014***		***Room - CC012***		***Room - CC021***		***Room - CC013***
10:30	Ritu Kataky	pg. 32	Wolfgang Kaim	pg. 101	Wataru Sugimoto	pg. 109	Carlos Ponce de Leon	pg. 121	
10:50									
11:10	Matej Velicky	pg. 33	Frantisek Hartl	pg. 102	Jacob Locke	pg. 110	Simantini Nayak	pg. 122	
11:30	Peter Toth	pg. 34	Nicolas Le Poul	pg. 103	Vivek Padmanabhan	pg. 111	Ian McPherson	pg. 123	
11:50	Virginia Ferreira	pg. 35	Maria Mercuri	pg. 104	Stephan L. Koch	pg. 112	Maria Kourasi	pg. 124	
12:10	Eden De La Pena	pg. 36			George Chen	pg. 113	Haitao Yu	pg. 125	
12:30	**Lunch, Posters and Exhibition** - *James France Exhibition Area*								
13:30	**Plenary Lecture** - Digby MacDonald *(CC011)*								
14:30	**Poster Prize Presentations** -*(CC011)*								
14:40	Anthony O'Mullane	pg. 37	Florence Geneste	pg. 105	Ian Godwin	pg. 114	Vivien Chapman	pg. 126	
15:00	Marc Ledendecker	pg. 38	Emilio Palomares	pg. 106	Noemi Aguilo Aguayo	pg. 115			
15:20	Asif Ali Tahir	pg. 39			Li Guan	pg. 116	Shangfeng Du	pg. 127	
15:40	**Refreshments and Exhibition** - *James France Exhibition Area*								
16:10	Ares Gomez Gallego	pg. 40			Fulian Qui	pg. 117	James Courtney	pg. 128	
16:30	Michael Mercer	pg. 41			Xiaoxiao Lu		Quentin Meyer	pg. 129	
16:50	Carina Grill	pg. 42			Jagdeep Sagu		Carsten Cremers	pg. 130	
17:10	Dave Cutler	pg. 43			Jorge O Gil Posada	pg. 118	Amrit Chandan	pg. 131	
17:30	**Close**								

ELECTROCHEM 2014

PLENARY SPEAKER ABSTRACTS

Probing Water Molecules at the Electrochemical Interface by Surface-Enhanced Infrared Absorption Spectroscopy

Masatoshi Osawa
Catalysis Research Center, Hokkaido University
N21-W10, Kita-ku, Sapporo 001-0021, Japan

Understanding the electric double layer is the most fundamental and challenging issue in electrochemistry. Since Helmholtz (1853), the electric double layer has been studied extensively and many models have been proposed, including the Gouy-Chapman-Stern and the Bockris-Devanathan-Müller (BDM) models. The BDN model assumes that water at the interface is isolated from hydrogen-bonded network in the bulk and changes its orientation depending upon the charge on the substrate (i.e., potential) [1]. X-ray scattering experiments showed that the spacing between the electrode surface and the first water layer changes with applied potential, which is consistent with the BDM model [2]. However, experimental supports of the models are still very limited. Infrared spectroscopy is another useful experimental tool for this purpose owing to its high sensitivity to the hydrogen bonding. The first application of IR reflection-absorption spectroscopy (IRAS) to electrochemistry aimed at characterizing interfacial water [3]. Nevertheless, IRA spectra of interfacial water reported so far in the literature are largely different from each other, mostly due to the interference from the bulk solution. To avoid this difficulty, we developped surface-enhanced infrared absorption spectroscopy in the ATR mode (ATR-SEIRAS, Fig. 1) [4]. SEIRA is an effect in which IR absorption of molecules in the near vicinity of metal surfaces is significantly enhanced. With the assist of the ATR mode, this technique enables us to prove the electrochemical interface with much less interference from the bulk solution than IRAS. The very high sensitivity of ATR-SEIRAS also enables us to investigate fast and ultrafast electrode dynamics (with ms-ps time resolutions).

In this talk, the following three topics related to interfacial water studied by ATR-SEIRAS will be presented: (i) potential dependent restructuring of interfacial water under steady states [5,6], (ii) dynamics of destructureing of hydration shells around cations at the interface under potential step conditions [7], and (iii) ultrafast change in the rest potential induced by the thermal agitation of water molecules at the interface [8].

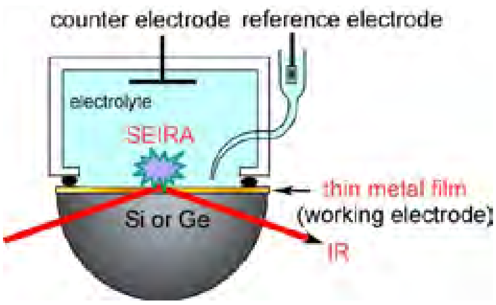


Fig. 1. In situ observation of the electro-chemical interface by ATR-SEIRAS

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Functionalized Solid-State Nanopores for Biosensing Applications

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Imperial College London
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t.albrecht@imperial.ac.uk

Solid-state nanopore devices are a new class of sensors for the structural and compositional analysis of biopolymers such as DNA, RNA and peptides, as well as biomolecular complexes.[1] Typically, they consist of a liquid cell, separated into two compartments by a thin, solid-state membrane. A single, nanometer-sized opening in the membrane (the "nanopore") connects these two compartments and allows for the exchange of ions and liquid between them. Upon application of an electric field across the membrane, charged biopolymers are pulled through the nanopore one-by-one, modulating the ion current in a characteristic way. This modulation in the current-time trace can then be related to the properties of the translocating biomolecule and perhaps even to the composition of the analyte. Therefore DNA sequencing has been a long-term goal and major driving force in the field, since the approach would be fast, inexpensive and not require any labelling. Unfortunately, the implementation of these promises has proven very difficult. Some of the reasons are the lack of control of DNA motion in the nanopore; insufficient spatial and temporal resolution (i.e. to resolve individual bases or base pairs); and the lack of specificity of the sensing region.[2] However, these challenges can be overcome, as we and others have shown. In my presentation, I will discuss a select number of examples from our own work and put them into context with the state-of-the-art in the field.

These examples include the use of bipotentiostatic electrodeposition, with *in situ* ion current feedback through the pore, as a tool for fabricating sub-10 nm metallic pores;[3] SERRS-based detection of translocation events and plasmonic enhancement in the nanopore;[4] embedding of electrode junctions in the nanopore and the notion of tunnelling-by-sequencing;[5,6] and the integration of glass nanopipettes with droplet microfluidics.[7] In addition to DNA, we have also studied small proteins, such as insulin, and complexes between DNA and proteins, for example p53, single-stranded binding protein (SSB) and methylation-specific antibodies. In this context, nanopore sensing proves to be a valuable biophysical tool and may find applications in gene profiling or molecular barcoding.

[1] M. Wanunu, Phys. Life Rev. 2012, 9, 125-158
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[3] M. Ayub et al., J. Phys.: Cond. Mat. 2010, 22, 454128
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[5] A.P. Ivanov et al., Nano Lett. 2011, 11, 279-285
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[7] T.R. Gibb et al., Anal. Chem. 2014, 86, 1864–1871

The Rechargeable Aprotic Li-O_2 Battery

Peter G. Bruce
University of Oxford

Energy storage is one of the great scientific challenges and societal needs of our time. Whether to power future portable electronic devices, to transform electric vehicles into a mass market product or to store electricity from renewable sources, a step-change in energy storage, especially the storage of electrical energy, is required. New science, new knowledge and new electrochemistry are essential to achieve this step-change. The rechargeable aprotic Li-O_2 battery, see figure below, in which O_2 is reduced to Li_2O_2 at the positive electrode on discharge then oxidised again on charge, offers the highest theoretical specific energy of any rechargeable battery (theoretically 3500Whkg^{-1} versus 800Whkg^{-1} for Li-ion). The promise of the aprotic Li-O_2 is great but so too are the challenges.

Schematic representation of a rechargeable Li-O_2 battery.

All aspects of the cell require advances in the science. In particular, new understanding of the electrochemical mechanism of O_2 reduction to Li_2O_2 in aprotic Li^+ containing electrolytes is required. So too is understanding the reactivity between the intermediates in the reduction and the electrolyte and electrodes. The use of redox mediating molecules to address the problem of how to oxidise solid Li_2O_2 at a solid electrode with sufficient rate to sustain adequate current densities will also be described.

References

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The Enabler of Our Reactive Metals-Based Civilization; Passivity

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For more than forty years, the conditions for the existence of the passive state, and hence for the existence of our reactive metals-based civilization, which is based upon the use of the reactive metals (Al, Cr, Fe, Ni, etc) to build precision machines, have been described in terms of equilibrium thermodynamics in the form of Pourbaix diagrams.[1] These diagrams plot equilibrium potential versus pH relationships for various reactions (e.g., Fe/Fe_3O_4, Fe/Fe^{2+}, Fe_3O_4/Fe^{2+}) to define regions of stability or predominance. However, Pourbaix diagrams provide an equilibrium view of passivity, whereas passive films are non-equilibrium structures, whose existence depends upon an appropriate relationship between the rate of formation and the rate of destruction. Accordingly, a more accurate and realistic description of the phenomenon of passivity must be found in the field of electrochemical kinetics. It is this kinetic theory for depassivation (loss of passivity) that is presented in this paper. It is shown that the kinetic theory for depassivation, which is based upon the Point Defect Model[1,2] not only accounts for transpassive dissolution, acid depassivation, flow-assisted corrosion, and fretting corrosion, but it also led to the discovery of a new form of depassivation, which is termed "resistive depassivation". This form of depassivation results from the passage of the passive current through a resistive outer layer to a remote cathode, such that when the IR potential drop is subtracted from the control voltage, there is insufficient voltage drop across the barrier layer to maintain a finite thickness. In that case, the barrier layer disappears and the surface becomes "depassivated". The kinetic theory of depassivation has led to the construction of Kinetic Stability Diagrams (KSDs)[2], which the author offers as kinetic alternatives to the classical, equilibrium Pourbaix diagrams for describing the passive state. Importantly, the KSD accounts for the high corrosion resistance of the chromium-containing alloys (e.g., stainless steels) in very acidic environments, such as concentrated nitric acid and oleum (SO_3/H_2SO_4), and resolves Faraday's paradox arising from his famous iron-in-nitric-acid experiments of 1833. Finally, the PDM provides a deterministic method of designing *ab initio* new, corrosion-resistant alloys[3], representing the first departure from empiricism since alloying began several thousands of years ago.

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ELECTROCHEM 2014

SPEAKER ABSTRACTS

Spatially Directed Electroactive Polymer Deposition for Visualizing Latent Fingerprints on Metal Surfaces

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Fingerprint evidence is central to the investigation and prosecution of property and violent crime. The majority of such evidence is in the form of *latent* fingermarks, i.e. those that are not immediately visible to the eye, so they require physical techniques or chemical reagents to make them visible. Over several decades diverse reagents have been developed for this purpose, ranging from coloured powders that interact by mechanical adhesion, through polymers (e.g. "superglue") that form on the fingermark, to (bio)chemically selective reagents that react with specific components of the fingermark residue. Surprisingly, despite considerable inventiveness, success is modest: for metallic objects, such as bullets and knives involved in crimes of violence, the recovery rate is typically less than 10%.

Motivated by these considerations, we have explored a complementary strategy based on electrochemical control, direction and visual optimization of the reagents [1],[2]. Specifically, we exploit the fact that the fingerprint deposit can act as a “mask” (template), such that electrochemical processes can be directed with spatial selectivity to the exposed metal between the fingerprint ridges. Electrodeposition of a visibly contrasting reagent then yields a negative image of the fingerprint. This strategy has the practical advantage that it may be used sequentially with traditional reagents without mutual jeopardy [3].

The attributes of this approach will be explored via electrodeposition of pyrrole-, thiophene- and aniline-based conducting polymers on a wide range of metal surfaces. These materials have the further advantage that they are electrochromic. By comparison with traditional monotone (commonly B&W) fingerprint images, this creates an additional dimension for optimization of the visual contrast with the surface; this process is reversible and permits local optimization for regions of the image that are strongly or weakly developed. The results of imaging methods operating at different length scales, associated with different features within the fingerprints, will be presented. Extension of the approach will be described in terms of co-polymer deposition. This permits use of a wider colour palette and application to more reactive metal surfaces of forensic interest. Speculation will also be made on the possibility of combining optical absorption with fluorescence.

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Electrochromic and Colorimetric Properties of Copolymer Films Based on Pyrrole and Quaterthiophene Derivatives

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Alkyl derivatives of oligothiophenes constitute an interesting class of electroactive polymers with potential application in electronic devices. 3,3'''-Dihexyl-2,2':5',2'':5'',2'''-quaterthiophene (DHQT) is often investigated for such applications, however, its electropolymerisation directly onto the electrode surface can lead to a loosely-adherent deposited film, as observed for other dihexyl-quaterthiophenes with similar structures [1]. In order to modify the properties of DHQT and thus enhance the adherence and film formation capability of this polymer, this work has focused on the electrochemical copolymerisation of DHQT with a pyrrole derivative, (*R*)-(-)-3-(1-pyrrolyl)propyl-*N*-(3,5-dinitrobenzoyl)-α-phenylglycinate, DNBP [2] (Fig. 1).

The copolymerisation of DHQT and DNBP was performed electrochemically in 0.1 mol L^{-1} $CH_3CN/(C_4H_9)_4NBF_4$ by oxidation of monomer mixtures in different feed ratios. Copolymerisation improved the properties of the films of both polymers PDHQT and PDNBP in respect to the adhesion of PDHQT onto ITO/glass surface and the chromatic contrast of these materials. Reversible changes in the colour occur in the all copolymer films from yellow or orange at 0.00 V *vs.* Ag/Ag^+ to green or blue at 0.45 V, but were dependent on the proportion of the comonomers used to prepare the copolymers. These changes are more significant for P(DHQT-co-DNBP) films deposited onto ITO/glass with 1:5 feed ratio (Fig. 2). Solutions of PDHQT and its copolymers with DNBP (independently of the feed ratio) in N- methylpyrrolidone are fluorescent with emission of yellow colour. Therefore, the copolymers might be potentially applicable in displays and optoelectronic devices as electrochromic and fluorescent materials.

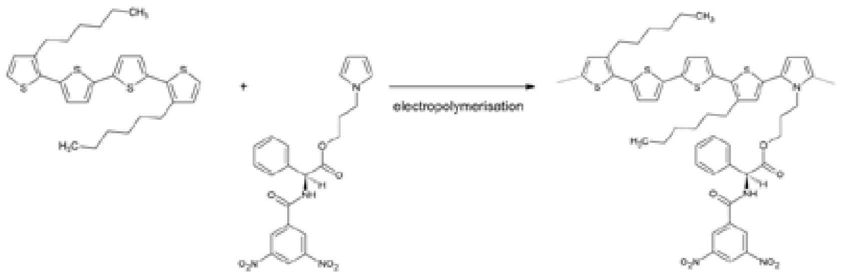

Fig. 1

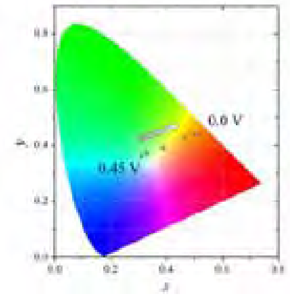

Fig. 2

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An Electrochemical Quartz Crystal Nano-Balance Study on Cu-Sn Codeposition from Methanesulfonic Acid

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Methanesulfonic acid (MSA) is an interesting supporting electrolyte for electrodeposition as it has many desirable properties such as high salt solubility, high conductivity, low toxicity and corrosivity which enables better waste management. Being an acidic electrolyte it has the added benefit of being compatible with photoresist materials and, therefore, offers the possibility of being useful for microfabrication. Various additives or complexing agents such as brighteners, antioxidants, and surfactants are usually added during Cu-Sn deposition. The simplest electrolyte has been shown to require an antioxidant and a fluorosurfactant [1].

Although the fluorosurfactant was initially used to reduce hydrogen evolution [2], more recently, it has been shown to also prevent the formation of metal oxides [3]. In addition, this additive shifts the metal reduction potential of Cu in the cathodic direction, thereby facilitating the co-deposition of the Cu-Sn alloy [4]. In this regard, the role of the fluorosurfactant is crucial and multifunctional, which is not fully understood.

In this work we have further examined the role of fluorosurfactant in shifting the electrochemical reduction potential for the more noble metal. The surface adsorption and desorption processes of the surfactant has been inferred through the use of an electrochemical quartz crystal nanobalance (EQCN). Copper and tin have been deposited individually and simultaneously from methanesulfonic acid electrolytes. The deposition potential of Sn is not affected by the presence of the surfactant. However, it was found that the adsorption of the surfactant blocks the reduction and oxidation reaction for copper. During the codeposition of Cu-Sn, the surfactant was found to adsorb to the surface and inhibit Cu deposition. Once the potential reaches a significantly negative value, the surfactant desorbs and the co-deposition of Cu-Sn can proceed.

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Co-electrodeposition of Co-nSiC Nano-Composite Coatings by Pulse Reverse Technique

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Cobalt-nano-silicon carbide Co-nSiC composite coatings have been successfully produced from a cobalt gluconate bath containing a dispersion of SiC nano particles (45-55 nm diameter). The particles were dispersed in the bath by use of an ultrasonic horn during deposition. The influence of anionic surfactant on particle content of the composite coatings produced using direct current (DC) and pulse reverse plating (PRP) are described. The effect of the varying the cathodic deposition time on the particle content of the coatings was determined. The coatings were assessed by scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX) to determine the dispersion of coatings

The particle content of the coatings was controlled by fixing the anodic cycle time t(a), and varying the cathodic cycle time, t(c). Improved particle content and distributions were obtained by PRP, with higher particle contents achieved using high anionic surfactant content and shorter t(c). Sound coatings with a high percentage (>10 vol.%) of particles were produced at t(c) of 60 s. This was encouraged by electrophoretic attraction of particles in the anodic phase and then encapsulation during the cathodic phase of the cycle.

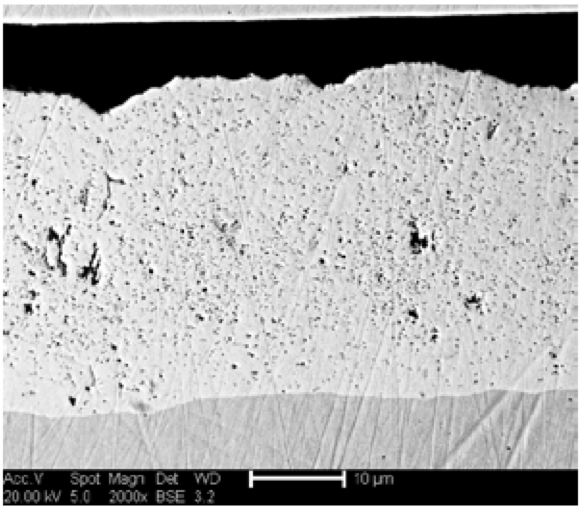

Figure 1 Co-nSiC with low particle content

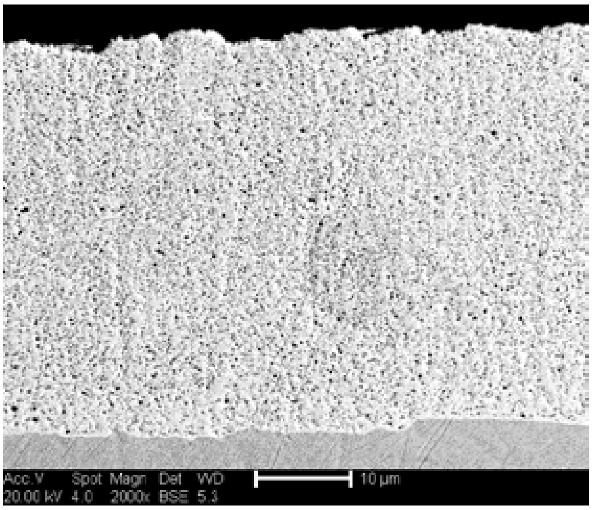

Figure 2 Co-nSiC with high particle content

Silicon Quantum Dots: Properties and Applications in Bone Biology

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We prepare silicon quantum dots (SiQDs) by an electrochemical etch followed by refluxing the porous silicon in toluene solutions of an alkene. The porous silicon layer is disrupted by the refluxing solvent and a transparent yellow dispersion of silicon quantum dots results. The dispersion shows strong orange luminescence. The particles are capped by an organic monolayer covalently bonded to the surface Si atoms through a robust Si-C bond that is formed by thermal hydrosilation of the alkene at the porous silicon surface. This monolayer greatly increases the stability of silicon quantum dots to aqueous environments and makes possible applications as a luminescent label in cell biology.[1] We have studied the time-dependence of the luminescence under CW excitation with laser light and find that although the PL intensity decreases to reach a steady-state value in a few minutes, the process is a photoionisation and does not involve irreversible chemical changes in the particles which would reduce the utility of the silicon quantum dots in confocal microscopy.[2] Finally, we have demonstrated a simple real-time assay for bone resorption based on confocal luminescence microscopy in which the release and subsequent cellular internalisation of silicon quantum dots by resorption of an artificial bone matrix is detected at the single-cell level.[3]

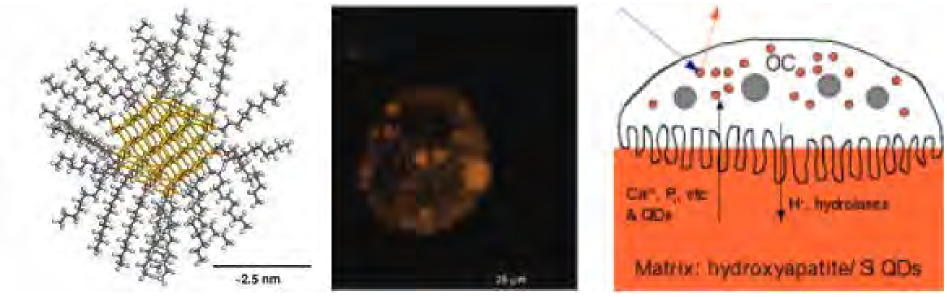

Figure 1 – (left) Alkyl-capped silicon quantum dot. (middle) Confocal luminescence image of an osteoclast resorbing the artificial matrix; the colour scale is a false colour, but is chosen to reflect the approximate true colour of the luminescence. (right) The schematic illustrates the assay concept with SiQDs indicated by the orange colour.

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Synthesis of p-block Nanowires by Supercritical Fluid Electrodeposition

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The deposition of nanowires of the p-block elements as a means to construct nano-devices is currently one of the great challenges in nanoscience. Interest in the p-block elements primarily stems from their semiconducting properties, and subsequent application in a wide variety of devices including transistors, thermoelectric generators and solar cells. Traditional deposition techniques for device fabrication, such as chemical vapour deposition and molecular beam epitaxy, are unsuited for filling extreme nanoporous templates (sub 10 nm) as the necks of the pores often become blocked. Supercritical Fluid Electrodeposition (SCFED) is an emerging technique that combines the benefits of electrodeposition and supercritical fluids (SCFs) to fabricate the next generation of nanotechnology and nanowire- based devices. The SCFED Project (www.scfed.net) is a multidisciplinary collaboration of British universities investigating the fundamental and applied aspects of SCFs.

Supercritical fluids (SCFs) are a distinct phase of matter, that exhibit a novel hybrid of gas- like and liquid-like properties. They are attractive as solvents for electrodeposition because the absence of surface tension and suppression of bubble formation allows them to fully penetrate extremely high aspect ratio, small diameter (sub 3 nm) nanopores. Furthermore, the high chemical stability and wide potential windows of many SCFs facilitates the electrodeposition of highly reactive materials that would be inaccessible from many liquid- state solvents.

Previous work in the SCFED Project has demonstrated the electrodeposition of copper[1], silver[2], and germanium[3] from SCFs. In this work we will present the preparation of a variety of p-block nanowires including bismuth, tellurium, germanium, tin and antimony into templates with pore sizes ranging from 55 to 3 nm. The prepared materials are characterised by scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD).

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Can Surfactant Effects be Beneficial for Electrocatalysis?

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Platinum (Pt) nanoparticles are currently the most effective catalysts used as cathode materials in proton exchange membrane fuel cells (PEMFCs).[1] Much research effort has been expended to identify and understand how catalytic activity and selectivity depend on the size, size distribution and shape of nanoparticles, as well as their dispersion on catalysts supports.[2] Two main problems can arise in the study of such nanoparticles: (a) the small size of nanoparticles leads to a tendency to aggregate, which reduces long-term efficacy of the catalyst and (b) the common use of surfactants to control the size, size distribution and shape has often led to loss of activity as a result of blocking of active sites by surfactants. For this reason, some studies have focused on means to "clean" nanoparticles of surfactants to enable their study in the absence of these blocking effects.[3] It would be advantageous if Pt nanoparticles could be utilised in catalytic reactions without extensive cleaning procedures, from the point of view both of reducing effort in their production and also from the potentially beneficial effects of reducing tendency to aggregate during operation.

We present a study of the effect of surfactant on the performance of Pt nanoparticles for the oxygen reduction reaction. Pt nanoparticles were synthesised using different surfactants and characterised with transmission electron microscopy, dynamic light scattering and cyclic voltammetry. The activity and the selectivity of the catalyst towards the four electron reduction of oxygen to water were determined with rotating ring disc electrochemistry. We show that the choice of surfactant is crucial to the electrochemical and electrocatalytic properties of the nanoparticles. Nanoparticles prepared with the cationic surfactant tetradecylammonium bromide exhibit poor performance for the oxygen reduction reaction, which we interpret as resulting from anion adsorption and shape effects. On the other hand, nanoparticles prepared with the non-ionic surfactant nonylphenolethoxylate perform well, both in terms of selectivity and activity, when compared with commercial catalysts. This possibility to synthesise surfactant-stabilised catalysts provides a potential means to protect catalysts from aggregation without loss in performance.

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High-Resolution Electrochemical Imaging of Nanomaterials for Energy Applications

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The ability to characterize the electrochemical behaviour of spatially heterogeneous electrode surfaces on a localized scale is essential to our understanding of interfacial processes and heavily impacts the development of nanomaterials for emerging energy conversion technologies. Scanning electrochemical microscopy (SECM) is a valuable tool for achieving spatially resolved electrochemical measurements and significant advances have been made over the past decade in high resolution electrochemical imaging. Major challenges include the reliable fabrication of nanoelectrode probes as well as the ability to precisely control their separation from the surface of interest during mapping experiments. The introduction of a topographical feedback mechanism has the advantage of enabling the correlation of electrochemical behaviour with surface structure and morphology.

This presentation will highlight the latest developments at NPL in the high-resolution electrochemical and topographical imaging of nanostructured electrode surfaces using two different approaches. We first present the characterization of new batch-fabricated conical probes for coupling SECM with atomic force microscopy (SECM-AFM). The probes generate high-quality Faradaic current maps alongside nanometre-resolved topographical information, as demonstrated by their application to imaging exfoliated graphene and graphite samples. We then explore progress in the combination of SECM with scanning ion conductance microscopy (SECM-SICM) through the development of double-barrelled pipette probes with functionalized carbon tips. We demonstrate the application of such probes to imaging electrocatalytic processes at nanostructured interfaces and take a step towards the measurement of intrinsic electro-kinetics at the single nanoparticle level.

Ultrasonically Enabled Resource Efficient Electrochemical Deposition

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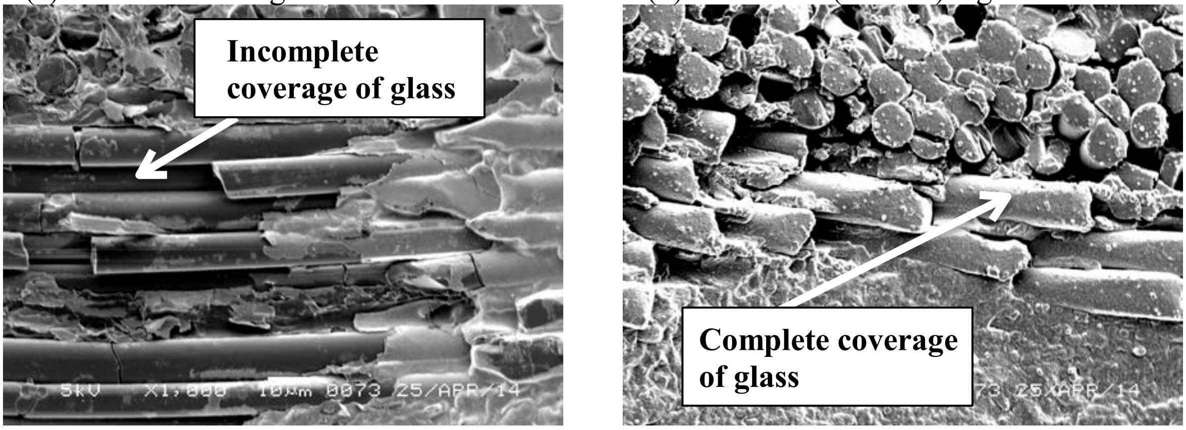
Electroless copper plating is an electrochemical deposition process used in a wide range of industries due to the fact that it enables the metallisation of non-conductive materials. For this reason it is used extensively for the metallisation of ‘through holes’ and ‘vias’ in printed circuit boards (PCBs) enabling their subsequent electroplating. In this application the non- conductive material must first be catalysed using a palladium based colloidal solution.

When ultrasound is applied to an electrolyte, a number of well-known effects occur which can influence an electrochemical process. In particular micro-jetting, brought about by the asymmetric collapse of acoustic cavitation bubbles at, or near, a solid surface, can improve mass transport, thin diffusion layers [1] and generate localised heating. Electroless plating is also electrochemical in nature and there has been much work performed on the effect of ultrasound on the electroless process [2] and benefits such as increased plating rates [3] and improved coverage [4] have been described.

This paper will demonstrate how ultrasound can be an enabling technology for more resource and energy efficient electrochemical deposition. It will be shown that by electroless copper plating in a 40 kHz ultrasonic field, significant improvements in plating coverage (Fig 1 (a) and (b)) can be achieved which will allow electroless copper plating temperatures to be reduced by at least 20 ºC and a 50% reduction in palladium concentration is facilitated.

Figure 1. Electroless copper coverage on glass fibres in through hole of a printed circuit board. Plating temperature 25 ºC, 50% Catalyst concentration



(a) Conventional Agitation

(b) Ultrasonic (40 kHz) Agitation

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Sonoelectrodeposition of Novel Thin Nickel-based Composite Coatings with Lubricant Particles

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The electrodeposition of Ni-based composites has received a wide attention in recent years due to the improved characteristics that these coatings may present [1]. In the study here presented, novel Ni-based composite coatings with embedded lubricant particles (hBN and WS_2) were electrodeposited on Cu substrates from a Ni Watts bath with no further addition of surfactants or dispersants with the aid of ultrasound [2]. The implementation of ultrasound did not only prove very effective in achieving a better dispersion of particles in the Ni Watts bath, but also in producing thin Ni composite coatings with a uniform distribution of finely dispersed particles.

The novel Ni/hBN and Ni/WS_2 composite coatings were characterised by different methods: Glow Discharge – Optical Emission Spectroscopy (GD-OES) to estimate the particle content in the coating, X-ray Diffraction (XRD) analysis to analyse the orientation of the Ni composite coatings, Focused Ion Beam – Scanning Electron Microscopy (FIB-SEM) to study the surface morphology and microstructure of the resulting composites and microhardness tests to evaluate effect of the presence of the particles on the hardness of the deposits. GD-OES results pointed a higher incorporation of WS_2 particles than hBN particles in the same conditions (15 g/L), which not only resulted in a remarkable change in the XRD spectra of the composites compared to pure Ni deposits (presence of particles promoted electrocrystallization in [211] direction, especially in the case of the Ni/WS_2), but also in the surface morphology and microstructure of the coatings, with the Ni/WS_2 composite coatings presenting a nanocrystalline structure, as opposed to the Ni/hBN composite coatings, where much larger Ni grains were observed. Such nanocrystalline structure was responsible for significantly enhancing the hardness of the Ni/WS_2 composite coatings (≈30%, of improvement compare to pure Ni coatings), despite the general idea that the presence of inherently soft particles should result in lower hardness, as observed in the Ni/hBN composite coatings.

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Speciation and Electrochemistry in Deep Eutectic Solvents; Applications in Immersion Coatings

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Here we discuss the speciation of metal ions in deep eutectic solvents (DES), showing how this can have a profound effect on their electrochemical behaviour. We go on to show how an insight into speciation is key to understanding the coating of immersion gold onto electroless nickel substrates (ENIG), an important process in the electronics industry.

Speciation controls many aspects of the electrochemical behaviour of metal ions in aqueous solutions, such as solubility, redox potentials and kinetics of deposition/dissolution. This can give large differences in the electrochemical behaviour of respective metal salts. Novel DESs have shown great promise for the processing of metals, with applications in electrodeposition, electropolishing, immersion coatings and metal recycling but there is a limited understanding of metal ion speciation in these media.

EXAFS studies show that usually metal solvation occurs through coordination with chloride ions in the DES, which are present in high concentration (c.a. 5.6 M Cl^-). An example of this is AuCl, that forms a linear $[AuCl_2]^-$ anion in the DES Ethaline 200, as determined through the EXAFS data shown in Figure 1(a). While most metal ions form chloro complexes, this is not always the case. EXAFS shows that $NiCl_2$ in Ethaline 200 is dominated by interactions with the ethylene glycol (eg) forming a cationic Ni complex where the Ni ion is coordinated by 3 eg molecules. Crystals were also obtained from a solution of 5 mM $NiCl_2$ and 10 mM phenanthroline in Ethaline where the speciation is dominated by the hydrogen bond donating ligands as shown in Figure 1 (b).[1]

This change in speciation manifests as markedly different electrochemical behaviour. For example, AuCl shows classic diffusion limited electrochemical behaviour indicating a kinetically fast process. Conversely, $NiCl_2$ has a much more complicated response with sluggish deposition kinetics and no distinct peaks in the CV indicating a more hindered deposition process as shown in Figure 1 (c).

The electrochemical properties of Ni and Au salts are of critical importance when considering immersion coating of Au onto Ni, affecting the deposit morphology, adherence and rate of deposition. To illustrate this we demonstrate how the speciation and electrochemical properties of various Au salts has a dramatic impact on the properties of immersion gold coatings onto electroless Ni substrates.[2]

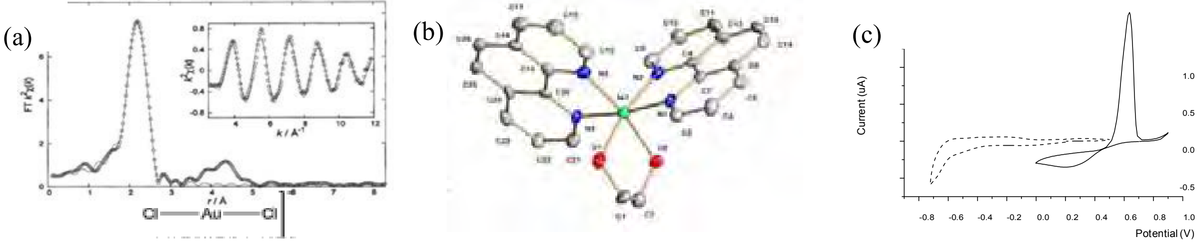

Figure 1: a) Fourier transforms of EXAFS data (circles) and fits (line) with raw unfiltered data (inset) for a 0.1 M AuCl solution in ethaline 200, b) crystal structure of $[Ni(phen)_2(eg)]Cl_2.2eg$ with olipsoids displayed at 50% probability and c) cyclic voltammograms for 5 mM solutions of AuCl (unbroken) and $NiCl_2$(dashed) on a 1 mm Pt disc w.e., Ag wire *pseudo* R.E., Pt flag C.E. at room temp and a scan rate of 5 mV s^{-1}

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Size, Charge and Concentration Effects on Modified Gold Nanoparticles

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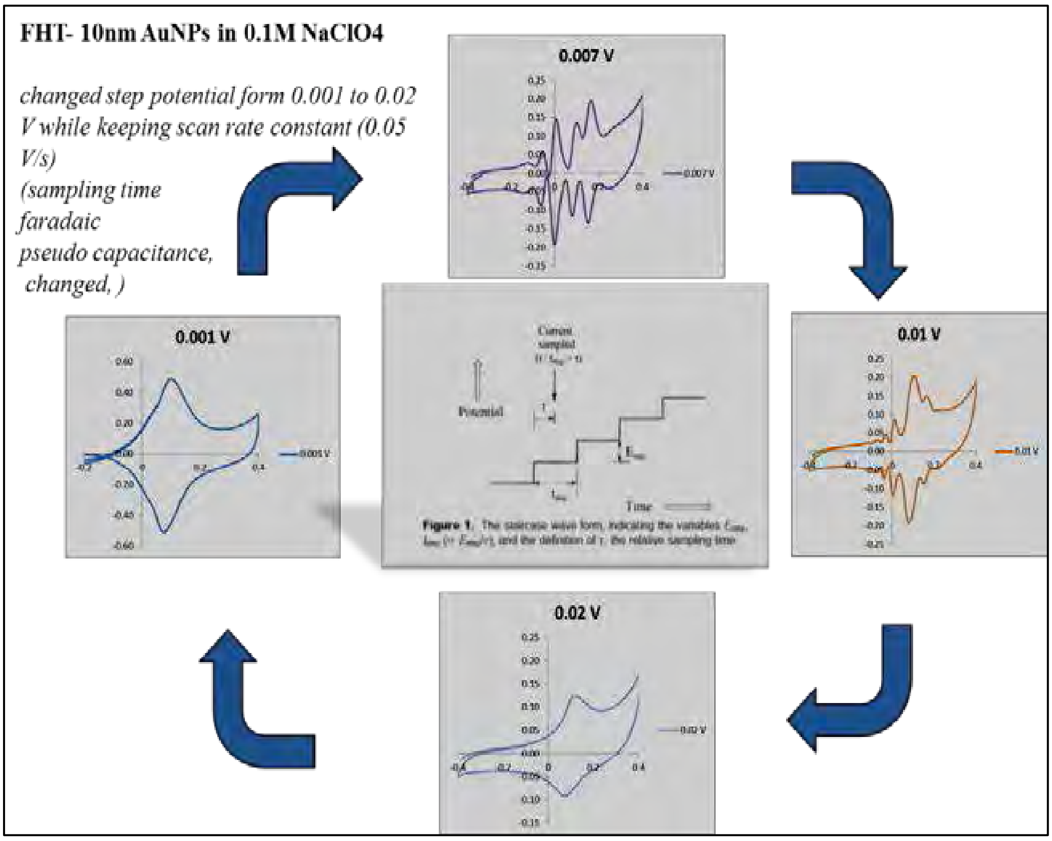
Modified Gold nanoparticles (AuNPs) of a range of sizes from 1.3nm-10nm, show charge, anion, concentration size and scan rate dependent electrochemical properties. The effects are clearly evident in cyclic voltammetric and differential pulse of square wave voltammetry as peak splitting. The observations are attributable to the double layer on the electrode surface , the different electrical fields experienced by the modified nanoparticles in different electrochemical environments ion-pair associations and permeabilty. Similar effects have been reported by Murray and co-workers[1,2]. In this work we will show the dependence on the electrochemical response on the position of the anion in the Hofmiester series. Modulation of amplitude and scan rates additionally has a spectacular effect of peak splitting depending on the AuNP size.



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Electron Transfer Kinetics on Mono- and Multi-layer Graphene and Other 2-D Layered Materials

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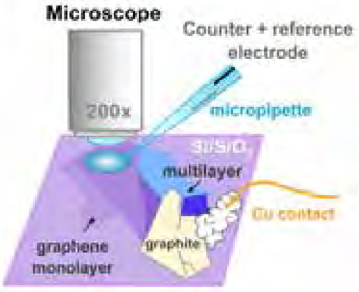
The unique properties of the two-dimensional crystal of carbon, known as graphene, such as high electron mobility, large specific surface area and high transparency, sparked an enormous research interest to explore the electrochemical properties of graphene sheets, with potential uses in many applications such as sensors, energy conversion/storage and corrosion protection. Furthermore, other 2-D layered materials, particularly transition metal dichalcogenides (TMDC) such as MoS_2, also show promising properties. Understanding how the electron transfer kinetics of a redox reaction between the surface of these 2-D crystals and a molecule, compare to bulk materials is crucial to the future use of graphene/TMDC as high-performing electrode materials. Herein, the electrochemical response of graphene/graphite and MoS_2 electrodes is presented. Experiments were carried out using a microinjector, micromanipulator and optical microscopy, enabling precise deposition of size-controlled droplets on the flake surface [1]. The insulating substrates used for flake preparation include inorganic materials and organic polymers. The electrode materials were characterised using optical microscopy, Raman spectroscopy, atomic force microscopy and X-ray photoelectron spectroscopy.

The electron transfer rate at the basal plane, edge plane and freshly cleaved surface of graphene/graphite and MoS_2 flakes was determined using voltammetric techniques. The number of layers and, in particular, local surface conditions are shown to have a significant effect on the electrochemical activity [2, 3].



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Electrochemical Investigation and Metal Nanoclusters Deposition at a Free-Standing CVD Graphene Monolayer

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Electrical polarisation of the interface between two immiscible electrolyte solutions (ITIES) generates electrochemical potential gradients capable of promoting ion and electron transfer across the molecular boundary. The nucleation of metallic structures, catalytic activity *e.g.* hydrogen and oxygen evolution, the assembly of nanoparticles or catalytic nanoparticles have received a great interest in the last years [1-2].

Graphene nanomaterials were prepared either by liquid exfoliation from natural graphite in 1,2-dichloroethane and by chemical vapour deposition (CVD) on copper foil. Both types of material were assembled at the ITIES. The graphene (GR) materials before and after assembly were characterized by microscopy techniques and Raman spectroscopy. The electrochemical reactivity of assembled GR was probed by model redox species at the ITIES and impedance spectroscopy was used to study the change of the interfacial capacitance and resistance. *In situ* electrochemical and spontaneous metal deposition of noble metals (Pd, Au) at the interface assembled CVD GR monolayer was studied (spontaneous deposition scheme and photographs in Fig 1). The identification and morphology of the deposited graphene-metal nanoclusters were determined using electron microscopy (SEM image in Fig 2). The 2D graphene-based metal nanostructures effects were studied for the model redox species process at the ITIES. The graphene-metal nanocomposites preparation procedure at the ITIES opens an alternative way to prepare low dimensional carbon-based catalyst materials.

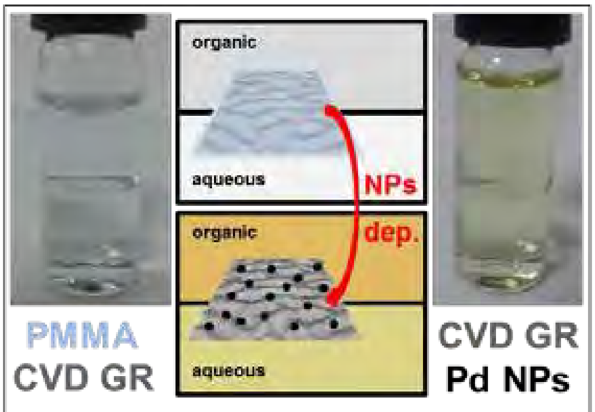

Fig 1: The interfacial assembled CVD GR

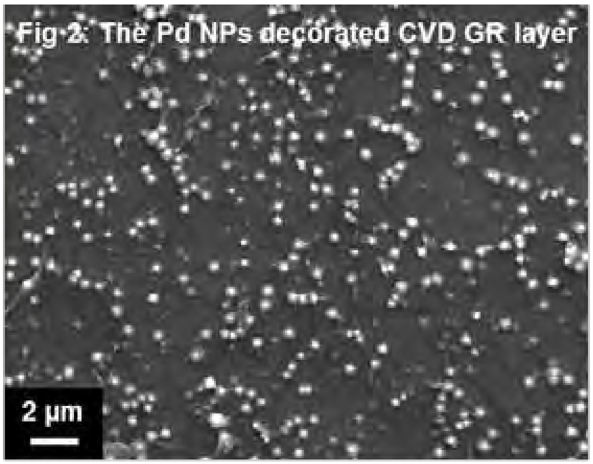
Fig 2: The Pd NPs decorated CVD GR layer

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The Effect of Electrochemical Control Function on Metal Alloy Deposition

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Here we describe an *in situ* study of the electrochemical deposition of metal films onto a gold electrode in a deep eutectic solvent (DES) electrolyte using neutron reflectivity measurements.

The aim is to study the effect of the deposition technique on the properties of the resultant metal films; two deposition protocols are characterised: (i) slow scan rate potentiodynamic and (ii) constant cathodic potential deposition. The ultimate goal is to elucidate whether systems in which two metal species are present alloy or co-deposit. To achieve this (i) the spatial profiles of the metal components, (ii) the effect of deposition methodology on the composition of the thin films and (iii) the compactness of the deposited layers will be investigated. Two very different co-metal systems have been chosen to characterise: (i) Ag/Cu where the reduction potentials of the metals are significantly different and (ii) Cu/Sn which has similar reduction potentials.

The formation of metal alloys is of significant academic and industrial interest due to large variety of applications such as electrical contacts in microelectronic devices and battery development[1-3]. The deposition of a bi-metallic alloy requires the simultaneous reduction of both metal ions; hence both species must have similar reduction rates. The electrodeposition of metals from DESs has become of particular scientific interest in the last 20 years as it has been found that the metal electrochemistry changes considerably in a DES in comparison to that traditionally found in aqueous solutions. In the DES of interest here, Ethaline 200 (1 choline chloride: 2 ethylene glycol), the reduction potentials of Ag(I) and Cu(I) ions are around 300 mV apart (-0.07 V and -0.39 V *vs* Ag/AgCl, respectively) as such the most likely outcome of depositing from a Ethaline solution containing both these ions is that segregated layers of each metal are formed[4,5]. An electrochemical quartz crystal microbalance-probe beam deflection (EQCM-PBD) study into the co-electrodeposition of silver and copper from a DES found that even though the deposition was carried out at a constant -0.4 V, upon subsequent dissolution of the metal coating from the surface of the crystal a step-wise electrochemical dissolution was observed; suggesting segregated phases of each metal present. Neither electrochemical nor EQCM-PBD data are spatially selective so neither technique can provide internal structural and compositional information which would be key to assessing whether an alloy or co-deposit had been formed; or whether any hydrogen embrittlement had occurred that may inhibit performance.

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The Effect of Additives on the Polarization of the EnFACE Plating Bath

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The EnFACE technology is a novel mask-less process that enables electrochemical metal deposition and etching with the use of just a single pattern. The process is seen to have potential in replacing costly photolithographic method. The EnFACE copper bath is atypical in composition as it is acid-less and has much lower copper concentration in comparison with conventional copper chemistry. However, it is unknown how bath additives would influence EnFACE plating processes.

This fundamental study looks at how additives are used in the electronic copper superfilling process; namely, PEG, SPS and Cl^-, affects the electrochemical behavior of the EnFACE bath. The study was done using a traditional electrochemical three-electrode set-up and a potentiostat for electrical response measurements. Single and mixed combinations of the additives were used with the EnFACE bath. Varying amounts of each additive were also tested to determine how additive concentration affects the bath. The polarization curves were derived by plotting the observed current density, i, with changing potential, V.

The three additives, when used separately, were observed to polarize the bath suggesting copper plating inhibition. The increase in polarization is caused by the adsorption of the additive molecules at the plating interphase which competes with copper ions and preventing the latter from undergoing chemical reduction. Increasing amounts of each additive is seen to lead to higher curve depression and appears to reach a saturation level where further rise in additive concentration does not yield an appreciable inhibition.

From Porous Metals to Liquid Metals and their Applicability in Catalysis and Sensing

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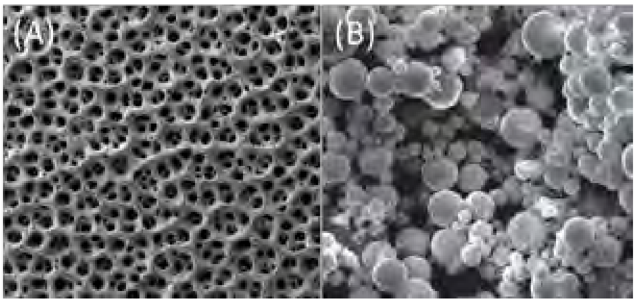
The fabrication of metallic nanostructures, and in particular bimetallic nanostructures, has received significant attention due to synergistic effects that improve electrocatalytic and catalytic activity of the bimetallic material over their individual counterparts. There are numerous ways to fabricate such nanostructures, however electrochemical approaches have advantages such as low cost, good control over morphology and composition and ease of use. In this presentation the co-deposition of porous Cu/M (M = Au, Pd and Ag) (Figure 1A) under hydrogen evolution conditions is discussed where Cu is used as a scaffold material in which the other metals are incorporated. Depending on the composition of the plating solution, alloys or phase separated materials are formed which has significant implications for catalytic processes such as nitrophenol reduction to aminophenol [1], a precursor used in the pharmaceutical industry. In particular it is also demonstrated that the substrate electrode material has a profound influence on the morphology and composition of the final electrodeposited material [2]. It is also shown for the particular case of Ag, Au and Pd electrodeposition on Cu electrodes that the deposit consists of a significant amount of Cu throughout the bulk of the electrodeposited material which is explained via a cathodic corrosion process occurring at the substrate electrode under vigorous hydrogen evolution conditions.

In the second part of the presentation the use of liquid metal galinstan (a eutectic of gallium, indium and tin) is discussed as a heavy metal ion electrochemical sensor whose sensitivity can be improved dramatically by surface modification with WO_3 nanoparticles [3] (Figure 1B). Significantly, liquid drops of galinstan, galinstan/native oxide and galinstan/WO_3 can be actuated in aqueous solution under an applied electric field, utilised as a liquid metal based pump as well as demonstrating photocatalytic properties for the destruction of organic dyes.



SEM images of (A) porous Cu/Au and (B) liquid drops of galinstan covered with nanostructured native oxide

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Highly Porous Materials as Tunable Electrocatalysts for Hydrogen and Oxygen Evolution Reactions

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The electrochemical water splitting reaction consisting of the oxygen evolution (OER, $4OH^-$ à $O_2 + 4e^- + 2H_2O$ in alkaline media) and the hydrogen evolution reaction (HER, $2H_2O + 2e^-$ à $H_2 + 2OH^-$ in alkaline media) plays a growing role in the fabrication of alternative energy devices due to the need of clean and sustainable energy.[1] By now, less abundant materials as Pt (HER) and Ru, Ir (OER) show prosperous performances but their high price make them rather unfavourable and alternatives are wished for. Thereby, Nickel as group 10 element show very promising properties as non-noble electrocatalyst in alkaline solution.

Here, we report the synthesis and characterisation of nickel sponge-like material embedded into a carbon and nitrogen matrix with high surface area (~900 m^2/g) for the use in the HER at pH 13.[2] The material was fabricated by an easy salt templating method using inorganic salts as templating agent and as reaction media. By easy doping of this material with manganese, higher current densities at lower overpotentials can be obtained. The activity of the material can be easily altered from a well working HER catalyst to a well working OER catalyst by simple surface oxidation as shown in Figure 1. Thereby, the surface area increases up to 1200 m^2/g while oxidising the metal to the respective metal oxide. A total voltage efficiency of 70% can be obtained for the water splitting reaction by dividing the theoretical cell potential (1.23V) by the necessary applied onset potential (1.76V).

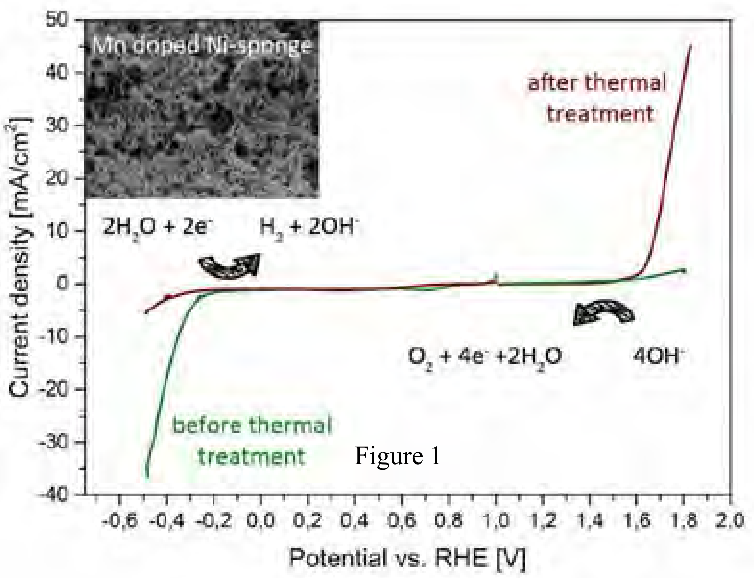

Figure 1

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Design and Development of Stable Metal Ferrites based Photocathodes for Solar Hydrogen Generation

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Abstract:

The photoelectrochemical (PEC) water splitting using semiconductor electrodes is the “Holy Grail” of solar energy conversion in the form of hydrogen, which is widely considered to be the sustainable solution for current energy crisis.[1,2] Since the pioneering work of Fujishima and Honda on photoelectrolysis on TiO_2 electrodes, a considerable amount of research has been conducted to explore suitable semiconductor electrodes.[3] The bottle-neck in realising the concept practically has been the difficulty in identifying stable low-cost semiconductors that meet the thermodynamic and kinetic criteria for photoelectrolysis of water.[4] Suitable materials for PEC should be capable of absorbing maximum photons from sunlight and function as effective catalyst for water splitting. Therefore, the semiconductor electrode must have low electron affinity, good stability against photocorrosion and bandgap of 1.8 - 2.2 eV for maximum solar to chemical energy conversion.[5]

There has been a considerable interest in recent years in the preparation, characterisation and testing of metal ferrites as a new class of potential semiconductor materials for water photoelectrolysis. This recent interest is ignited by a number of factors; (i) ferrites are a class of oxides hence capable of withstanding rigorous water redox reactions (ii) many metal ferrites have moderate band gaps, hence absorb visible light (iii) ferrites are available as anodes as well as cathodes (iv) they are easy to fabricate. Hence, metal ferrites have been considered as potential candidate materials that fulfil most of the stringent requirements (i.e. optical, energetic, chemical, electrochemical, photoelectrochemical, economic, and environmental requirements) demanded in water photoelectrolysis process.[6,7]

We have recently studied metal ferrites as a candidate photoelectrodes for water photoelectrolysis. Photoelectrochemical properties of those electrodes show that they are suitable for the photoelectrolysis of water. The present work describes our latest efforts on the fabrication and characterisation of metal ferrites ($LaFeO_3$) as potential *p*-type semiconductor electrodes for water electrolysis in PEC cells.

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Surface finish study of Electrochemical Machined Stainless Steel 316

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Electrochemical Machining (ECM) is capable of machining complex shapes in high performance materials (in terms of their toughness, hardness and elasticity) that have wide use in aerospace, medical and other high-value industries. It is desirable that ECM behavior of various systems can be accurately simulated, as this minimizes e.g. the experimental iterations associated with the design of the tool required to produce the shape and surface finish of the workpiece. This will reduce the cost and time of the process and would diversify the application of ECM in industry. Earlier experimental studies [1-3] of various metals showed that ECM and the resulting surface finish is dependent on parameters such as the overpotential and the flow rate of the electrolyte, due to variation in the underlying dissolution electrochemistry. This is particulary evident in ferrous alloys with a high chromium content, and makes accurate simulation challenging.

Based on these studies, in this presentation we present an enhanced model developed for accurate simulation of the ECM process. This aims to account for non-idealities by incorporating such factors as Joule heating, mass transfer and the measured i-V characteristics of the electrochemical dissolution process to enable the more accurate simulation of ECM as a factor of control parameters such as voltage, electrolyte flow rate and electrolyte inlet temperature. Simulation results will be presented from this enhanced model and compared to experimental ECM measurements for an industrially relevant Stainless Steel 316 (SS316) workpiece, for which the surface finish of the metal after the process was found to be non-uniform along the electrolyte flow path length and to vary with the control parameters. The accuracy and applicability of this simulation model will be discussed, along with its potential in simulating other materials.

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Design of Ultra-Thin Pt_xPb_{1-x} Films and Study of their Electrochemical Adsorption Properties

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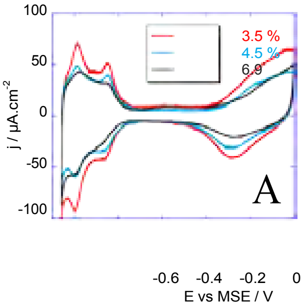
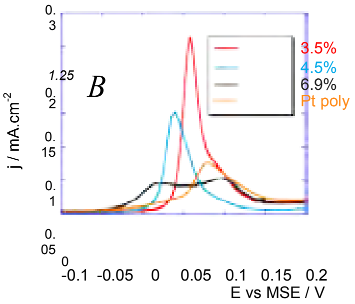
The development of inexpensive, highly active and stable Pt catalysts relevant to fuel cell applications remains a very important area of research. The most successful approaches to improve the performance of Pt catalysts include Pt thin-film overlayers[1] and Pt-X alloy skin and skeleton structures that comprise a Pt-rich surface supported on a Pt-X alloy[2]. In such structures, electronic and geometrical effects alter the catalytic activity and adsorption binding energies with respect to pure Pt. Furthermore, this work is motivated by promising results concerning the catalytic activity of Pt_xPb_{1-x} alloys for formic acid oxidation[3]. Thus, in this work we have explored the effect of controlling Pb content and film thickness on adsorption and catalytic activity.

One of the most successful methods to grow thin film overlayers is known as Surface Limited Redox Replacement (SLRR)[4]. In SLRR, a monolayer of underpotentially deposited (UPD) metal is galvanically displaced by Pt. Recently, epitaxial growth and negligible roughness evolution was demonstrated when SLRR was performed in a single cell configuration, using Pb UPD as a mediator[5]. In this work, we explored the SLRR-based deposition of Pt_xPb_{1-x} alloys in a single solution. Variations in surface composition with potential limits in SLRR and thickness have been verified by XPS measurements. The coverage of H UPD has been shown to decrease with Pb content, as shown in Figure A. The estimated Pt areas obtained from H UPD charges are much lower than the ones measured by XPS on the same alloys. This effect is due to a screening influence from Pb.

In this work, we have also examined the CO stripping behaviour on alloys. Linear sweeps in the CO free solution are presented in Figure B. A negative shift of the onset potential for CO stripping and change in peak shape as the Pb content increases can be observed. The charges obtained by integration of the stripping peaks are in quantitative agreement with those obtained by H UPD.





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Electrodeposition of Combinatorial Thin Film Material Libraries and their Investigation

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Combinatorial electrodeposition provides a time-saving and cost-efficient opportunity of producing a multitude of different materials on one single sample, a so-called material library, which can be prepared using a geometrically adapted Hull cell [1,2].

In this work, modified Hull cells were developed and utilised to electrodeposit binary and ternary material libraries (e. g. Cu-Ni, Ni-Zn, Co-Ni-Zn) exhibiting a large composition gradient, by means of normal and anomalous codeposition [3]. The compositions were determined using XRF, revealing for example respective Co, Ni and Zn contents of 25.7 –43.2 at.%, 13.8 – 51.2 at.%, and 5.6 – 60.5 at.% (Fig. 1) for a ternary Co-Ni-Zn material library.

Further examination of the material libraries was carried out by SEM imaging, XRD, and SKP. Scanning droplet cell microscopy (Fig. 2) allowed localised studies of the corrosion behaviour of the coatings over the whole composition range by means of potentiodynamic polarisation experiments. In this way the properties of an entire class of materials can be explored comprehensively.

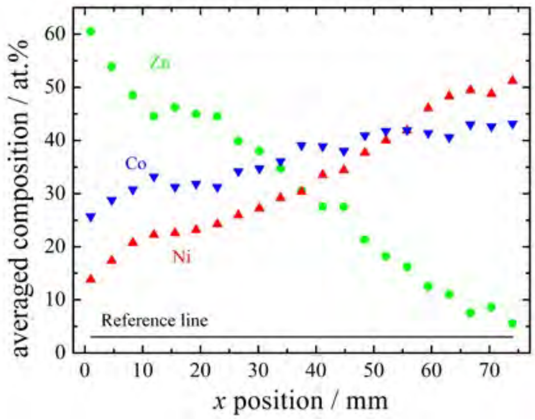

Fig. 1

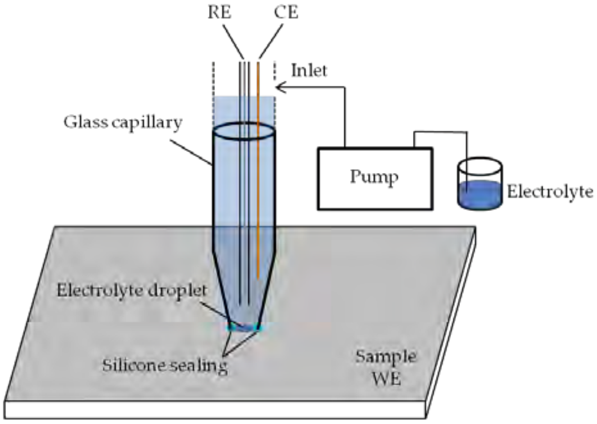

Fig. 2

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Dynamic *in situ* Spectroelectrochemical Cell to Study Nickel Hydroxide Thin Films using Synchrotron Techniques

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Diamond light source, a synchrotron facility in the Oxfordshire countryside (figure 1), is one of the world's most advanced scientific machines [1]. Synchrotron's produce intense beams of X-rays which can be used for many different spectroscopic, diffraction and mapping techniques of biological, geological and material samples which is not possible with lab based X-ray sources. Synchrotron facilities are shared by the international scientific community and time is allocated on individual beamlines through a competitive application process. A spectroelectrochemical cell will be used to measure *in situ* x-ray techniques such as microfocus extended x-ray absorption fine structure (µEXAFS), X-ray absorption near edge structure (XANES) and X-ray diffraction (XRD) of electrodeposited doped nickel hydroxide thin films. Nickel hydroxide is an important material in electrochromic [2], battery [3] and supercapacitor [4] applications. However a new technique is now also available at Diamond Light Source known as scanning x-ray microscopy (SXM), this beamline is capable of measuring a large number of different chemical elements as it has broad photon energy range. In addition multiple detectors using florescence and transmission mean that more data can be collected simultaneously, these detectors are capable of mapping chemical elements at a resolution down to 20 nanometers. For this beamline an *in situ* electrochemical cell will be based on designs from Bozzini et al three electrode system [5].

Figure 1 - Arial view of Diamond Light Source

Figure 2 - SXM in situ Spectroelectrochemical cell

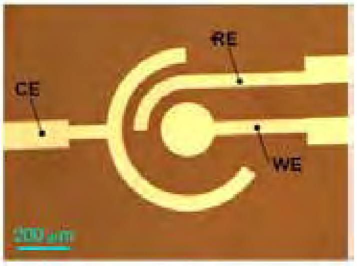

Figure 3 - Gold three electrode system

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ELECTROCHEM 2014

SPEAKER ABSTRACTS

ENERGY HARVESTING AND CONVERSION

Engineering of Advanced Functional Ceramic Thin Films from Single Molecular Precursors for Solar-Activated H_2 Generation

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Inorganic functional materials thin films are high sought for their employment in solid oxide fuel cells [1] and photoelectrochemical cells (PEC) [2] as alternative and renewable energy sources in addition to their applications in electronic devices [3], gas sensors [4] and solar cells [5].

In this context, the molecular route to advanced functional materials offers precise control over purity, composition, homogeneity and nanostructure of the resulting materials. This presentation explains the synthetic strategies for the design of single source molecular precursors that are capable of delivering all the elements of interest bonded in one structure and are capable of delivering the desired functional metal oxide/sulphide thin films of controlled composition and architecture onto the target substrate using Aerosol Assisted Chemical Vapour Deposition (AACVD). We, therefore report the design, synthesis, characterization and disposal of a series of specifically tailored new single source molecular precursors $[PbTi(\mu_2\text{-}O_2CCF_3)_4(C_4H_8O)_3(\mu_3\text{-}O)]_2$ (**1**), $[Cd_3(TFA)_4(OAc)_2(THF)_4]_n$ (**2**), $[Mn_2Zn_2(TFA)_8(THF)_4]$ (**3**),$[Mn_2Ti_4(TFA)_8(THF)_6(OH)_4(O)_2]$ (**4**), $[Sn(dmae)(OAc)]_2$**(5)**, $[Ag_4(S_2CN(Et)_2)_2(py)_2]_2\cdot 2(H_2O)\cdot(NO_3)$ **(6)**, $[Bi(S_2CN(Et)_3]$ (**7**) and $[In(S_2CNRR')_3]\bullet n(py)$ [where py = pyridine; R,R' = Cy, n = 2 (**8**); R,R' = ^{i}Pr, n = 1.5 (**9**); NRR' = Pip, n = 0.5 (**10**) and R= Bz, R' = Me, n = 0 (**11**)] their use for the deposition of nano phased solid solutions of $PbTiO_3$ (**1**), $Cd_{0.17}Zn_{0.83}O_3$ (dual source) (**2**), $MnZnO_3$ (**3**)**,** and composite of Mn_2O_3-$4TiO_2$ (**4**), SnO_2 nano-balls (**5**), Ag_2S (**6**), Bi_2S_3 (**7**) and In_2S_3 (**8**)-(**11**) thin films respectively on plain and FTO glass substrates using AACVD and tested their PEC properties for their possible technological applications in the green energy sector.

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Red-absorbing Cationic Acceptor Dyes for Photocathodes in Tandem Solar Cells

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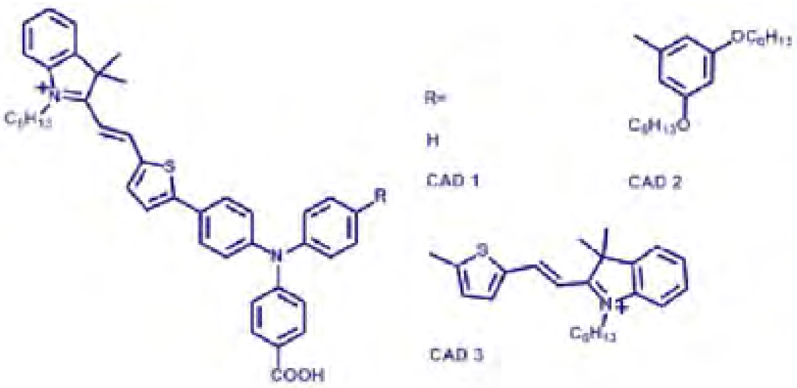
Tandem Dye sensitised solar cells (DSSCs) are a promising modification to existing n-type DSSCs. Wherein a dye sensitised photocathode is used in place of the passive counter electrode, enabling the absorption of a broader range of photons. However the majority of high performance dyes for photocathodes absorb higher energy photons causing spectral overlap with the n-type photoanode. A series of new donor-π-acceptor dyes which absorb towards the red region of the visible spectrum (**CAD 1-3**) were synthesised incorporating indolium cationic acceptor units. Their optical and electrochemical properties show the energy levels are better matched for use with the I_3/I redox couple in NiO-based p-type DSSCs, which has been the main shortcoming of previously reported 'blue' dyes. NiO-based p-type DSSCs with **CAD 1, CAD 2** and **CAD 3** gave photocurrents of **3.6**, **3.3** and **7.0 mA cm^{-2}** respectively. The photocurrent given by **CAD 3**, to our knowledge, matches the highest photocurrent for a p-type DSSC. This can be attributed to a very broad absorption across the visible-NIR spectrum making it ideal for use in tandem DSSCs. In addition the effect of dye structure on charge recombination processes has been studied using **S**mall **S**quare **W**ave **M**odulated **P**hotovoltage measurements and ultra-fast transient spectroscopy (TA/ TRIR).



1)C. J. Wood, M. Cheng, C.A Clark, R. Horvath, I. P. Clark, M. L. Hamilton, M. Towrie, M. W. George, L. Sun, X. Yang, E. A. Gibson*, J. Phys. Chem. C.,* **2014 DOI:** 10.1021/jp4119937

Photoelectrochemical Defect Mapping in Low Cost Metal-Oxides Energy Harvesting and Conversion

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A common issue in photoelectrochemical devices such as dye sensitised solar cells and artificial photosynthesis is the decrease in efficiency due to defect states acting as recombination centres. Two common oxides for dye sensitised cells and the next generation of inorganic extremely thin absorbers are titanium dioxide and zinc oxide. In this work ZnO was grown onto fluorine doped tin oxide glass (FTO) via seeding with zinc acetate and hydrothermal growth in a bath of zinc nitrate and hexamethylenetetramine. This grew nanorods with diameters ranging from 50 nm to 150 nm, with n-type conductivity and optical band gaps of 3.1 eV (405 nm). TiO2 was grown through the annodisation of titanium foil in ethylene glycol and ammonium fluoride forming nanotubes with diameters of ~125nm and ~10nm walls. Again they show n-type conductivity and have a similar band gap of 2.9 eV (425 nm). TiO2 can also be used in water splitting to generate oxygen, but has the disadvantage of not being able to be grown on a transparent electrode. Using photocurrent measurements and optical spectroscopy the effects of different growth techniques and thermal treatments have been investigated. The electrolyte used was sodium sulfite and illumination was provided via a 375 nm LED. Photogenerated holes are quickly scavenged by the sulfite and the electrons are collected through the substrate. The response to illumination can be modelled via the continuity equation allowing for the existence of electron traps. At potentials where the traps are initially empty through thermal equilibration the photocurrent is slow to reach its maximum as the photogenerated electrons fill up the traps. Performing transients at different potentials allows for the measurement of unfilled trap states which build up to give a Gaussian distribution of states and provide an accurate measurement of the central potential of these states. Growing the TiO2 to different lengths has provided a measure of trap states per length of tube. TEM analysis has potentially related the size of crystal grains to the distribution of trapped electrons. For the zinc oxide samples an annealing step is able to remove the photocurrent rise time dependence on potential, a good indication that the annealing removes the defect states and may be a step towards determining the cause of the trap states.

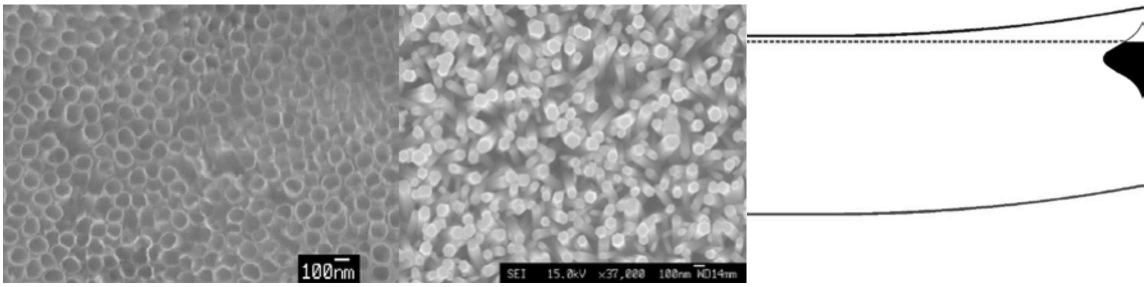

Fig. 1 TiO_2 nantubes, ZnO nanorods and a diagram representing defect states within a semiconductor bandgap.

Next Generation Solar Cells Based on Graded Bandgap Structures Utilising Low-cost Electroplated Semiconductors

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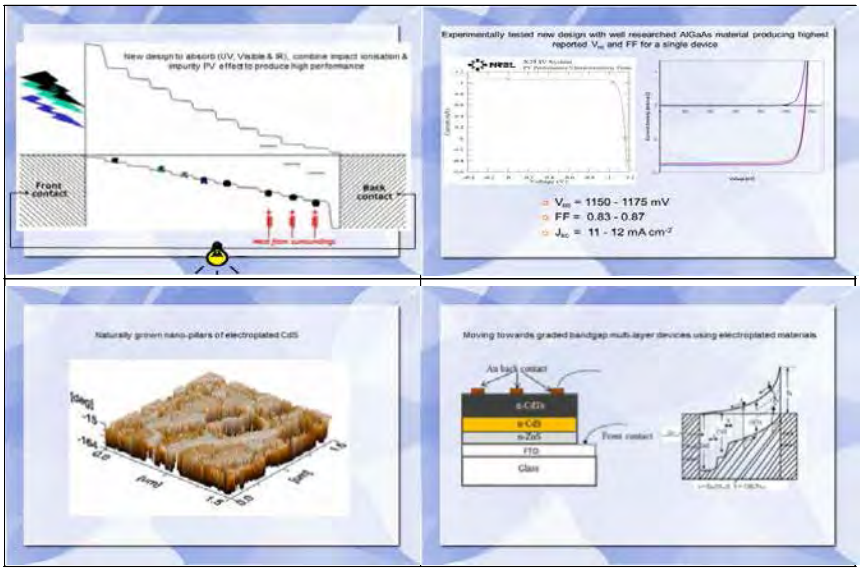
Abstract: A graded bandgap solar cell has been designed for moving towards the next generation high efficiency solar cells [1]. This design was experimentally tested using well-researched AlGaAs alloy, and highest reported open circuit voltage (V_{oc}=1175 mV) together with highest possible fill factor (FF=0.85) were obtained for a single device. These devices are capable of harvesting UV, visible and infra-red (IR) radiation, and combine impact ionisation and impurity PV effect within one device. Therefore, these devices are PV active even in complete darkness and produce V_{oc} values exceeding 800 mV, due to utilisation of IR radiation from the surroundings [2]. The second growth of this device using MOCVD-AlGaAs alloy produced ~20% efficient solar cells confirming the validity of the new design [1]. Since the concept is experimentally proven, the present work is focussed on fabricating and developing graded bandgap multi-layer devices utilising low-cost electroplated materials. These materials consist of naturally grown nano- and micro-rod type grains and enable the exploitation of extra-ordinary electronic properties such as extremely high charge carrier mobilities and reduced recombination process. Preliminary devices show 10-12% efficiency exhibiting expected high short circuit current density close to J_{sc}≈48 $mAcm^{-2}$ [3]. The results of materials growth by electroplating and characterisation, device fabrication and assessment will be discussed in this presentation.



New design to absorb (UV, Visible & IR), combine impact ionisation & impurity PV effect to produce high performance

Experimentally tested new design with well researched AlGaAs material producing highest reported V_{oc} and FF for a single device

- V_{oc} = 1150 - 1175 mV
- FF = 0.83 - 0.87
- J_{sc} = 11 - 12 mA cm^{-2}

Naturally grown nano-pillars of electroplated CdS

Moving towards graded bandgap multi-layer devices using electroplated materials

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Oxygen-deficient Metal Oxides for Photoelectrochemical Water Splitting

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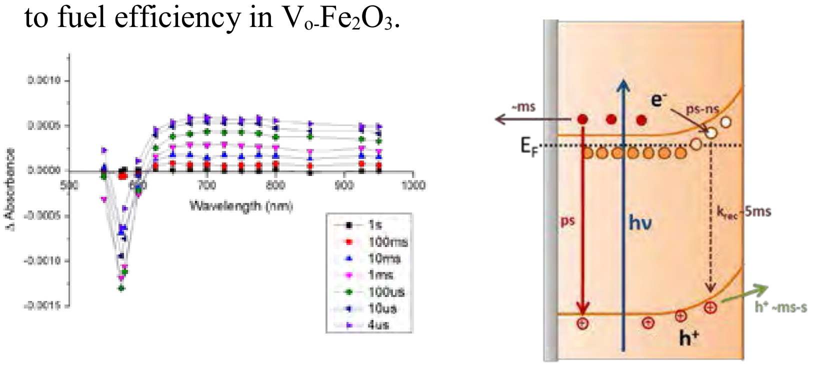
There is intense interest in the development of more efficient materials for photocatalytic water splitting as a route to harvest and store solar energy in the form of a fuel, H_2. Recently oxygen-deficient metal oxide photoelectrodes such as "black" TiO_2 and α-Fe_2O_3 have been dramatically improved the photocurrent densities, compared to pristine samples. In the case of TiO_2 photoanodes IPCE's of > 95% are obtained.[1,2]

It is proposed that improved electronic properties in oxygen deficient materials leads to enhanced transportation and charge separation at the semiconductor/electrolyte interface,[1,2] however there have also been conflicting reports on the potential role of oxygen vacancies as they can also act as trap and recombination sites.[3]

It is therefore important that the factors behind the remarkable enhancements in solar to fuel efficiencies of oxygen deficient materials are fully elucidated. Here we report on a range of transient spectroscopic and electrochemical measurements to monitor electron/hole populations in oxygen deficient metal oxide electrodes. Experiments on hydrogen treated TiO_2 nanowires show that rapid charge separation due to a greatly enhanced band bending leads to very high energy conversion efficiencies.[4] Studies on α-Fe_2O_3 will also be reported where in contrast to the TiO_2 excessive trapping of photoelectrons is measured and found to be a key factor limiting the solar to fuel efficiency in V_{o}-Fe_2O_3.



Transient absorption spectra of V_o-Fe_2O_3 under PEC conditions with an applied bias of 1.4V vs RHE and proposed mechanism for charge carrier dynamics under PEC conditions

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Is the Spin Seebeck Effect a New Route to Explore for Thermoelectrics?

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The Peltier and Seebeck effects are thermoelectric phenomena that are defined by the generation of a temperature- or potential- difference, respectively (see Fig. 1). This can be used to fabricate reliable solid state cooling (the Peltier cell) or to scavenge waste heat (the thermoelectric energy generator, TEG). Typically, a Peltier cell or TEG consists of pillars of n- and p- type semiconductors connected electrically in series and thermally in parallel, an arrangement that maximises the efficiency of the device (for a given choice of materials). The high cost and relatively low efficiency of these devices, however, prevents widespread application of TEGs for waste heat harvesting. Although there has been some advancement with regards to the performance of materials used for this technology (e.g. Bi_2Te_3, Bi_2Te_3:Sb_2Te_3 superlattices, and Si nanowires)[1], the co-dependence of electric and thermal conductivities inevitably limits the efficiency of such devices.

It was demonstrated recently that a thermal gradient applied across a metallic, insulating, or semiconducting magnetic material can result in the generation of a spin polarized current [2]: the spin Seebeck effect. This observation has stimulated a wealth of theoretical output on potential applications such as magnetic heat valves [3], position sensitive heat detectors [4], and spin caloritronic nanomachines [4],[5]. Critically, however, it has also led to the suggestion of further improvements to the conversion efficiency of TEGs. This is due in part to a key feature of this effect that the electric conductivity can depend on the spin state of the electron, as well as the potential simplification of the device itself. A broad overview of the current state of the art with regards to thermoelectric materials will be presented, followed by a discussion of the merits of integrating the spin Seebeck effect in TEGs.

Fig. 1 Left: For a material with two junctions the Seebeck effect is defined as the voltage generated (ΔV) due to a temperature difference (ΔT), whereas the Peltier effect is the reverse process. Right: Schematic of a standard Peltier cell where p- and n-type pillars of material are connected electrically in series and thermally in parallel.

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A Study of the Photoelectrochemical Response of Metal Oxyhalides

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Hydrogen is a clean, chemically stable fuel which can easily be stored and transported. Currently the most common means of hydrogen production is through steam reforming which relies on the use of fossil fuels and emits harmful greenhouse gases into the atmosphere [1]. Water is an abundant natural resource which can be electrochemically split to produce hydrogen and oxygen. Solar water splitting takes advantage of the natural resources of sunlight and water. By photoelectrochemically splitting water molecules, no external bias is required and no polluting by-products are formed [2]. There are, however, still issues with this approach. While the hydrogen evolution reaction occurs readily, the oxygen evolution reaction (OER) is a multi-electron transfer process that suffers from slow kinetics. This work concentrates on driving the OER at a semiconducting photoanode based on thin films of novel metal oxyhalides. The metal oxyhalides are synthesised via a low temperature ionic liquid phase transfer method [3], yielding phase-pure materials

Highly crystalline, phase-pure BiOCl microsheets have been synthesised via the low temperature ionic liquid method. X-ray crystallography studies confirmed the highly crystalline, phase-pure nature of the powders. TEM and HRTEM studies show a crystal structure with very few defects. A thin film of the BiOCl was dropcast onto fluorine-doped tin oxide, a transparent conducting substrate, and electrochemical and photoelectrochemical studies carried out. The distinctive photoresponse of BiOCl makes it an intriguing prospect for further investigation as a component of a mixed metal oxyhalide thin films for use in photoelectrochemical water splitting.

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Mixed Oxides Photocathodes for Water Splitting

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Over the course of the last decades, the increasing worldwide demand for energy has driven the search for new and clean sources of energy. In this context, solar energy emerges as the most promising energy source in terms of abundance and sustainability. Different ways have been investigated to convert solar energy into a chemically stored form such as H_2.[1] Since the original use of rutile TiO_2 for water electrolysis by Fujishima and Honda, a plethora of compounds have been investigated as a photoanodes, exhibiting, however, large band gaps and not adsorbing in the visible region.[2] In contrast, studies of metal oxide semiconductors as photocathodes where hydrogen is generated are scarce.[3]

$CuBi_2O_4$ has been studied as a promising photocathode material due to its narrow band gap (~1.8 eV). However, due to its poor electronic conductivity, the material is unfavourable for certain applications; making doping and morphology control at the nanoscale worthwhile exploring. In general the synthesis of $CuBi_2O_4$ has been limited to solid state, electrodeposition or hydrothermal syntheses, which generally require high temperature, voltages or pressures.

In this work, $Cu_xZn_{1-x}Bi_2O_4$ powders were prepared by a new route based on an ionic liquid/cellulose/chitin system. In the presence of both cellulose and chitin two distinct coral and rod like morphologies are formed. XRD, EDX and TEM provide strong confirmation of the BSCF composition and phase purity. A systematic study of photoelectrochemical properties with composition was conducted. $Cu_xZn_{1-x}Bi_2O_4$ materials showed a potential applicability as photocathodes for water splitting.

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Organometallic Iridium Complexes for Highly Efficient Water Oxidation Catalysis

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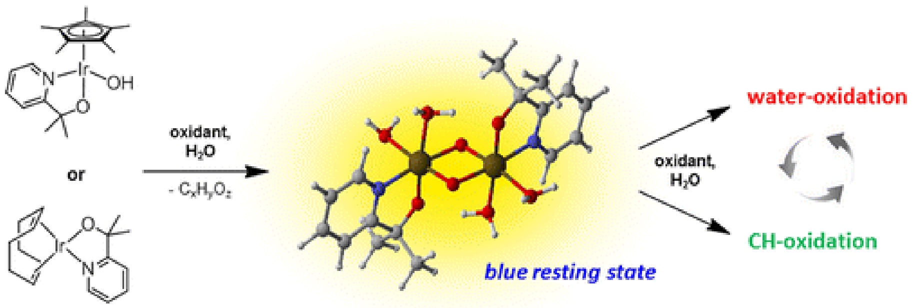
The production of sustainable chemical energy carriers (fuels) through light-driven water splitting (artificial photosynthesis) is important for securing our future energy supply.[1] A plethora of different materials and configurations are currently being investigated, but a crucial step common to all schemes is the oxidative half reaction of water splitting: $2\ H_2O \rightarrow O_2 + 4\ e^- + 4\ H^+$. Efficient and durable water oxidation catalysts are thus urgently needed.[2]

In recent years organometallic iridium complexes have emerged as promising candidates, and half-sandwich Cp*Ir(III) complexes in particular have attracted much attention.[3] While initially little experimental insight was available as to how these systems function we have recently been able to distinguish homogeneous from heterogeneous (nanoparticulate) catalysis using time-resolved dynamic light scattering during periodate-driven oxygen evolution.[4] Subsequently, using a variety of spectroscopic techniques, we gained deeper insight into precursor transformation under reactions conditions,[5] revealing that the Cp* ligand is merely a sacrificial placeholder which is quickly lost under turnover conditions to yield *μ*-oxo-aqua coordination compounds as the active species:



We now report on the electrochemical activation and electrode-driven water oxidation activity of these compounds. Both processes can be performed electrochemically without the need of chemical oxidants, resulting in homogeneous electrocatalytic oxygen evolution with high rates and Faradaic efficiency. Furthermore, strategies for binding these molecular water oxidation catalysts to oxide surfaces to yield functionalised electrodes are presented.[6]

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Highly Robust Sn/C_{GDE} for the Electrochemical Reduction of CO_2

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The electroreduction of CO_2 into formic acid on solid cathodes has slow kinetics and therefore higher cathodic potentials are required [1]. Due to the low solubility of CO_2 in aqueous solution (0.034 M), there is a need of using gas diffusion electrodes to overcome mass transport limitation that led to lower CO_2 conversion efficiency. Hence, this study focuses on a flow cell system including Sn gas diffusion electrode (GDE), where the catalyst was immobilized by electrodeposition on a carbon paper r egarding to the loading and morphology of the electrocatalyst. A series of cell potentials ranging from -1.0 to -3.0 *V* were tested for two different electrolytes to determine the highest catalytic activity towards the conversion of CO_2 into formic acid. Also operating conditions such as flow/area ratio and applied current density were taken into consideration. The maximum efficiency towards formate formation was 75 % at -1.78 V vs. Ag/AgCl and 71 % at -1.71 V vs. Ag/AgCl with 0.5M $KHCO_3$ and 0.5M $NaHCO_3$ electrolytes respectively, which are one of the highest values found in the literature on Sn electrode of 200C charge conversion so far to the best of our knowledge [2]. An interest on novel alloy-catalysts by electrodeposition and catalytic activity of Sn deposits at extended periods will also be highlighted.

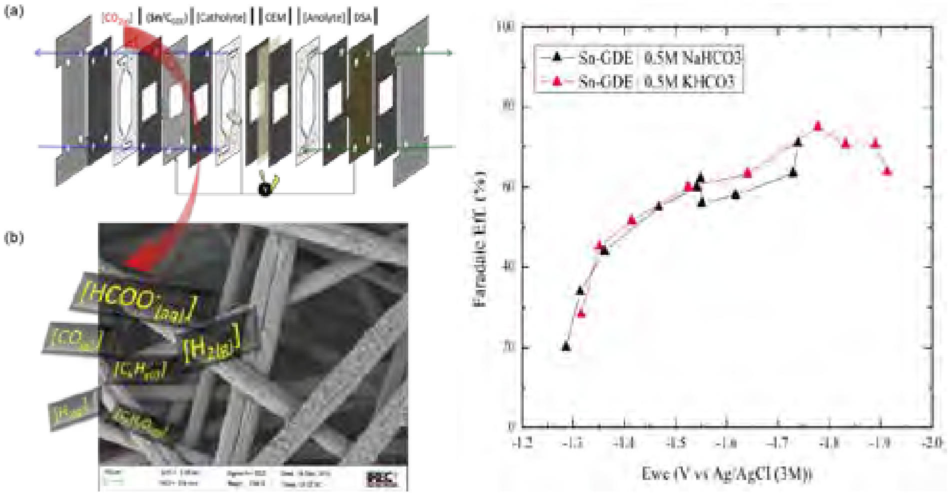

Fig. 1. (a) The flow cell stacks showing the route of gas and electrolytes, (b) electrodeposited Sn catalyst layer on carbon fibers of GDE (c) Faradaic efficiency and total current values respect to Sn/C_{GDE} potential for two different electrolytes are presented.

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Effects of Different Produced CuZn and CuNi Thin Films on the Electrocatalytic Oxidation of Formaldehyde

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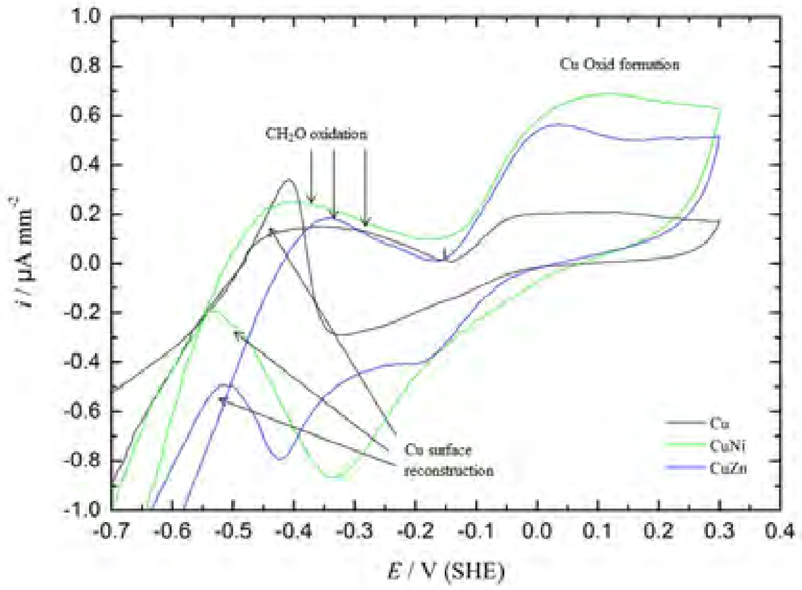
The catalytic properties of copper are a result of the Cu(II)/Cu(I) redox system. Copper is used as catalyst for anodic formaldehyde oxidation in alkaline solutions, which was investigated in connection with fuel cells. Because of good physical properties, corrosion resistance and reasonable price copper alloys are used in many applications [1-3]. CuZn and CuNi thin films were examined for their electrocatalytic oxidation of formaldehyde in alkaline solutions using cyclic voltammetry. A scanning flow cell was investigated for the electrochemical studies on thermally evaporated Cu alloys. In Figure 1 the cyclic voltammograms of the electrocatalytic oxidation of formaldehyde is shown. Between the potential from -0.5 to -0.15 V (SHE) an anodic current peak as a result of the CH_2O oxidation was received [4]. Hence the Cu_2O formation, which inhibits further CH_2O oxidation, the anodic current drops. The CV shows the occurrence of the formaldehyde oxidation leading to formic acid. In further experiments the oxidation of the formic acid leading to CO_2 was examined. The electro oxidation of the formaldehyde is a surface sensitive method and depends on the formation conditions of the electrode surface. Thermally evaporated, electro- and electroless deposited Cu based alloy were produced and the activity of these thin films are reported. One possible application for these electrodes could be the usage of a formaldehyde sensor. Further the peak current depends on the formaldehyde concentration in the solution, so it is possible to use the copper based alloy electrode for analytical applications.



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High Resolution Electrochemical Imaging in Ionic Liquids: Surface Structure Effects on Triiodide Reduction at Platinum Electrodes

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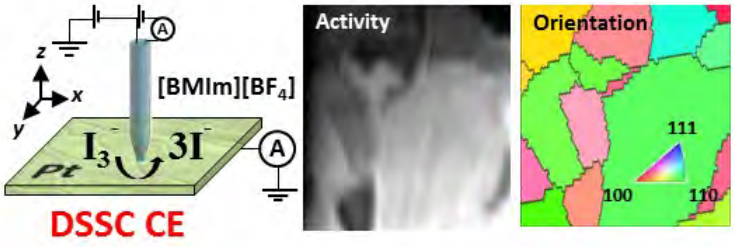
Room temperature ionic liquids (RTILs) are emerging as promising alternatives to the volatile and toxic solvents employed in dye sensitized solar cells (DSSCs) [1], which in turn are attracting attention as low cost alternatives to standard silicon-based solar cells [2]. However, efficiencies of DSSCs are still to be improved significantly in order to become commercially viable. Thus, understanding fundamental processes occurring in these devices is of paramount importance. Moreover, standard electrochemical techniques are technically challenging in RTILs and often miss vital structural information. Here, we introduce scanning electrochemical cell microscopy (SECCM) [3] in which a sub-micron sized droplet, creating a confined electrochemical cell, is scanned across a surface of interest. The reduction of I_3^- to I^- in 1-butyl-3 methylimidazolium tetrafluoroborate ([BMIm][BF$_4$]) RTIL is investigated on polycrystalline platinum using SECCM and correlated to the crystallographic orientation obtained with electron backscatter diffraction (EBSD). Significant grain-dependent variations in current exchange densities are revealed and are related to the interaction between solvent ions and the platinum surface. We thus present an effective electrochemical technique to investigate spatial variations in electro-activity across a sample in RTILs, not only to identify the best catalyst for the counter electrode in DSSCs but also providing a new platform for structure-activity investigation in RTILs [4].



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Thin Film Electrodes for Photoelectrochemical Water Splitting

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In recent years there has been considerable interest in developing semiconductor materials capable of harvesting energy from sunlight to split water[1]. These can be used as electrodes in photoelectrochemical (PEC) cells. PEC cells are typically made up of a photoanode (which drives the water oxidation reaction) and a photocathode (which drives the hydrogen evolution reaction). Metal oxides show the most promise for this application due to their ease and low cost of fabrication and their relatively good resistance to chemical and photo corrosion relative to other semiconductor materials (such as nitrides and phosphides).

In this presentation we will outline some of our recent work directed at the development of simple and scalable methods for the synthesis of thin film metal oxide electrodes for photoelectrochemical water splitting and the investigation of the photoelectrochemical properties of previously unstudied metal oxide materials[2-4].

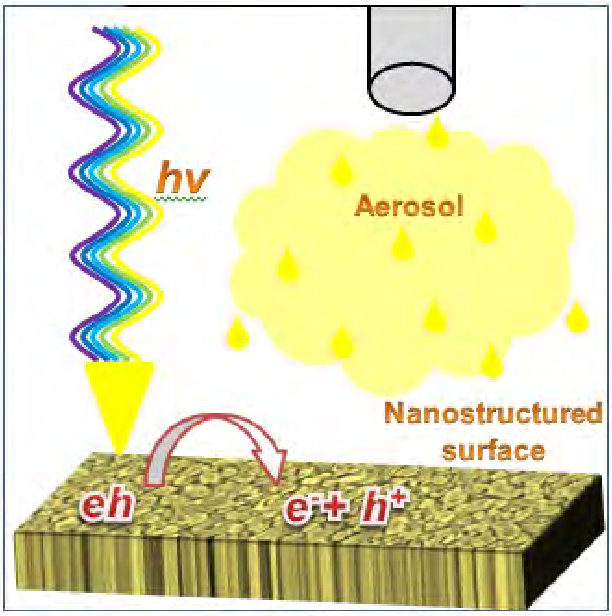

Figure 1 A graphical illustration of a simple and scalable technique, aerosol assisted chemical vapour deposition

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ELECTROCHEM 2014

SPEAKER ABSTRACTS

FUNDAMENTAL ELECTROCHEMISTRY

Pitfalls in the Quantitative Evaluation of Fast Electrode Kinetics at Stationary Macrodisk Electrodes

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The evaluation of the thermodynamics and kinetics of an electron transfer reaction is frequently the objective of a voltammetric study. The simplest possible case of an E reaction may be fully characterised by the determination of the standard potential (E^0), the heterogeneous charge transfer rate constant (k^0) and the charge transfer coefficient (α) if Butler-Volmer electron transfer theory is employed. In dynamic electrochemistry, electron transfer is coupled to mass transport, as an electroactive species must be able to move from the bulk solution phase to the electrode, or if generated at the electrode, away from the electrode into the bulk solution. If the voltammetry is carried out in a still solution and in the presence of excess electrolyte, diffusion will be the dominant form of mass transport. Another key parameter determining the response to a dynamic electrochemical experiment is the uncompensated resistance (R_u) which is governed by Ohm's Law. In transient voltammetric studies at macrodisk electrodes, the magnitude of double layer capacitance (C_{dl}) also needs to be known as this term will be used to define the background current which contributes to the total current (sum of faradaic current from electron transfer and capacitance current).

Quantitative evaluation of electrode kinetics for even the simplest process given in Equation 1 is therefore a complex matter requiring evaluation of E^0, k^0, α, D, R_u, C_{dl} as a minimum number of parameters, assuming that terms like electrode area (A) and temperature (T) are known from independent sources. Another ubiquitous mechanism considered in this lecture involves electron transfer followed by a chemical reaction in the so-called EC electrode process. In this case, all the parameters relevant to the quasi reversible reaction viz., E^o ,k^o, α,, R_u and C_{dl} in addition to the homogenous chemical forward and backward rate constants (k_f and k_b respectively) that describe the kinetics of the C step following electron transfer need to be evaluated, giving rise to even more possibilities for non-unique solutions to be available within experimental uncertainty. The complexity now is such that the reliable use of heuristic methods is almost impossible and computationally intensive e-science approaches become essential in determining in as far as possible that a unique solution has been obtained for all of E^o k^o, α,, R_u, $C_{dl,}$ kf, and k_b and any other parameters that are relevant.

Probably as a result of the substantial complexity in terms of the number of parameters required in the modelling and their widely varying magnitudes, and the common lack of analytical mathematical solutions to the theory, the reproducibility of electrode kinetic parameters reported from laboratory to laboratory remains poor, despite the fact that the basics of the theory and use of numerical methods for its solution are now very well understood.In this lecture, a critical review of quantitative electrode kinetic studies of reactions using the ubiquitous macrodisk electrode under conditions of transient voltammetry with a focus on the analysis of the seemingly simple process given in equation 1 and the more complex EC mechanism. In the last 50 years, the most commonly used voltammetric method for quantifying electrode kinetics has been DC cyclic voltammetry at a stationary macrodisk electrode. However, there are numerous other waveforms and procedures now available. Advantages provided by AC waveforms superimposed on the DC potential as employed in the technique of AC voltammetry will be considered as will the use of modern *e*- science and statistical methods to provide the basis of experiment- simulation comparisons and generation of sets of optimised parameters relevant to electrode kinetic studies.

Electron Transfer at Liquid/Liquid Interfaces Photoinduced by Colloidal Semiconductor Nanostructures

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Polarisable liquid/liquid interfaces have been studied for a number of years, with ion and/or electron transfer across the phase boundary promoted by potential gradients and evidenced by electrical currents.[1] Recent research, has reported photoinduced biphasic hydrogen evolution and the nucleation of metallic phases at the phase boundary.[2,3] However, development of these molecular interfaces has generally focused on applications such as ion sensors, leaving more complex phenomena, such as photoelectrochemical and multiple electron transfer, to be less studied and consequently less well understood.[4] Herein we take a close look at the potential-dependent assembly of colloidal TiO_2 nanostructures at the liquid/liquid interface and its effect on photo-induced electron transfer. The figure below shows an asymmetric capacitance-potential curve at the water/1,2-dichloroethane (DCE) interface, indicating the potential-induced interfacial assembly of the positively charged TiO_2 aqueous colloid at positive potentials. The figure also presents the photocurrent values obtained as a function of potential (and consequently interfacial TiO_2 concentration) in the presence of octane in the organic phase upon UV-illumination; this demonstrates that complex multi-electron transfer reactions, such as the oxidation of short-chain alkanes, can be promoted at these unique polarisable interfaces. The processes underpinning these photoresponses will be discussed.

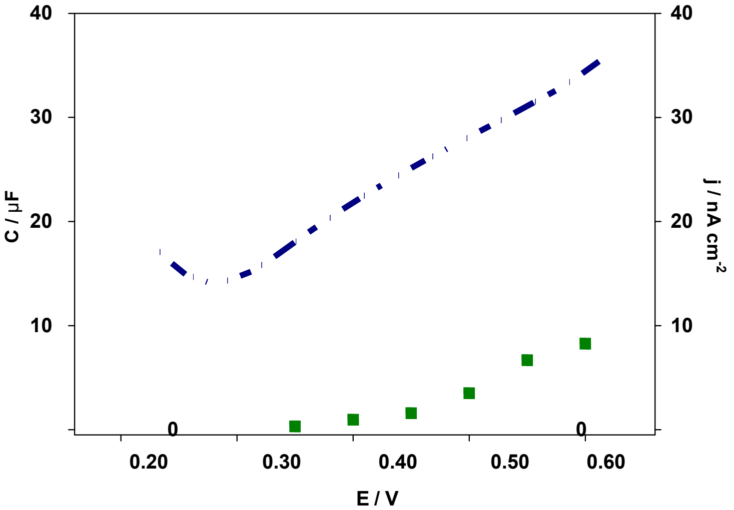

Figure 1. Capacitance as a function of potential at the water-DCE interface in the presence of TiO_2 nanoparticles (blue trace) and photocurrent response in the presence of octane in the organic phase (green squares).

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Electrochemical Behavior Pt - Pd Thin Overlayers on Au

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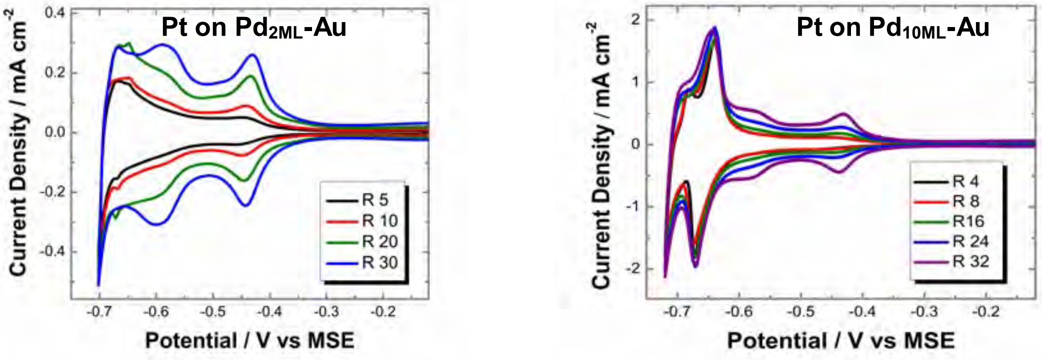
Epitaxially grown Pd overlayers on Au (111) are well known for their unique hydrogen- sorption behaviour different from the bulk Pd.[1] They have been extensively studied for their unique properties in many electrochemical reactions such as formic acid oxidation, carbon monoxide oxidation, and oxygen reduction.[2] Recent studies on the Pt-on-Pd and Pt-Pd-Au showed that this system is of interest for both electrocatalysis as well as H- storage potential.[3]

Here we will present the study of electrochemical behaviour of 2D Pt-Pd structures on Au created by hydrogen as mediator. Among different electrochemical methods the surface limited redox replacement (SLRR) has an important place for design of epitaxial Pt films.[4] The deposition of Pt on Pd has been achieved by using controlled amount of the electrosorbed H as the sacrificial "layer" in the galvanic replacement protocol similar to the SLRR.[5] The properties of the deposited epitaxial Pd and Pt-Pd films were studied by EQCM, STM and electrochemical methods. Cyclic voltammetry results showed interesting H- sorption behaviour of deposited Pt films. As illustrated in the Figure, Pt films grown on Pd films of 2ML and 10 ML thickness show distinctly different behaviour. Films grown on 2ML Pd have all the characteristics of typical Pt behavior. In contrast, Pt films on 10 ML Pd exhibit H- sorption behavior with features of both adsorbed and absorbed H similar to Pd. Moreover the H-absorption peaks are more reversible and have a charge similar to that obtained on underlying Pd film. The changes of H-sorption behaviour of Pd-overlayers (>2ML) with the sub-monolayer coverage of deposited Pt were studied too and they show correlation with the behaviour of epitaxial Pt-overlayers.



Cyclic voltammetries of Pt films deposited using H-absorbed on 2ML and 10 ML Pd films on Au in 10^{-1} M H_2SO_4. Scan rate 50 mV/s and R presents number of

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Electrochemical Interfaces and Butler-Volmer equations

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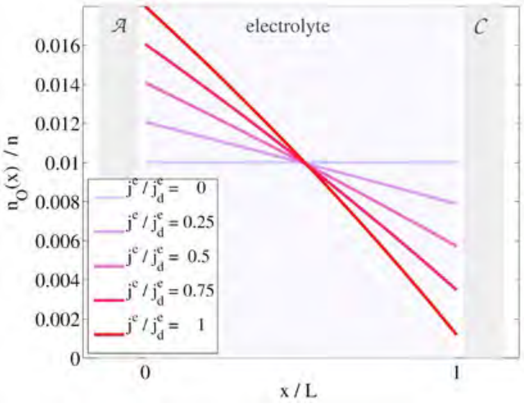
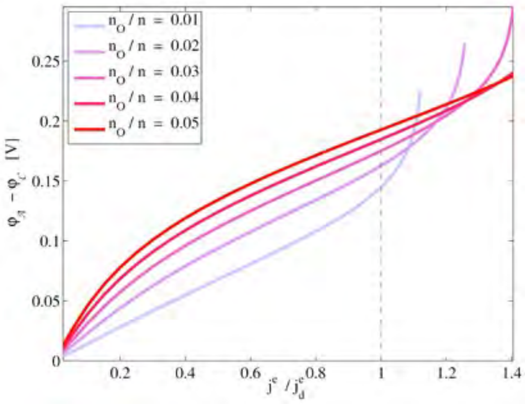
We consider the contact between electrochemical systems and derive model equations based on non-equilibrium thermodynamics [1]. Typical solutions of these equations exhibit very sharp boundary layers where an electrolyte cannot be assumed to be diluted. To confine the concentrations to a physical meaningful range, the classical Poisson-Nernst-Planck equations must be corrected by taking into account the momentum balance [2]. Instead of postulating a compact Stern layer, a saturation layer at the boundary is then a consequence of this theory [3]. We apply formal asymptotic analysis to derive a reduced system of equations with electro- neutrality in the bulk and consistent boundary conditions that include all effects of the boundary layers. Two scenarios are analyzed in detail: first, we study a liquid electrolyte between blocking electrodes with no adsorption reactions. For moderate frequencies, the bulk transport is decoupled from the development of the layers that is hidden in the new boundary conditions. Second, we consider Faradaic electrode reactions and their coupling to bulk transport processes. The asymptotic limit allows us to recover Butler-Volmer equations and to identify necessary restrictions on the exchange currents to maintain thermodynamic consistency [4].





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Plasma Electroanalysis using Voltammetry

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Gases are normally considered as very effective electrical insulators however, plasmas are defined by the ability to act as ionic and electronic conductors. Plasmas are formed by the excitation of gaseous components to the point of ionisation, either by applying an electrical discharge or electromagnetic radiation. The common property in these gases is the presence of charged species, which are responsible for charge transfer.

This project stems from recently published work on the electrochemical approach of redox reactions at a solid/gas interface.[1],[2] By adopting a seemingly uncomplicated experimental approach, a new analytical tool has been developed. We focus on the control and measurement of redox chemistry through the integration of plasmas with surfaces.

Organic based aliphatic and aromatic compounds have been added to the flame and the corresponding CVs recorded. Reduction signatures obtained not likely originate from distinct fragmentation products from the incomplete combustion of the native molecules. Results are very encouraging and certainly contribute to our confidence that the physical basis of the peaks measure is Faradaic.

In situ diagnostic techniques have been applied to seek unambiguous evidence to support gas phase cyclic voltammograms.

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Discovery of a Single Molecule Transistor in Photosystem II

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The oxidation of water to oxygen is essential for all oxygen-breathing life on Earth. Inside plants, this process is carried out by Photosystem II, which extracts energy from sunlight and converts it into a flow of electrons. However, even after a century of effort, it is still a mystery how plants actually control the electron flow. In the present work, quantum theory is applied to the results of recent high precision x-ray diffraction studies of photosystem II, and it is suggested that a single molecule transistor regulates the flow of electrons through this remarkable system. At the core of the device, electrons flow through an iron(II) *d*-orbital by a process of superexchange, at a rate which is gated by the ambient ligand field. The transistor operates in the negative feedback mode, and its existence suggests that man- made molecular logic gates are technologically feasible. We believe this is the first recorded example of a single molecule electronic transistor in a living system.

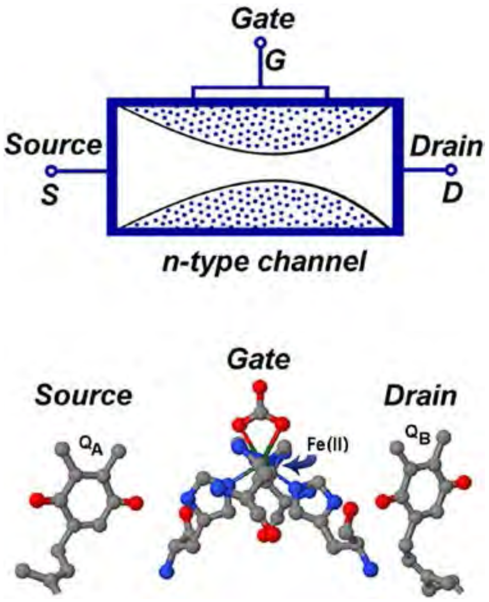

*Fig.1. Comparison of a JFET (top) with the newly-discovered single molecule transistor in PSII (bottom). Both are three-terminal devices, consisting of a source, a gate, and a drain. **Top**: The JFET uses an electric field to "gate" the conduction of electrons between source and drain. **Bottom**: The single molecule transistor (an Fe(II) ion) uses the bicarbonate ligand field to "gate" the superexchange of electrons between the quinones Q_A and Q_B.*

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Detection of DNA Damage with the Latch Constriction of α-Hemolysin

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The protein α-hemolysin forms a pore with nanometre dimensions in a lipid membrane through which single-stranded DNA (ssDNA) can transit. As the DNA transits through the pore, there is a momentary reduction of the current due to blockage of the ion flow as the as the DNA passes the tightest 0.14 nm constriction in the pore. This system has been extensively studied as a potential method for rapid and cost effective sequencing of ssDNA.[1]

However, the interactions of double-stranded DNA (dsDNA) with α-hemolysin are less well- studied. Whilst dsDNA can enter from the wider (vestibule) side of the pore it does not transit fully because its diameter is larger than the tightest constriction. With sufficient energy dsDNA can unzip (denature) inside the vestibule, and the blocking current observed during dsDNA residence is due to its presence within the vestibule.[2]

In this report, we describe a previously unrecognised sensing zone for dsDNA, in the vestibule of α-hemolysin that is sensitive to the presence of an abasic site (a missing base) within the DNA sequence.[3] The presence and position of an abasic site can be detected over a 4-5 base (1.36 nm) range centred near to the entrance to the vestibule, with a sensitivity that is dependent on the precise position of the abasic site within the sequence. We demonstrate through temperature-dependent ion channel recordings that the detection of an abasic site in this newly-discovered sensing zone is possible because of a decrease in the activation energy required for transport of the electrolyte through the pore when an abasic site is in proximity to the constriction site. Whilst previous efforts at nanopore DNA sequencing have focussed on characterising and sequencing ssDNA, The discovery of this new sensing zone offers exciting possibilities for characterising and sequencing more biologically-relevant dsDNA instead.

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Rotating Discs Galore!

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After a brief look back at the early days of rotating disc electrodes with John Albery in Oxford, we shall discuss how related principles of momentum, mass, and heat transfer can be applied to two very different applications of rotating discs.

The first example will be the plating of epitaxial silicon at temperatures in the range 900 to 1250°C. It is shown that the results for growth from $SiCl_4$ and H_2 in a rotating disc reactor can be described by a single equation, analogous to the Koutecky-Levich equation, in terms of homogeneous kinetics and mass transport. The rate determining kinetic step is found to be the homogeneous conversion of $SiCl_4$ to $SiHCl_3$. Using the kinetic parameters determined with the rotating disc system, results from other workers obtained with reactors of very different geometries when normalised are in excellent quantitative agreement with the results found in this work – Fig. 1.

The second example of a rotating disc application is to the identification of proteins and nucleic acids after separation on a gel by electrophoresis. Traditional methods rely on staining with agitation of dissolved organic dyes which bind to the biomolecules followed by de-staining of unbound dyes. These processes give inhomogeneous staining and de- staining and are time consuming. Reproducible, rapid and uniform gel development can be achieved with the Phast rotating disc system – Figs. 2 and 3. A general theoretical analysis has been developed for the effects of mass transport and kinetics on dye binding.

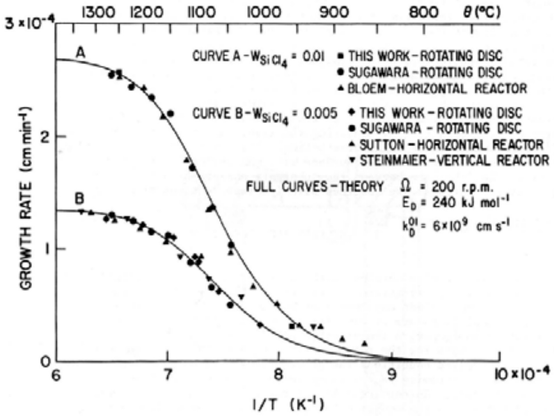
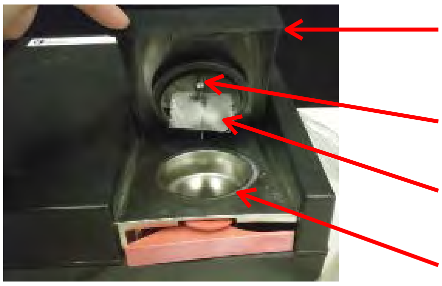


Fig.1 Experimental and theoretical growth rates for Si

Fig. 2 The Phast high speed electrophoresis system

Fig. 3 Rotating disc gel development unit of the Phast system



Metastable Ionic Diodes Based on a Rigid Intrinsically Porous Polymer-Amine

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Polymers of intrinsic microporosity (PIM) have been applied for gas storage,[1] gas separation and as sensors component.[2] To date, applications are all based on PIM-gas interactions, but our recent publication[3] has opened the way for the study of PIM-electrolyte interactions and applications in solution phase. PIM-EA-TB[4] (see Figure 1) exhibits permanent microporosity and ultra-microporosity with permeability for small molecules and ions.

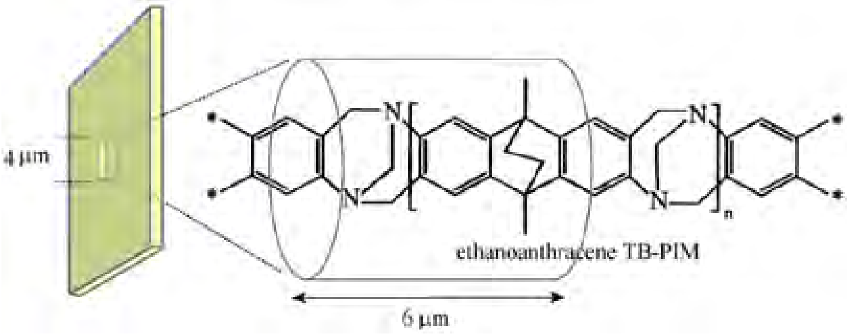

Figure 1. Schematic depiction of molecular structure of PIM-EA-TB filled into a pore in a PET membrane.

Membrane electrochemistry experiments were carried out by immobilisation of PIM-EA-TB into a single micropore PET film. Ion currents were measured using an H-cell with a four electrodes system where the modified PET film was supported between the half cells. The compartments of the cell were filled with different electrolyte solutions and cyclic voltammograms were recorded. "Bistable ionic diode"[5] characteristics were observed.

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Enhanced Oxidation Catalysis at Superactivated Gold Surfaces

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It is well established that solid metals can trap and store energy and exist in metastable or non-equilibrium superactivated states[1]. Metastable states are generally assumed to involve lattice defects of low lattice coordination and as a result are thermodynamically active[1,2]. In aqueous solution, these metastable metal clusters can become significantly hydrated when oxidised, aquiring a relatively large ligand coordination sphere to form an assembly of hydrated metal surfaquo clusters[1]. This is the basis for the Incipient Hydrous Oxide/Adatom Mediator (IHOAM) model of electrocatalysis. In this model the metal surface is considered as a chemically or redox modified electrode with equilibrated, low energy surface atoms functioning as a relatively inert support, and low coverage, high energy protruding atoms, or minute clusters of the same, functioning as electrocatalytic redox mediators. This concept of mediated electrocatalysis via highly energetic surface species is outlined in Fig. 1a, where electrocatalytic reductions are shown to be 'hot' metal atom nanocluster (M*) mediated and electrocatalytic oxidations are incipient hydrous oxide mediated

Although the coverage of the M* species is very low, their influence on interfacial catalytic processes is significant, and their presence often results in the catalysis of multi-electron transfer surface processes in potential regions where traditionally no such surface chemistry should occur[3]. In this work we report the cathodic superactivation of Au surfaces using potentiostatic and potentiodynamic methods. The influence of the superactivation procedure on the electrocatalytic properties of these surfaces is outlined in relation to two important electrocatalytic reactions: the oxidation of glucose and the oxygen evolution reaction. Significant catalytic enhancement was observed in both cases. The sensitivity of the gold electrode towards glucose oxidation was shown to increase over a series of superactivation treatments (Fig. 1b) from ca. 15.3 μA mM^{-1} cm^{-2} to ca. 76.4 μA mM^{-1} cm^{-2}. On the other hand, the OER tafel slope decreased from ca. 120 mV dec^{-1} to ca. 60 mV dec^{-1} with superactivation, suggesting a change in reaction mechanism at the superactivated surfaces. Building on these observations, this work will discuss the influence of superactivated metal clusters in surface catalysis and highlight their potential importance for targeted catalyst design.

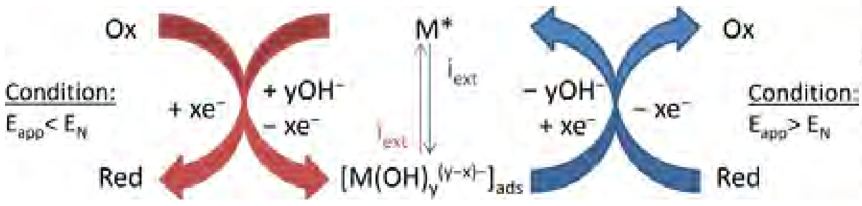
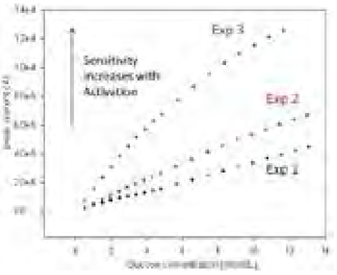


Fig. 1(a)



(b)

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CO_2 Electroreduction at Au-Pd Core-Shell Nanoparticles: Effect of Shell Thickness on Reactivity

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The use of bimetallic nanostructures for catalytic applications has been widely studied. This is due to the ability to tune the reactivity of the catalyst by controlling the metal ratio, as well as their unique behaviour compared to their monometallic counterparts. Experimental observations can be rationalised in terms of geometric (strain) effects on the position of the metal *d*-band, which consequently impacts on the binding energies of reaction intermediates.[1] Correlation between catalyst reactivity and electronic/strain parameters have been investigated for a number of reactions including oxygen reduction as well as methanol and CO oxidation. These concepts have been relatively less exploited with regards to CO_2 electroreduction. In the present contribution, we investigate the effect of the effective lattice strain on ultrathin Pd shell at Au nanocores on the reduction of CO_2. As shown in Figure 1, the faradaic current associated with CO_2 reduction and HER can be affected by the thickness of the Pd shell.[2] Our previous studies have shown that varying effective lattice strain between 1 and 3.5% can lead to significant changes in CO coverage as well as the reactivity of the catalysts towards formic acid oxidation.[3] In this presentation, we shall discuss mechanistic aspects of CO_2 reduction by analysing the faradaic responses as well as the products generated from the reaction based on spectroscopic techniques.

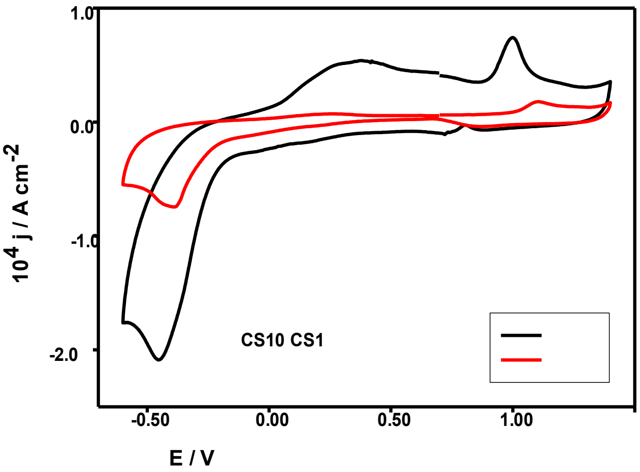

Figure 1. Cyclic voltammetry of Au-Pd CS nanoparticles, of shell thicknesses between 1 (red) and 10 nm (black), in CO_2 (red) saturated aqueous 0.1 M Na_2SO_4 (20 mV s^{-1}).

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ELECTROCHEM 2014

SPEAKER ABSTRACTS

ELECTROANALYSIS AND SENSORS

Exploring the Electroanalytical Opportunities of Nanoscale Liquid- Liquid Interfaces

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Electrochemistry at the interface between two immiscible electrolyte solutions (ITIES) has attracted increasing interest for a range of reasons, including insight into mechanisms of ion and electron transfer, energy conversion and chemical sensing [1]. A key advantage of this electrochemistry is that it can be used for the detection of non-redox-active species. Since the introduction of microscale ITIES by Taylor and Girault [2], this area of electrochemistry has sought to take advantage of the ensuing enhanced mass transport and reduced interfacial capacitance. Micropipettes and microholes have enabled the creation of single and arrayed micro-ITIES [3]. Electrochemistry at nano-ITIES has also been growing in popularity, with an emphasis on kinetic studies [4], which may enable insights into the behaviour of small interfaces and offer benefit for improvement in electroanalytical performances.

In this presentation, the use of silicon nitride nanoporous membranes to form nano-ITIES arrays will be discussed, together with the voltammetric and chronoamperometric responses at such interfaces. In comparison to micro-ITIES arrays, nanoscale ITIES provide increased sensitivity for electrochemical detection of ions. An interesting feature of voltammetry at nano-ITIES array is a sloping diffusion-controlled current rather than a steady-state plateau, as observed at micro-ITIES arrays. This presentation will present and discuss data on the electroanalytical behaviour of nano-ITIES arrays and also demonstrate the detection of various ionised molecules based on ion-transfer voltammetry.

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Electroanalytical Sensing Properties of Pristine and Functionalised Multilayer Graphene

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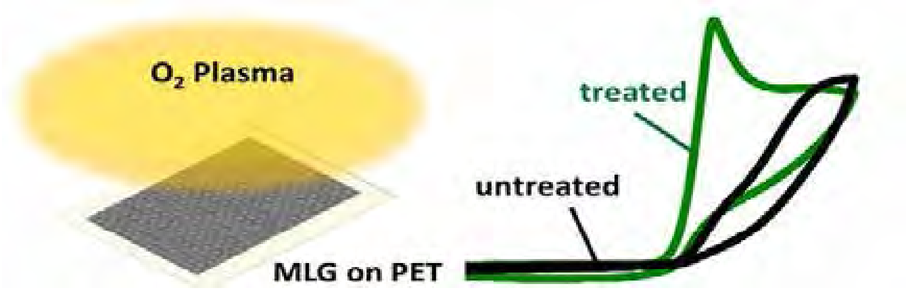

We have recently published a paper[1] describing the heterogeneous electron transfer (ET) properties of high-quality multilayer graphene (MLG) films grown using chemical vapor deposition (CVD) on nickel and transferred to insulating poly(ethylene terephthalate) sheets. An oxygen plasma treatment is used to enhance the ET properties of the films by generating oxygenated functionalities and edge-plane sites and defects. Scanning electron microscopy, Raman, and X-ray photoelectron spectroscopy, along with voltammetry of the standard redox probes $[Ru(NH_3)_6]^{3+/2+}$, $[Fe(CN)_6]^{3-/4-}$, and $Fe^{3+/2+}$ are used to demonstrate this effect. The biologically relevant molecules dopamine, NADH, ascorbic acid, and uric acid are employed to show the improved sensing characteristics of the treated films. Control experiments involving commercially available edge-plane and basal-plane pyrolytic graphite (EPPG and BPPG) electrodes help to explain the different responses observed for each probe, and it is shown that, in certain cases, treated MLG provides a viable alternative to EPPG, hitherto considered to be the “best-case scenario” in carbon electrochemistry. This is the first comprehensive study of the electroanalytical properties of pristine and functionalised CVD- grown MLG, and it will serve as an important benchmark in the clarification of ET behaviour at graphene surfaces, with a view to the development of novel electrochemical sensors.

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Three-phase Boundary Processes on Porous Carbon ‘Droplet’ Electrode: and its Application in Natural Oil Analysis

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Porous carbon materials’ high conductivity and surface area makes it an ideal interface for three-phase boundary processes. It was previously demonstrated that coating randomly aligned carbon nanofibres with thermally reduced graphene oxide can dramatically improve the activity of the electrode [1]. Here, graphene oxide is electrochemically reduced onto a network of carbon spheres held together with some polystyrene (ca. 4% weight) to form an active porous electrode material (see fig.1). Multiple coatings of reduced graphene oxide are shown to improve the activity further to an extent.

Three phase boundary electrochemistry of oil droplets not supported with intentionally added electrolyte is demonstrated for coenzyme Q10 in methyl laurate. Micromolar detection limit was achieved. Application for quantification of Q10 in natural products (olive oil) is investigated

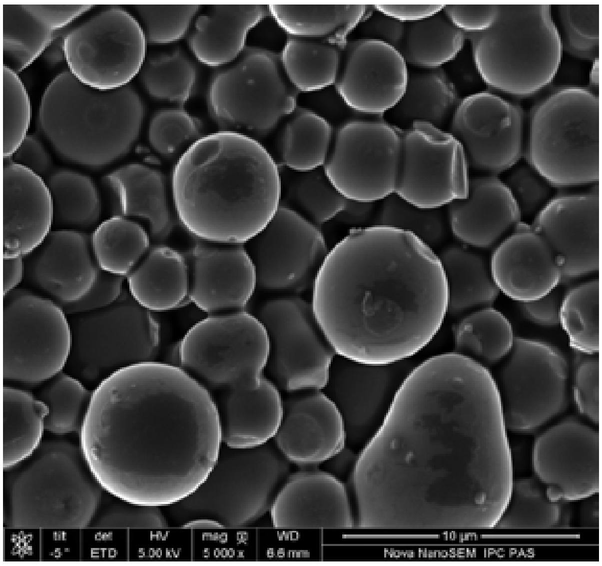

Fig 1. SEM image at a magnification of 5000 showing carbon spheres lightly coated by polystyrene (ca. 4% weight). Carbon spheres range from 2-12um and are held together to form a porous material.

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Amperometric Gas Sensors: New Developments for Low Concentration Measurements

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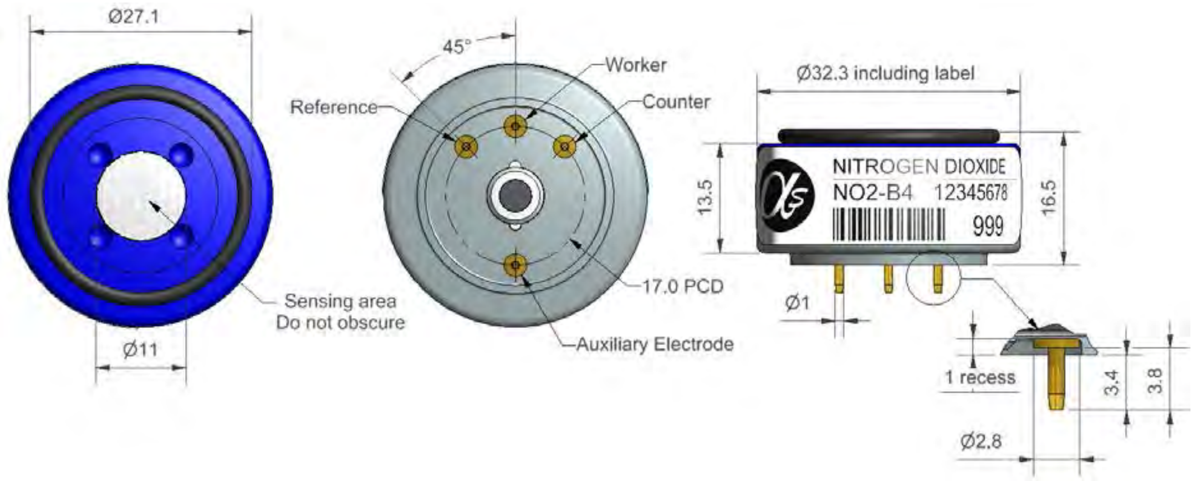
Amperometric gas sensors are well established in the gas monitoring industry [1-3]. They are used both in portable and fixed instruments, with the advantage of being affordable and robust. In fact today many workers in the world rely on amperometric gas sensors for their immediate safety. Besides conventional gas sensing applications there is now a growing demand for air quality monitoring instruments and the use of amperometric gas sensors would be a cost-effective alternative to existing technologies [4]. The concentrations of common pollutants in the air are, however, 2-3 orders of magnitude lower than the concentrations involved in traditional applications and a certain number of issues need to be carefully considered when measuring gases at ppb levels. One of the main issues involved is the stability of the background current. We propose to present studies dealing with the background current dependence on environmental factors such as temperature and humidity. Experimental results identify the sources of these background currents, which are challenges for air quality monitoring applications.



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Electroanalysis at Discrete Nanowire Arrays: Quantitative and Qualitative Detection of Nitroaromatic Explosives

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Recently 1-dimensional nanoelectrodes fabricated at silicon substrate have been demonstrated as practical alternatives to traditional nanodisc and nanopore electrodes. [1-4] 1-dimensional nanoelectrodes, such as nanowires, benefit from nanoscale critical dimensions (width and height) ensuring enhanced mass transport, while the high aspect ratio permits higher measurable currents in the ≥1 nA regime and with uniform current densities. In this work, we report simulation, fabrication and characterisation of discrete gold nanowire electrodes arrays, fabricated using a hybrid E-beam /photolithography approach, for use in electrochemical applications.

We simulated diffusion profiles existing at nanowire electrode arrays with various inter-electrode distances. Experiments show that nanowires that are sufficiently spatially resolved (diffusionally independent) demonstrate superior electrochemical performance, when employing sweep voltammetric techniques such as cyclic voltammetry, compared to nanowires that are relatively close to each other (overlapping diffusion profiles), which is in good agreement with the simulated results. By contrast, arrays with diffusionally overlapping profiles exhibit enhanced performance when employing step voltammetric techniques such as square wave voltammetry.

We explore application of nanowire array electrodes to the detection of different nitroaromatic species. Characteristic reduction peaks of nitro groups are not observed at nanowire array electrodes using sweep voltammetric methods. By contrast, clear and well-defined reduction peaks are resolved using potential step square wave voltammetry. A Principle Component Analysis technique is employed to discriminate between nitroaromatic species including structural isomers of DNT. The analysis indicates that all compounds are successfully discriminated by unsupervised cluster analysis. Finally, the magnitude of the reduction peak at ~671 mV for different concentrations of TNT exhibited excellent linearity with increasing concentrations enabling sub-50 ng mL^{-1} limits of detection in water samples; see Figure 1.

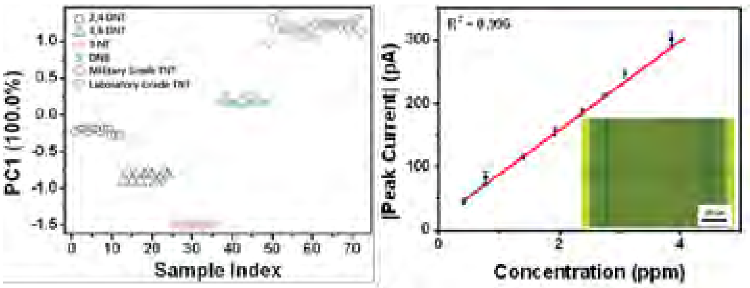

Fig 1 (a) PCA discriminating different nitroaromatic species and (b) TNT calibration curve in water

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Anodic Stripping Voltammetry using Nanoband Array Electrodes

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Anodic stripping voltammetry is an important technique for the detection of trace metals. The technique is very sensitive but requires careful control of a range of parameters including the conditioning of the working electrode, the pH and the hydrodynamics[1, 2]. In this paper we discuss the detection of arsenic using a commercial nanoband array electrode structure which allows for sub ppb detection limits with no stirring of the electrode and much milder conditions than is standard for this technique. We also report of preliminary studies of mercury detection using the same technique described. In both cases we have demonstrated that the absence of mass transport limitations[3] allows us to determine trace levels of the target analytes without the need to control the hydrodynamics thus simplifying the measurement process.

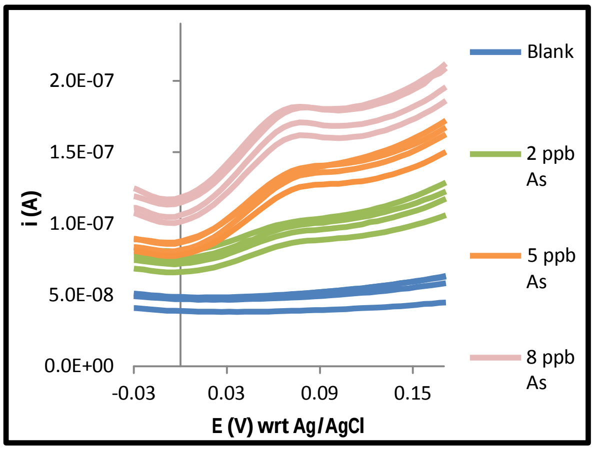

Figure 1: ASV of varying quantities of As in deionised water

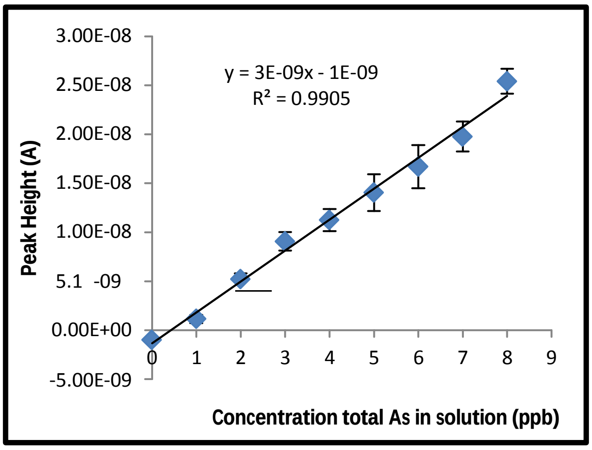

Figure 2: Calibration curve of As in deionised water

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Development of Robust Microelectrodes for Electroanalysis in Molten Salts.

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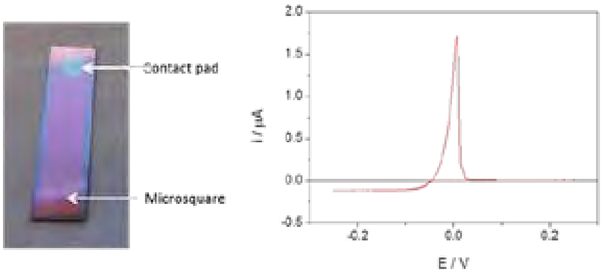
Molten salts are an extremely useful medium for chemical processing. Examples of industrially important chemical processes carried out in molten salts include, the FFC process[1], electrodeposition[2] and pyrochemical processing of spent nuclear waste[3]. Currently there is significant interest in improving yields for uranium recovery from used fuel rods, the overall aim being to dramatically increase the efficiency of the nuclear cycle by recycling more fissile material and avoiding the requirement for long term storage of radioactive waste. Molten salts are being extensively explored for effective pyroprocessing of spent nuclear fuel. The EPSRC funded REFINE collaboration is leading the UK's pyrochemical research effort. In this collaboration our work is specifically concerned with "online" monitoring of chemical processing in the molten salt lithium potassium eutectic (LKE). The chemical species of interest for online monitoring are redox active e.g. Uranium and Plutonium, making electrochemical techniques a promising set of approaches for real time measurements. Using photolithography, we are developing a range of microelectrode sensors for use in LKE. Microelectrodes have the advantages of high signal to noise ratio, insensitivity to convection and rapid development of steady state diffusion profiles. The major challenge associated with the work is developing a sensor capable of withstanding the harsh environment in the melt (temperatures up to 500°C and often highly corrosive). This talk will detail our research in this area, highlighting initial studies, optimisation work, materials choices, electrochemical characterisation of redox agents in LKE and deployment of the sensors for online monitoring in LKE.



Left – image of a microelectrode chip designed for use in molten salt
Right – Cyclic voltammogram recorded using a sweep rate of 100 mVs^{-1} and a 50 µm tungsten square electrode in LKE + 10 mM Bismuth (III) chloride at 450°C.

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Design and Development of an Electrochemical Sensor Based on 3,4-Ethylenedioxythiophene and Polystyrene Sulfonic Acid for the Detection of Small Molecules

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Poly(3,4-ethylenedioxythiophene) (PEDOT), one of the most studied conducting polymers, usually tends to form uniform and adherent films on most of electrode substrates. This polymer has biocompatibility and good stability in aqueous electrolytes [1-4]. Moreover, it shows satisfactory anti-fouling properties which is beneficial to achieve good repeatability of the electrochemical response. These merits make it a material for the electrochemical sensors. Due to their properties glassy carbon is employed as an electrode material for the fabrication of electrochemical sensors. Chemically modified electrodes have been employed for the analysis of organic molecules (viz., Paracetamol, aspirin, caffeine, phenol, catechol, resorcinol, hydroquinone, dopamine, L-dopa, epinephrine, norepinephrine, methyl parathion, ethyl parathion, venlafaxine, desvenlafaxine, imipramine, trimipramine, desipramine etc) as well as inorganic compounds (bismuth, antimony, etc.) [1].

This work describes the characterization of two glassy carbon electrodes modified (GC). The first one is a GC electrode modified with PEDOT (GC/PEDOT), through the electropolymerization of 3,4-Ethylenedioxythiophene (EDOT) in presence of polystirene sulfonic acid, and the second one is a modified GC electrode (GC/PEDOT-SiO_2) in which initially a SiO_2 layer has been electrochemically deposited, and then the PEDOT is electropolymerizated in the same conditions than GC/PEDOT. of GC/PEDOT by sol gel (SiO_2). the second step we modified . The electropolymerization has been performed by cyclic voltammetry between -0.3 and 1.0 V at different scan rates during 25 cycles. From cyclic voltammetric experiments at scan rate 50 $mV.s^{-1}$, it was observed that the GC/PEDOT electrode presents a redox pair corresponding to ferrocene/ferrocenium process with a peak-to-peak separation of 153 mV. When the GC/PEDOT-SiO_2 electrode is used, a important decrease in the redox potential occurs maintaining the peak-to-peak (ΔE= 158 mV). Then an catalytic effect is observed with this GC/PEDOT-SiO_2 electrode.

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Novel Reductive-Reductive Mode Electrochemical Detection of Rohypnol Following Liquid Chromatography and Its Determination in Coffee

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Rohypnol (flunitrazepam) has been determined by high performance liquid chromatography dual electrode detection (LC-DED), both in the redox mode and the dual reductive mode. Initial studies were performed to optimise the chromatographic conditions and these were found to be 50 % acetonitrile, 50 % 50 mM pH 2.0 phosphate buffer at a flow rate of 0.75 ml/min, employing a Hypersil C_{18}, 5 µm, 250 mm x 4.6 mm column. Cyclic voltammetric studies were made to ascertain the redox behaviour of Rohypnol at a glassy carbon electrode over the pH range 2-12. Hydrodynamic voltammetry was used to optimise the applied potential at the generator and detector cells; these were identified to be -2.4 V and +0.8 V for the redox mode and -2.4 V and -0.1 V for the dual reductive mode respectively. A linear range of 0.5 µg/ml to 100 µg/ml, with a detection limit of 20 ng/ml was obtained for the dual reductive mode. Further studies were then performed to identify the optimum conditions required for the LC-DED determination of Rohypnol in beverage samples. A convenient and rapid method for the determination of Rohypnol in beverage samples was developed using a simple sample pre-treatment procedure. A recovery of 95.5 % was achieved for a sample of white coffee fortified at 9.6 µg/ml Rohypnol.

Redox-Cycling Sensors Based on Microscaled Plate-Plate Double- Electrodes

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Micro- and nano-scaled electrode systems having two independently controlled working electrodes provide excellent opportunities in electroanalysis with applications ranging from mechanistic studies to single molecule detection [1]. In this work generator-collector electrochemistry is exploited in which one electrode (“the generator”) is used to convert an electroactive species which is then rapidly transported to the second electrode (“the collector”). This approach offers signal enhancement through current amplification, chemical filtration and spatial separation effects.

Here we report new methods of fabricating microscale double-electrodes with the plate-plate of “trench” geometry. The developed methods are straightforward, easy to replicate and provide access to trench electrodes with a small microscale inter-electrode gap and proportionately large electrode areas. Applications of these electrodes for fast feedback redox cycling of ions such as nitrate and chloride [2, 3] as well as biomolecules including dopamine [4] will be described. New experiments performed in biological media are reported. Advantages and disadvantages of the microtrench electrodes will discussed.

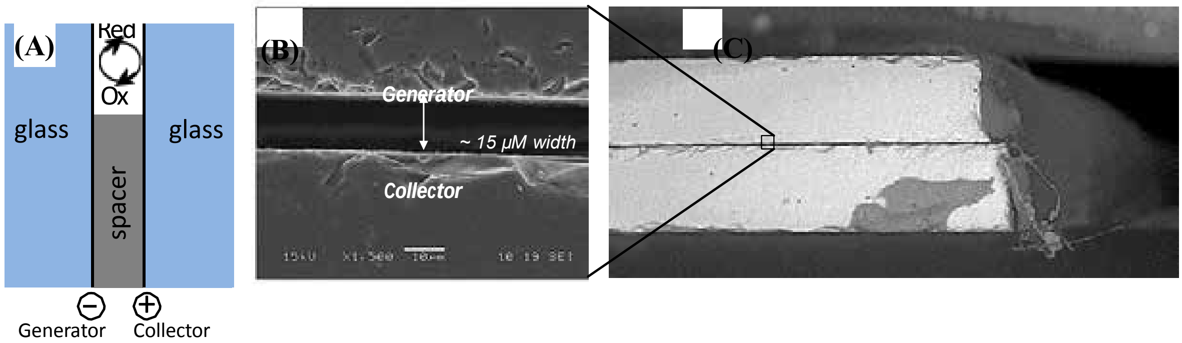

Figure 1: (A) Schematic drawing of a microtrench sensor in “generator-collector” mode (B, C) SEM micrographs of a boron-doped diamond microtrench electrode.

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Glucose Detection using Nanoband Array Electrodes

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Development of biosensor devices is of key importance to optimise detection for a range of biomolecules relevant to healthcare applications. Amongst these devices, the most widely characterised and commercially available is the glucose biosensor. A range of sensors based on the enzyme glucose oxidase (GOx), which catalyses the oxidation of β-D-glucose to δ-gluconolactone have been reported using macro and micro electrodes [1, 2,]. However, the use of nano-scale electrodes is limited [3]. Nanoband array electrodes offer the enhancement of electroanalysis via enhanced mass transport, high signal-to-noise ratio, faster response time and increased sensitivity [4, 5]. In this paper, we use the glucose biosensor model as a platform to demonstrate the immobilisation of an enzyme, GOx onto a commercial gold nanoband array electrode structure using simple covalent linkage methods and the subsequent detection of glucose. We have demonstrated that the absence of mass transport limitations using nanoelectrodes allows determination of glucose levels without the need to control hydrodynamics thus simplifying and speeding up the measurement process. The limits of detection, reproducibility of measurements and the stability of such nanoband array electrodes relative to biosensors reported in the literature is also discussed.

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Possibilities of Selective and Sensitive Electrochemical Monitoring of Purine Derivatives in Real Biological Samples Though Nanostructuring of Carbon-based Material Surfaces

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Recent research shows that surface nanostructuring of materials that have long been used in electrochemistry plays a key role in the production of electrodes enabling the selective and sensitive electrochemical detection of individual fractions of biologically important molecules that normally coexist in real matrices, such as body fluids, hair or environmental samples [1,2]. Sensitive determination of a deviation in the concentrations of substances, which are found in body fluids as metabolic products of different biochemical reactions, from their standard values can be used as an indicator of many started metabolic disorders, genetic mutations or serious diseases. For example, our group recently showed the electrochemical protocol for monitoring transformation of purine catabolites (hypoxanthine, xanthine, and uric acid) catalyzed by xanthine oxidase as well as inhibition of this pathway by allopurinol and its active metabolite oxypurinol [3]. In the case of DNA sensing, the position, size and shape of the oxidation signals of purine nucleotides (purine nucleobases in hydrolyzed DNA samples) displayed on nanostructured carbon-based electrodes can be advantageously used for a label-free sequence-specific DNA sensing [4], detection of DNA hybridization or sensitive detection of single nucleotide polymorphisms [1,2].

This contribution deals with the use of a few graphene-based surface structures that have been produced either by mechanical machining operations of compact carbonaceous materials or by electrochemical anodization of the carbon materials, which include also disposable and screen printed electrode concepts, in acidic solutions under specific conditions for sensitive and simultaneous electrochemical detection of purine derivatives in selected biological matrices:

(i) monitoring of purine catabolites and oxypurinol in urine and blood plasma samples of patient under allopurinol therapy
(ii) monitoring of methylxanthines in urine samples of patient treated for asthma
(iii) monitoring of purine nucleobases as a powerful tool for label-free DNA sensing

Acknowledgments: This work was supported by the Grant Agency of the Czech Republic, grant project P205/10/2378.

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A Novel Efficient Combined Process for Nitrate Treatment and Hydrogen Production — coupling of an Electrochemical System with a Biological Treatment

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Nitrate ions (NO_3^-) contamination of water sources has become a serious problem around the world. They cause methemoglobinemia in infants and eutrophication of water bodies. Several processes are used for removing NO_3^- ions from contaminated waters. But, these techniques present considerable drawbacks, which limit their use for large scale application. One promising and attractive way of treatment, which can lead to interesting solutions consists in coupling electrochemical and biological treatments [1]. The feasibility of such coupled process to treat NO_3^- from waters has not been yet investigated. Moreover, nitrate can be used as an expensive and direct source for ammonia manufacturing, which has an important potential as nitrogen source for microorganism cultures producing biohydrogen. For this reason the first objective of this study was to develop a flow electrochemical process, allowing a selective and quantitative transformation of NO_3^- to ammonium (NH_4^+). Then the obtained NH_4^+solution will be used to produce biohydrogen (H_2) via heat-treated activated sludge culture.

The first step in the present study was the preparation of a porous copper electrode by a suitable electrodeposition method that has been developed in the laboratory [2]. The electro- deposition of copper on graphite felt and the electroreduction of NO_3^- (3gL^{-1}) were performed on a home-made flow cell, where the solutions percolate through the porous electrode. Homogeneous Cu coating of all fibres in the 3D porous structure was successfully obtained using low concentrations of copper salts and high applied current intensities. The porous copper electrode was then used as cathode in the flow cell to achieve the transformation of NO_3^- into NH_4^+. The nitrate solution was quantitatively reduced into NH_4^+ with high selectivity of 97% and current efficiency of 72% in only one pass through the electrode and using phosphoric acid 10^{-2} M as an electrolytic solution. Finally, under the optimal conditions corresponding to pH 6.5 and initial glucose concentration of 25 g L^{-1}, the use of the collected effluent containing 1g L^{-1} of NH_4^+ as nitrogen source to convert anaerobically glucose to H_2 in a batch system involving heat-treated activated sludge led to a high biohydrogen yield (1.1 mol H_2/mol glucose) with total consumption of the produced ammonium. The pollutant, nitrate, was therefore valorized as a nitrogen source for biohydrogen production.

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ELECTROCHEM 2014

SPEAKER ABSTRACTS

(Electro)catalytic C-C Bond Formation Reactions with Redox-Active Metal Complexes

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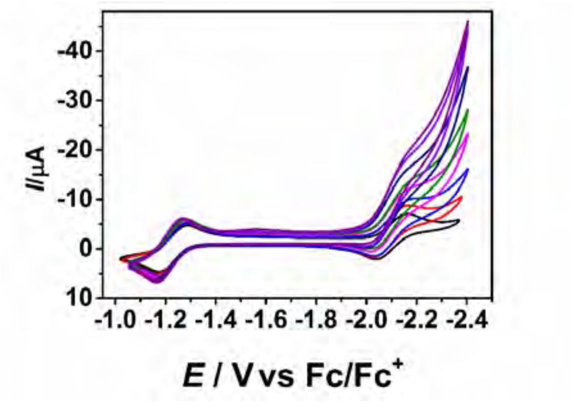
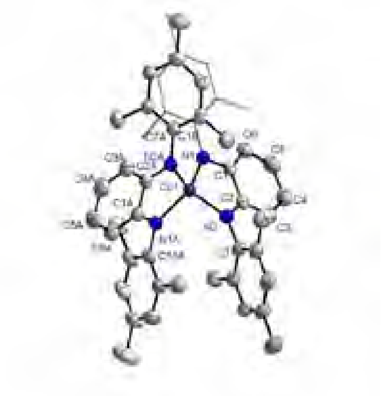
Metal complexes of redox-active ligands, once considered spectroscopic curiosities, are finding increasing use in catalytic bond formation reactions.[1] In this contribution we will discuss recent results from our laboratories[2] on the use of cobalt complexes of diiminosemiquinone ligands for the (electro)catalytic C-C bond formation reaction. Cases of homo as well as hetero C-C coupling reactions will be discussed. Results obtained from electrochemistry, UV-vis-NIR and EPR spectroelectrochemistry will be used to shed light on the catalytic mechanism. We will also touch upon the topic of nickel complexes of "click" derived triazole ligands for catalysing similar bond formation reactions.[3]





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Electrochemical Deposition of Metal Dithiolene Complexes and Cu- Phthalocyanine, Illustrating a Novel Route to Molecular Films for Optoelectronic Applications

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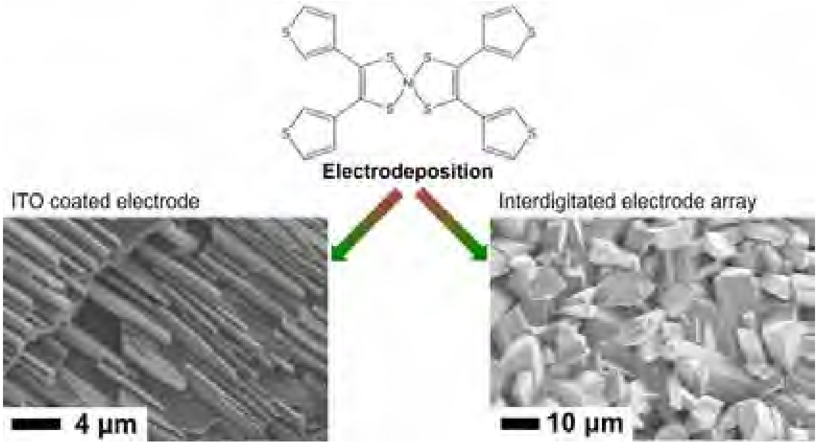
Molecular semiconductors are under intense study for low-cost, flexible electronic and optoelectronic devices. Thin film organic or molecular semiconducting materials are typically prepared by either vapour processing or coating from solution, however extended delocalised molecules suitable for molecular semiconductors are often of low solubility and low volatility. In addition, good structural control can be hard to achieve by solution coating and vapour processing can involve expensive equipment. We report electrodeposition as a novel alternative approach to molecular film formation that combines a low-cost, versatile solution method with good structural control. Our work shows molecular deposition by electrochemical oxidation of the monoanionic species leading to controlled film formation of the insoluble neutral complex [1,2,3]. We show some advantages compared with typical solution coating, such as better film crystallinity than a drop coated film of the same molecules; film formation with low-solubility molecules not suitable for normal solution coating; and formation of a film of molecules not stable in solution hence otherwise unobtainable in a neutral form.



We will discuss our recent work applying this technique to metal-dithiolene complexes and Cu-phthalocyanine, with emphasis on structural control and its impact on the photo-responsive characteristics of the devices. This work opens a unique new direction in molecular electronic materials, as a complementary fabrication process in comparison with vapour deposition or solution-coating

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Electrochemical Reductive N-H Bond Cleavage in Imidazole Coordinated in Rhenium(I) Carbonyl α-Diimine Complexes

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The redox activity, photophysical properties and synthetic flexibility of rhenium(I) carbonyl *α*- diimine *(N,N)* complexes make them very useful sensitizers of electron and energy transfer processes [1]. In particular, proteins such as *Pseudomonas aeruginosa azurins* allow the redox-active Re metallolabels to be attached in defined positions at their surface through the histidine side chains, thereby providing an ideal system to mimic active sites in metalloproteins for investigating relaxation dynamics and long-range electron transfer reactions (tunneling) between a metal center and the distant electronically excited $[Re(imidazole)(CO)_3(N,N)]^+$ chromophore [2]. Thus, deprotonation of the monodentate imidazole ligand becomes a crucial step in the synthesis of the dyads, using the metalloligand approach.

Here, we report on the electrochemical reduction of 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) ligands in the complexes $[Re(imidazole)(CO)_3(N,N)]^+$, which induces rapid N-H bond cleavage in the axial imidazole (imH) ligand at both ambient and low temperatures. While this process is straightforward for $[Re(imH)(CO)_3(bpy)]^+$ (Fig.1), being triggered by the initial 1e$^-$ reduction of the bpy ligand [3], the phen complexes with imH and *N*-methylimidazole (imMe) show a more peculiar behavior [4]. The oral presentation will also involve most recent results obtained with the neocuproine (2,9-dimethyl-phen) ligand.

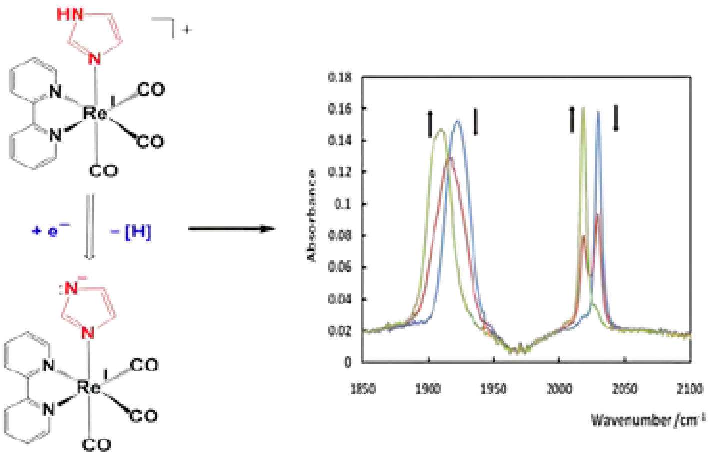

Fig.1. Reductive electrochemical conversion of $[Re(imH)(CO)_3(bpy)]^+$ to $[Re(im^-)(CO)_3(bpy)]$ (im^- = 3-imidazolate) monitored in situ by FT-IR spectroscopy.

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Electrochemical Behavior of Surface Immobilized Ru Complexes with Sequential Layered Structures

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Our research interest is focused on surface confined architectures on electrodes by use of redox-active metal complex as a modular unit, which have potential applications in molecular devices, sensors, and catalysis. Using phosphonate as both tethering on an ITO surface and linker groups, we have reported the layer-by-layer growth of redox-active Ru complexes with tetrapod phosphonate anchors on an ITO electrode[1, 2]. In order to achieve the potential asymmetry in the multilayer films, two dinuclear Ru complexes having different bridging ligand of 2,3,5,6-tetra(2-pyridyl)pyrazine (tppz) or 1,2,4,5-tetra(2-pyridyl)benzene (tpb) with tetrapod phosphonate anchors were synthesized. Oxidation potentials are +0.84 and +1.06 V vs Fc0/+ for the tppz-bridged complex (Ru-N), and -0.40 and 0.07 V for the tpbbridged (Ru-C) [3]. Surface confined assembly was achieved by applying the sequential coordination-driven assembly of Zr(IV)-phosphonate bonds on the ITO electrode (Fig. 1 and 2). As a result, unique molecular sequences of two Ru-N and Ru-C units in the films were fabricated and examined for both cyclic voltammetry in solution (Fig.3) and current-voltage (I-V) measurements on thin films. These molecular hetero-layer films showed rectification effect, which depends on the structure of the molecular junctions. In addition, novel photodiode behavior was observed. The role of molecular junctions will be discussed.

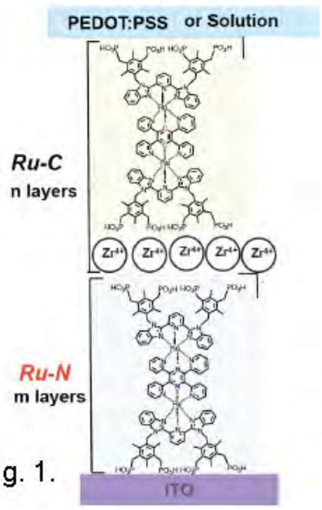


Fig. 1.

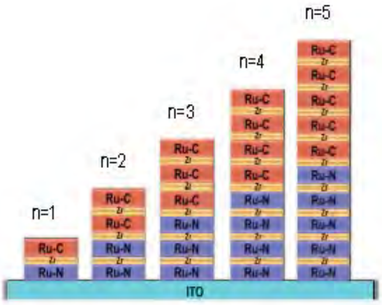
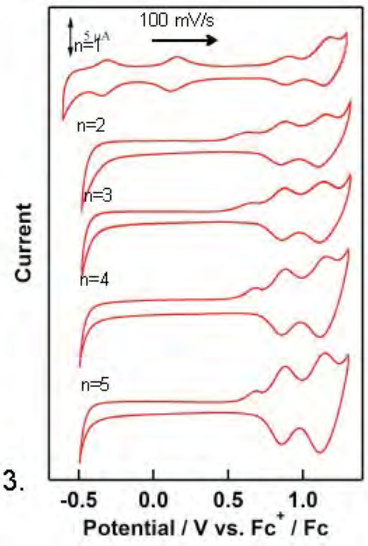


Fig. 2.



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Probing Mechanisms in Transition Metal Catalysed Oxidation Chemistry with (Spectro)electrochemistry

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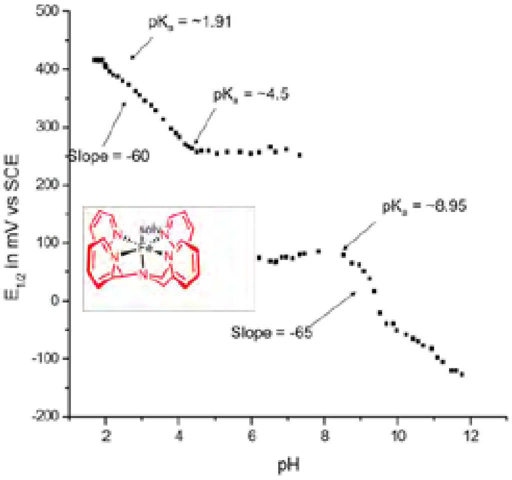
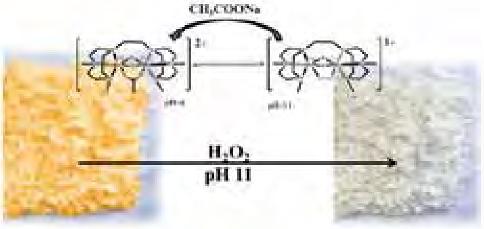
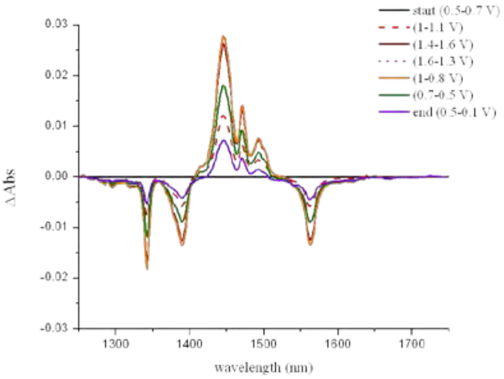
Electrochemical methods have a proven track record in facilitating our understanding of the complex reaction mechanisms that are encountered, not least, in transition metal oxidation catalysis. In regard to 1st row transition metal based oxidation catalysis, the dependence of both coordination mode and the rates of ligand exchange creates tremendous opportunities in terms of reactivity but, equally so, increases the challenge in understanding their redox chemistry. In this contribution, the focus will be on the application of electrochemistry and in particular spectroelectrochemical techniques, to understand specific aspects of the chemistry of several well-known iron [1] and manganese [2] oxidation catalysts.







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Electrochemistry of Covalently Connected Bis(Ferrocenylethynyl)s, and Coordination-driven Self-assembled Multi-Ferrocenyl- and Multi-Ferricenyl- Materials

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A range of bis(ferrocenylethynyl) complexes and a mono(ferrocenylethynyl) complex have been synthesized incorporating conjugated heterocyclic spacer groups with the ethynyl group facilitating an effective long-range intra-molecular electronic interaction.[1] To generate higher nuclear complexes, coordination chemistry approach involving copper clusters are utilized. Ferrocenylethynyl functionalized pyridine ligand provided the coordination site to connect ferrocenyl units through the copper clusters.

The bis(ferrocenylethynyl) complexes were investigated by electrochemical and spectro-electrochemical methods and complimented by DFT calculation. The ferroenylethynyl-copper cluster materials oxidize under mild condition giving electro-crystallization of partially- and fully- oxidized products. The oxidation products show distinct morphologies.

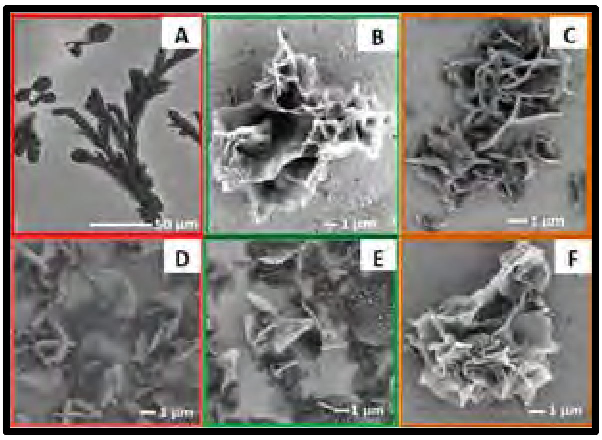

Figure 1 SEM images of electro-crystallized products from oxidation of $Cu_4I_4Fcpy_4$ (**A**), Cu_2X_2 $Fcpy_4$ (**B-C**), $[(Fcpy)(Ph_3P)CuX]_2$ **(D-F)**

The partial and fully oxidized materials hold promise for ferro-electronic applications.[2] Further the control over morphology present their potential for generating novel microstructures.[3] The convenient synthesis, investigation by electrochemistry, SEM, EDX, etc and future prospect of the electro-crystallized materials will be presented.

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Low pH Electrolytic Water Splitting Using Earth-Abundant Metastable Catalysts That Self-Assemble in Situ

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Typical catalysts for the electrolysis of water at low pH are based on precious metals (Pt for the cathode and IrO_2 or RuO_2 for the anode). However, these metals are rare and expensive and hence lower cost and more abundant catalysts are needed if electrolytically-produced hydrogen is to become more widely available. In this talk, I will show that electrode-film formation from aqueous solutions of first row transition metal ions at pH 1.6 can be induced under the action of an appropriate cell bias, and that in the case of cobalt voltages across the cell in excess of 2 V lead to the formation of a pair of catalysts that show functional stability for oxygen evolution and proton reduction for over 24 hours [1]. I will show that these films are metastable, and that if the circuit is opened they re-dissolve into the electrolyte bath with concomitant O_2 and H_2 evolution, such that the overall Faradaic efficiency for charge into the system versus amounts of gases obtained approaches unity for both O_2 and H_2. This work highlights the ability of first row transition metals to mediate heterogeneous electrolytic water splitting in acidic media by exploiting, rather than trying to avoid, the natural propensity of the catalysts to dissolve at the low pHs used. This in turn we hope will encourage others to examine the promise of metastable electrocatalysts based on abundant elements for a range of reactions for which they have traditionally been overlooked on account of their perceived instability under the prevailing conditions.

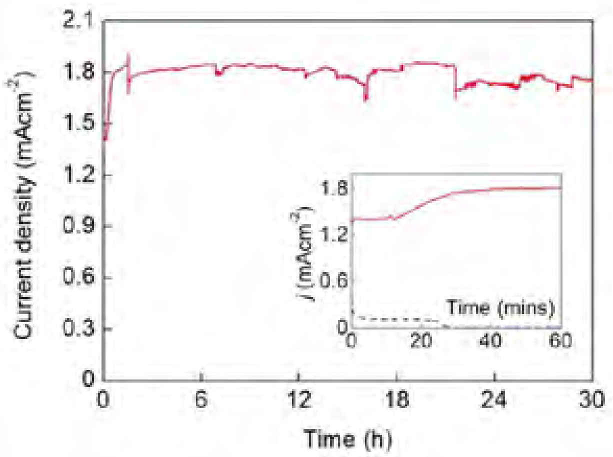

Figure: Red line (main figure and inset): electrolysis in 0.2 M $Co_3(PO_4)_2$. Blue dashed line (inset only): electrolysis under the same conditions but in the absence of Co(II).

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Photoelectrochemistry of 2D-confined systems: From Simple Logic Devices to Artificial Neurons

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Information, along with energy and matter, is one of the fundamental entities that built the Universe.[1] Light, usually considered as the cleanest form of energy is also a powerful information carrier. While interaction of light with molecules is studied in detail, these processes are very seldom associated with information processing.[2, 3] Dye-sensitized solar cells, devices which utilize photoelectrochemical processes involving dye molecules immobilized at semiconducting surfaces are efficient systems for energy conversion.[4, 5] Slight modification of these structures may lead to devices perfectly suited for information processing.[6, 7]

Our current approach combines paradigms of molecular logic devices with classical, semiconductor-based electronics. While the elementary acts of information processing occur at the molecular scale (molecules adsorbed and the surface of nanoparticulate semiconductors), both the input and the output have the form of current pulses easily understood by classical electronic devices. Novel materials are synthesized via chemisorption of organic redox-active chromophores or chromogenic molecules onto wide bad gap semiconductors. These materials are characterized by pronounced photoelectrochemical photocurrent switching effect (PEPS) or other photoelectrical instabilities. Variable state of the device upon application of optical and/or electrical stimulation can be described using Bollean logic.[8] By careful selection of substrate potential and incident light wavelength different information processing devices have been demonstrated. These simple logic devices can be subsequently connected into larger circuits. This in turn leads to construction of various optoelectronic computing circuits.[6, 7, 9] Moreover, in the presence of appropriate charge-trapping agents, pseudo-synaptic behaviour and short memory effects can be observed. These phenomena may lead to future computing devices based on neuromimetic architectures.

The most common feature of information processing devices based on the PEPS effect is the lack of predefined structure, conversely, their operation relies only on moleculr scale interactions between semiconductor, surface molecules and electrolyte components.

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Spectroelectrochemistry of New Metal Complexes with Hemilabile Redox-Active Ligands

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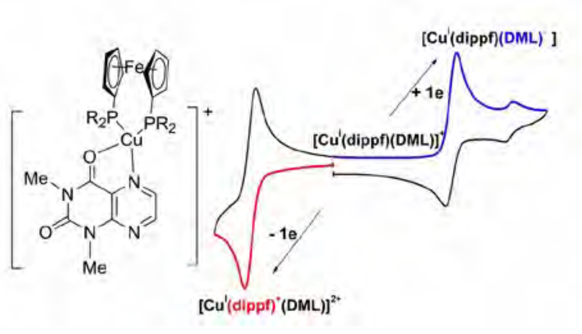
Non-innocently behaving redox-active ligands (1,2) with hemilabile chelate coordination functions have been used in two kinds of organometallic complexes [1,2].

1. Reducible 1,3-dimethyllumazine (1) contains an N,O chelate function with weak bonds between O and Cu^I of a 1,1-bis(diorganophosphino)ferrocene-copper unit [1].
2. Oxidisable *o*-amidophenolate N,O-chelates can be modified with an additional labile S-, Se- or O-donor function (2) which may coordinate to areneruthenium or areneosmium moieties, depending on the oxidation state [2].

The structurally characterised complexes were investigated by variable temperature cyclic voltammetry and spectroelectrochemistry (uv-vis-nir, ir, epr) [3,4] to reveal the effects of hemilability.



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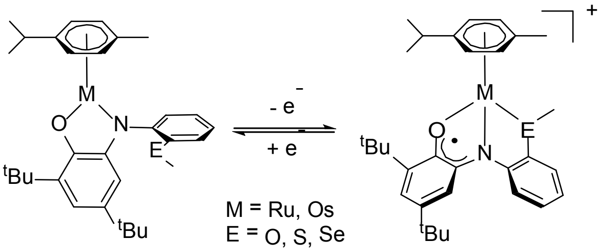

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A Thin-Layer Electrochemical Cell for the Study of Vibrational Circular Dichroism of Chiral Redox-Active Molecules

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VCD studies on synthetic ferrocene-containing peptides bring new insights into the real- space dependence of VCD signal-amplification due to low-lying electronically excited states. Through electrochemical switching of the redox state of substituted ferrocene covalently bound to a peptide-like bio-functionality, an amplification of VCD signal intensities of vibrational modes along the peptide backbone has been induced. Investigation of the distance-dependence of the amplification indicates a localized character of the enhancement. Our results[1] may inspire the development of chiral signalling prototypes based on redox sensing and chiral recognition by means of a localized amplified VCD response. The incorporation of a redox-switchable unit like ferrocene provides a powerful means to probe locally – and at user-defined locations – the structure of large systems.

The experimental work was performed with an adapted optically transparent thin-layer electrochemical (VCD-OTTLE) cell that features a relatively long optical path (1.2 mm) in the probed area. Details of the cell have been published elsewhere.[2]

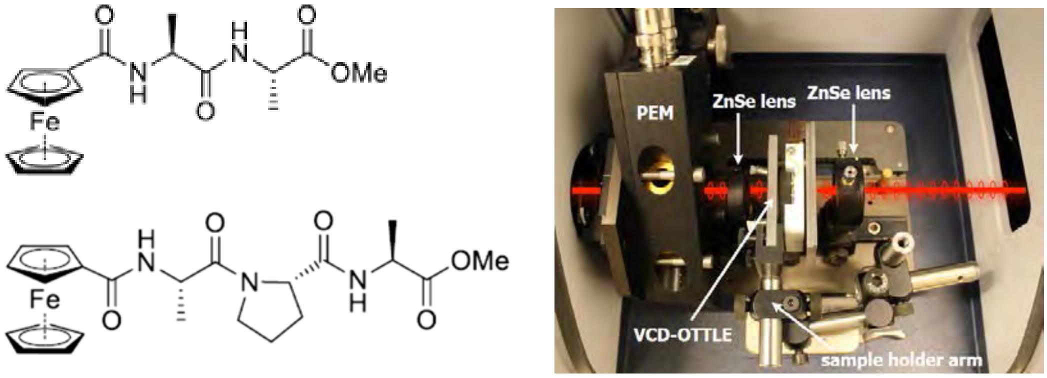

Figure 1 The chemical structures of investigated *N*-(ferrocenylcarbonyl)-L-alanyl-L-alanine methyl ester (top) and *N*-(ferrocenylcarbonyl)-L-alanyl-L-prolinyl-L-alanine methyl ester (bottom), and the VCD-OTTLE cell in an adapted sample compartment of a Bruker PMA 50 VCD module connected to a Bruker Vertex 70 FT-IR spectrometer.

References:
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“Self-induced Electroclick” Immobilisation of Cu Complexes on Gold for Enhanced Electrocatalytic Reduction of Nitrite Ions and Surface Addressing

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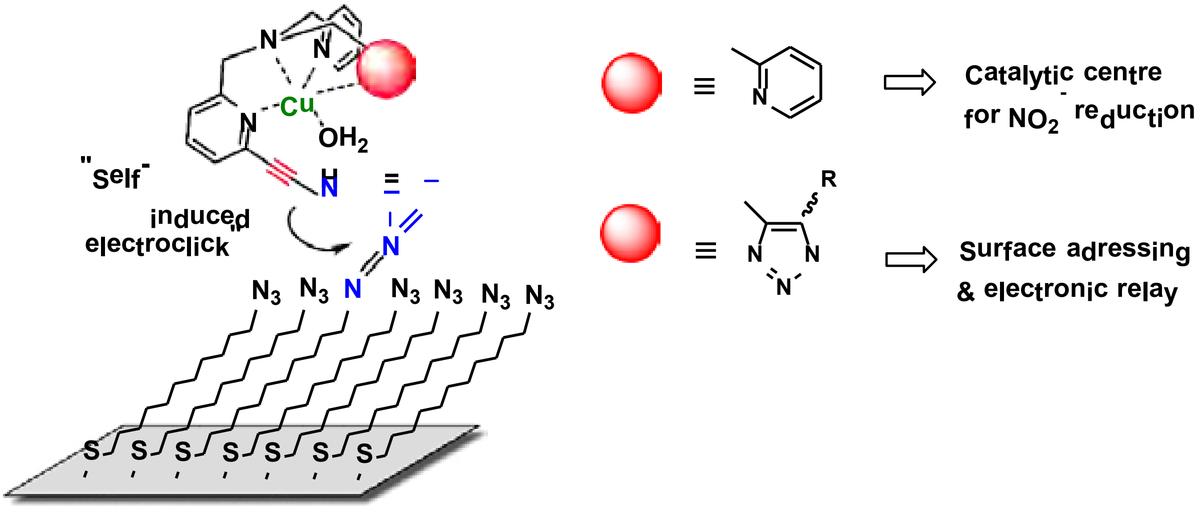
We have developed a strategy for surface functionalization inspired by the “click” Cu-catalyzed Huisgen’s cycloaddition reaction. The grafting is operated by simple electrochemical reduction of an ethynyl-based Cu(II) complex at an azido-undecanethiol pre-modified gold electrode without additional catalyst (“self-induced electroclick”).[1] The in-situ control of the surface coverage during the grafting process by the electroclick approach has been recently exploited to rationalize the influence of surface concentration on the electro- catalytic properties of the immobilized Cu complex towards nitrite reduction.[2] In addition, we have developed a versatile platform which allows the attachment of any object of interest R (R = electro active complexes, biomimetic compounds, proteins…) as SAMs on gold.[3,4] This method opens the way for surface addressing by a simple electroclick procedure.



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Functional- and Multifunctional Materials based on Redox-Active Ligands

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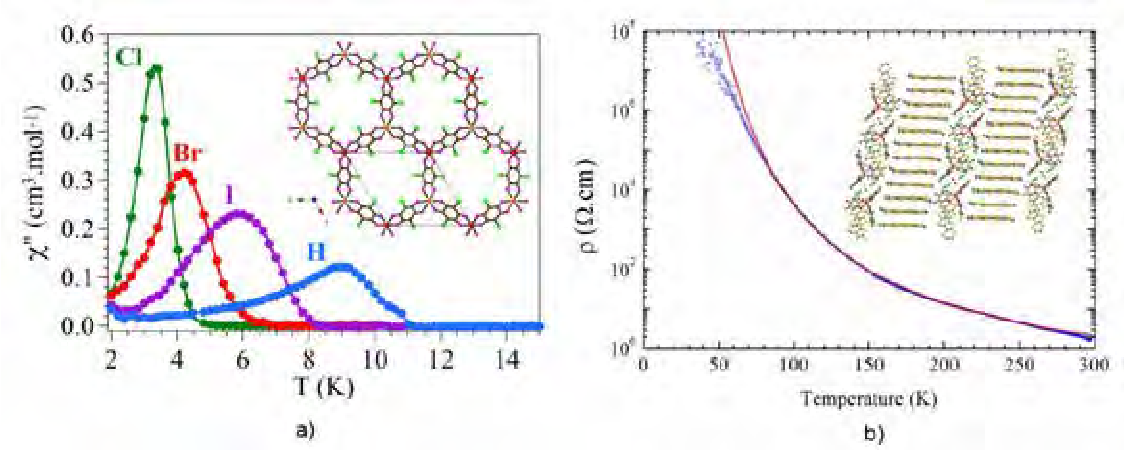
In the search for new functional molecular materials whose physical properties can be easily tuned by simple changes on the molecular structures of their building units, we have focused our attention on the redox-active anilato ligands X_2An (X = Cl, Br, I; An = 2,5-dihydroxy-1,4- benzoquinone). We have synthesized the new family of paramagnetic metal complexes of general formula $[M^{III}(X_2An)_3]^{3-}$ (M^{III} = Cr, Fe;) [1] which are challenging building blocks for the preparation of new molecule-based ferrimagnets and novel magnetic conductors, where the nature of the halogen atom can play a key role in determining their physical properties.
Here we report the synthesis and the full characterization of a novel family of molecular ferrimagnets formulated as $A[Mn^{II}Cr^{III}(X_2An)_3]$ (A = $(n\text{-}Bu)_4N^+$, $[(phen)_3(H_3O)]^+$, X = Cl, Br, I). In this family, a simple change in the halogen atom (X) on the bridging ligand allows for a fine tuning of the magnetic properties: the ordering temperature increases from 5.5 to 6.3, 8.2 and 11.0 K for X = Cl, Br, I, H, respectively.[2] Furthermore the role of the electrocrystallization technique in the synthesis of novel paramagnetic molecular conductors by combining the paramagnetic metal complex $[Fe(Cl_2An)_3]^{3-}$ with the organic donor BEDT-TTF (bis-ethylenedithio-tetrathiafulvalene) will be also highlighted in this communication.



a) b)

Figure: (a) AC susceptibility for the series $[Mn^{II}Cr^{III}(X_2An)_3]^-$ (X = Cl, Br, I, H) with a partial view of the crystal structure; (b) Conductivity measurements for the salt α'''-$[BEDT\text{-}TTF]_{18}[Fe(Cl_2An)_3]_3\cdot 3CH_2Cl_2\cdot 6H_2O$ with a view of the crystal structure.

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Dehalogenation Reduction of a Chlorinated Solvent by a $[Ni(tmc)]Br_2$-modified Nafion Electrode

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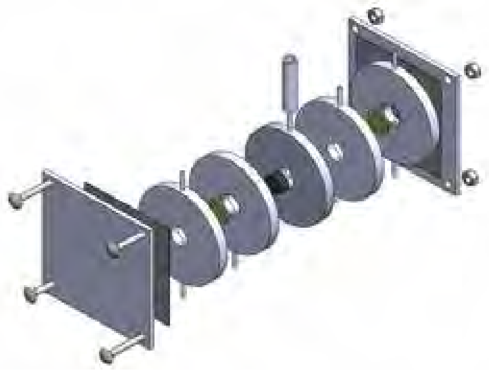
The chlorinated compounds are the most frequently observed contaminants in grounds and groundwaters due to their high use as solvents and degreasers. Since they are characterized by a density higher than water, they penetrate the full depth of the aquifer and accumulate on its bottom. Chlorinated solvents are difficult to eliminate because they are generally non-biodegradable and destructive methods such as incineration are very expensive and can produce more toxic by-products like dioxins.

In this work, we investigated the dechlorination reaction of 1,3-dichloropropane, a contaminant solvent, by electrochemical reduction in aqueous medium using a $Ni(tmc)Br_2$ (tmc=1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetra-decane) complex, known as an effective catalyst in dehalogenation reactions [1]. The complex was immobilized on a graphite felt electrode in a Nafion® film. Flow heterogeneous catalytic reduction of 1,3- dichloropropane was then carried out with the $[Ni(tmc)]Br_2$-modified Nafion® electrode in a flow electrochemical cell:



GC analyses underlined the total degradation of the substrate in only 3.5h with a substrate/ratio catalyst of 100. A dechlorination yield of 80% was obtained, as seen with Ionic chromatography analyses of chlorine ions. Comparison of homogeneous and heterogeneous reactions highlighted the interest of the $[Ni(tmc)]Br_2$-modified Nafion® electrode that led to a higher stability of the catalyst with a turnover number of 180 (instead of 4.5) and a higher current efficiency.

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Charge Transfer Reactions that Limit the Efficiency in PhotoElectrochemical Dye Sensitized Solar Cells.

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In my lecture I will present several examples of Dye Sensitized Solar Cells (also known as Grätzel solar cells) which efficiencies range from 5 to 11% using either organic[1] or organometallic[2] molecules as sensitizers. I will analyse the limiting reactions that prevent these devices to achieve their maximum theoretical efficiency and the differences that exists between the different dye structures and the device efficiency. A short introduction of advanced photo-induced transient absorption techniques (L-TAS) and photo-induced transient photovoltage (TPV) will be also given[3].

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ELECTROCHEM 2014

SPEAKER ABSTRACTS

4 V Hybrid Supercapacitors with Oxide-Based Positive Electrodes: Effective Usage of the Pseudocapacitance in Aqueous Media

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Although oxide electrodes have been highlighted as materials with high specific capacitance, this properties can only be acquired in aqueous electrolytes. This limits the operating voltage of the cell to less than 2 V maximum, and as a consequence restricting energy density. The 'best-match' combination would be to take advantage of the high specific capacitance of pseudo-capacitive oxides that can only be realized in aqueous electrolytes and concurrently push the voltage of the negative electrode beyond the hydrogen evolution potential. Here we report our efforts to use a water stable, multi-layered negative electrode (protected negative electrode), which allows the voltage to be extended to as high as 4.3 V in a mild aqueous electrolyte [1].

A typical protected anode consists of a lithium foil, a LISICON-type solid glass ceramic (LTAP) as the water-stable solid electrolyte, and a buffer layer consisting of PEO-LiTFSI between lithium and the solid electrolyte.

Figure 1 illustrates the cell configuration of the advanced hybrid electrochemical capacitor (AdHiCap™). Cells were constructed either as a beaker-type flooded cell with the positive electrode and protected negative electrode placed in an aqueous electrolyte or as laminated pouched cell (Fig. 1). Values reported for specific capacitance, energy and power density are normalized by the mass of the positive electrode unless otherwise noted. For a cell using RuO_2 nanosheet [1] as the positive electrode, specific energy of 544 Wh (kg-RuO_2)$^{-1}$ was achieved with a cell voltage of 3.9 V in a Li_2SO_4. By using acetic acid-lithium acetate buffered electrolyte, specific energy of 724 Wh (kg-RuO_2)$^{-1}$ was attained [2]. For a cell using MnO_2 as the positive electrode, the cell voltage can be expanded to 4.3 V [3]. A fully laminated pouched cell (Fig. 1) was constructed with a MnO_2 electrode prepared by electrodeposition onto porous carbon paper. The high capacitance (348 F g^{-1}@2mV s^{-1}) high cell voltage leads to specific energy of 753 Wh (kg- MnO_2)$^{-1}$, which is the highest reported a hybrid supercapacitor device.

Fig. 1 (left)Schematic representation of the aqueous hybrid EC using multi-layered Li electrode and (right) AdHiCap prototype cell.

The new advanced hybrid capacitor technologies can conceptually provide specific energy exceeding that of LICs and has the potential to compete with LiB technology. It also has the advantage of using a mild aqueous electrolyte, which is environmentally benign and safe.

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Silicon Nanowire Composite Negative Electrodes for Future Higher Energy Density Lithium-ion Batteries

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[4]Centre for Microscopy and Microanalysis, University of Queensland.

The chemistry of traditional electrode materials used in current commercial lithium-ion batteries is now well understood [1] and current commercial cells have almost reached practical limits of performance. As new mobile device technology demands ever more from re-chargeable batteries there is a growing demand to increase the energy storage capacity of batteries; this has led researchers to develop alternative electrode materials with greater performance for future higher energy density batteries [2].

Ex-situ bright field TEM image of silicon nanowire based composite electrode

Silicon based materials are an important set of future negative electrode materials as silicon theoretically provides the possibility of a 900% gain in charge stored per unit mass of active material compared to current graphite technology [3]. Silicon based negative electrodes are expected to play a major role in both future lithium-ion batteries. Nano-structuring of silicon materials has been recognised to allow for improved performance by alleviating structural stresses associated with the alloying process which involves a volume expansion of the silicon host of up to around 280% [4,5].

In this work silicon nanowires (supercritical fluid synthesis) were selected as the active material in composite electrodes as they allow for a reduction in stress during expansion and contraction via two nano-scale dimensions; preventing pulverisation, whilst also providing the possibility for maintaining long range electronic contact along the length axis [6]. The research presented includes work to understand the structural changes associated with the electrochemical insertion and removal of lithium from silicon nanowires tested within composite electrodes.

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The Electrochemistry of Dioxygen in Non-aqueous Electrolytes for Lithium-oxygen Cells

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Laurence Hardwick
Stephenson Institute of Renewable Energy, Department of Chemistry,
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The non-aqueous lithium-oxygen battery is one of a host of emerging opportunities available for enhanced energy storage [1]. Unlike a conventional battery where the reagents are contained within the cell, the lithium-oxygen cell uses dioxygen from the atmosphere to electrochemically form the discharge product lithium peroxide. Degrees of reversible oxidation and formation of lithium peroxide has been demonstrated in a number of non-aqueous electrolyte classes, mostly notably in dimethysulfoxide based electrolytes [2], thus making the Li-O_2 cell a potential energy storage device. A schematic representation of the rechargeable non-aqueous Li-O_2 cell is shown in Fig. 1. On discharge, lithium ions formed at the lithium metal anode are transported across the electrolyte and into the pores of the air-cathode. O_2 from the atmosphere enters the cathode, and dissolves into the electrolyte within the pores. It is then reduced at the porous carbon electrode surface by electrons from the external circuit and combines with Li^+ from the electrolyte, leading to the formation of solid Li_2O_2 as the final discharge product. Li_2O_2 can be then oxidised, releasing oxygen gas. The challenge for the Li-O_2 cell is the progress of development of the air-cathode that allows highly reversible formation of Li_2O_2 in a stable electrolyte within its pores [3].

This talk will present our groups recent results of the electrochemistry of dioxygen in non-aqueous electrolytes on planar carbon and gold electrodes, of which particular electrolytes could have practical application within a Li-O_2 cell. Discussion will touch upon how the electrochemistry can be related to electrode substrate and will be presented with *in situ* spectroscopic studies that identify intermediate and surface species during the oxygen reduction reaction.

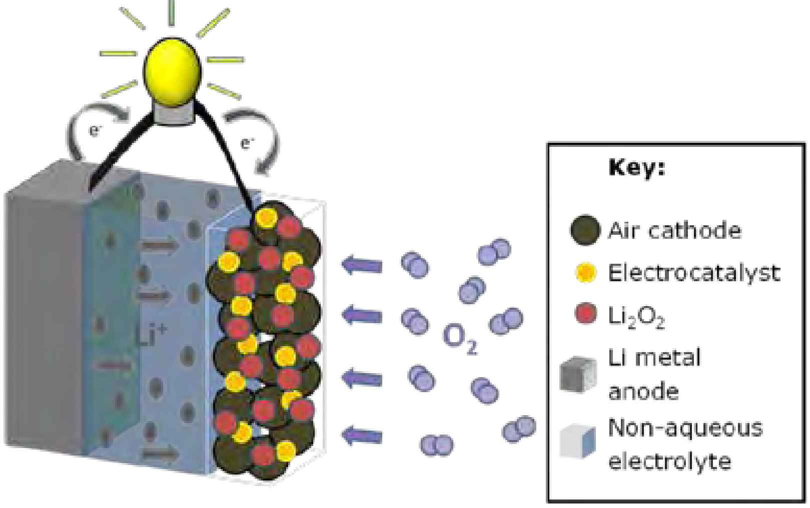

Fig. 1 The Li-O_2 cell

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In situ Investigation of Lithium Dendrite Growth

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Lithium metal is the ideal anode material for next generation batteries because of its high theoretical specific capacity of 3,860 mAh g^{-1}. Combined with a high-capacity cathode (e.g. in Li-O_2 or Li-S batteries), it is possible to overcome the power density limitations of Li-ion batteries and to allow a further driving range of EVs or longer charge intervals for consumer electronics.

The major problem for the application of metallic lithium in anodes is the growth of dendrites during cycling (Figure 1). The effects causing dendrite growth are not fully understood yet.[3] Due to the extremely low potential of Li, it forms a passivation layer, the commonly called Solid Electrolyte Interphase (SEI). The detailed composition is strongly dependent on the utilized electrolyte. The SEI built by conventional Li-ion electrolytes does not allow a high and safe cycle life. Applicable solvents for lithium metal anode based batteries are ionic liquids (e.g. $Pyr_{14}TFSI$ or $Pyr_{14}FSI$)[1,2] which form a stable SEI on lithium metal and exhibit unique solvent properties like non-flammability, great thermal and chemical stability and negligible vapor pressure.

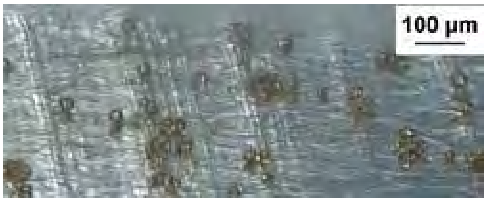

Figure 1: Dendrites grown on Li metal and observed *in situ* with optical microscopy

We developed a new cell setup to study dendrite growth *in situ* with optical microscopy. This setup features a heating device as well as the free choice of the Li deposition substrate. We will present our recent results from our *in situ* investigations. We will demonstrate the importance of the substrate as well as the current density on the dendrite growth. In addition, we will show that the activity of the observed dendritic structures can vary strongly in close proximity.

Acknowledgement: The research leading to these results has received funding from the European Union's Seventh Framework Programme under EC-GA No. 265971 'LABOHR' and EC-GA No. 608502 'SIRBATT'.

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Electrochemical Cycling between Carbon Dioxide and Carbon in Molten Salts for Energy and Materials

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Carbon dioxide can react readily with many metal oxides to form the respective carbonates. When this reaction occurs in an appropriate molten salt, carbonate ions form and can be electrochemically reduced to solid carbon as it was possibly first demonstrated in the 1960s. Interests in these molten salt supported reactions have grown again in recent years due to largely the needs to reduce carbon dioxide emission to avoid the detrimental climate change and, more importantly, to utilise this waste gas for material and energy applications. In this presentation, it will be shown that in comparison with the "hydrogen-water" cycle which has been widely promoted for energy applications in past decades, the "carbon-carbon dioxide" cycle, see Fig. 1, is far more efficient, practical and economical. More importantly, the electrochemical "carbon-carbon dioxide cycle" can proceed very fast and efficiently in molten salts without the need for any precious metal catalysts. Several examples will be provided to show the technical feasibility of the molten salts based electrochemical cycle of carbon-carbon dioxide with a brief energy and cost analysis.

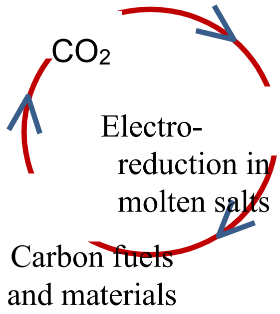

Fig 1. Electrochemical cycling between carbon dioxide and carbon for fuels and materials.

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Acknowledgement:

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Water Oxidation Catalysis at RuO_2/NiO Mixed Oxide Electrodes

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Electrochemical water splitting via alkaline water electrolysis is currently an extremely active research area of intense topical international interest. This is due to the need for the development of a clean, reliable and sustainable method for large scale production of high purity hydrogen gas for use as a fuel in a potential hydrogen economy. [1,2] However, one of the grand challenges fully utilising alkaline water electrolysis for hydrogen production is in the large anodic overpotential associated with the oxygen evolution reaction (OER). Over the past 30 years considerable research effort and resources have been focused on the development and improvement of novel anode materials, with the aim of achieving useful rates of the OER at the lowest possible overpotential and cost in order to improve the economic viability of this technology. Dimensionally stable anode (DSA®) electrodes, based on RuO_2 and IrO_2 currently exhibit the lowest overpotential for the OER at practical current densities [3] Despite their excellent OER performance, the relative high cost of these materials, in particular iridium, combined with their poor long term chemical stability in alkaline media renders their long term use as anode materials for water electrolysers impractical. Because of this problem we have attempted to overcome this problem by using oxides/hydroxides/ oxyhydroxides of first row transition metals which offer comparable OER performance but at significantly lower cost. [4,5] In this work [6] we have studied RuO_2/NiO mixed oxide electrodes prepared by thermal decomposition for use as potential water oxidation catalysts. Addition of just 10 mol% RuO_2 to a NiO electrode was found to decrease the oxygen evolution reaction (OER) onset potential by 20% with increasing additions having significantly diminishing returns. The OER current densities for the RuO_2/NiO electrode were found to increase when preconditioned by application of prolonged polarisation regimes with the Tafel slope also decreasing when conditioned. NiO prepared by thermal decomposition was found to behave in a similar manner to other nickel oxides [7,8] prepared using different methodologies.

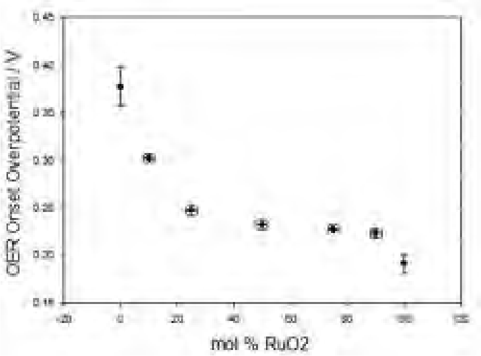

Fig. 1: Oxygen evolution reaction onset overpotential as a function of oxide composition.

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Innovative Embroidered Three-Dimensional Porous Electrodes used as Current Collectors for Li-ion Batteries

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There are different strategies to improve lithium-ion batteries. Many research groups focus their efforts on modifying the particle morphology and the structure by decreasing the particle size [1], adding a carbon coating [2] or doping the active material [3]. Other research groups have developed novel electrolytes to improve the thermal and electrochemical stability of the batteries [4].

Our aim is to improve the performance of the battery by means of innovative embroidered three-dimensional (3D) porous electrodes (Fig. 1) prepared by technical embroidery to be used as current collectors. Galvanostatic charge and discharge measurements in lithium iron phosphate batteries under the same current densities (~ 0.5 mA/cm^2) and geometric area (4 cm^2) for the embroidered 3D electrodes and plain configuration have been investigated. This new design of 3D current collectors allow better electronic conductivity, a higher amount of loading mass per unit area, and higher thicknesses compared to the plain electrode configuration. In addition, they offer a promising option for flexible electronics. The results provide a new outlook for advancement in Li-ion batteries.

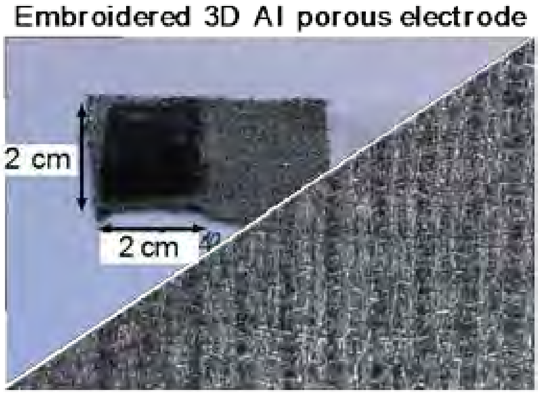

Fig. 1

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Investigation on the Stability of Polyaniline and its Carbon Nanotube Composite in the Solution of Fenton's Reagent

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Fenton's reagent, an aqueous mixture containing H_2O_2 and Fe^{2+}, is recognised as one of the most effective methods for oxidising organic pollutants. Fenton's reagent exhibits a high oxidising power via the following reaction to generate the OH• radicals [1,2] which are capable of indiscriminately mineralising most organics into CO_2, H_2O and inorganic salts.

$$H_2O_2 + Fe^{2+} + H^+ \rightarrow Fe^{3+} + OH\bullet + H_2O$$

In this work, attempts are made to investigate the chemical oxidation of polyaniline (PAn) or its carbon nanotube (CNT) composite as a thin coating on a platinum disc electrode [3] whose potentiometric response, *i.e.* the plots with open circle potential (OCP) vs. time, was recorded in Fenton's reagent. It was hoped that the OCP can be correlated with changes in the PAn or its CNT composite coating during their charging and discharging processes, for example, in supercapacitors. It was found that after immersion into the solution of Fenton's reagent, the PAn and PAn-CNT coatings were quickly oxidised and then gave rise to a fast OCP increase. This demonstrates that both materials are highly reactive with Fenton's reagent, showing a constant potential increase of around 0.54 V. However, PAn can also be partially over-oxidised by Fenton's reagent, causing its redox activity loss. Therefore, the stability of PAn (on its own or in its CNT composite) against Fenton oxidation has been investigated by means of repeating the OCP measurement in the same solution. The results had shown that in the first 10 cycles, the plateau potential of the OCP-time plot generally deceased with the number of times of the PAn coating used, but the rate to reach the plateau increased correspondingly. At the end, a steady state was reached where the respective OCP-time plots almost overlapped and had a common plateau potential at around 0.49 V vs. Ag/AgCl. Such an oxidation process can be explained by conversion of the PAn in the coating between its different oxidation states under the attack of Fenton's reagent. Moreover, the loss of PAn's electrochemical activity has been evidenced by a significant current decrease on the cyclic voltammograms recorded after each OCP measurement.

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Coaxial Weaveable Supercapacitors Using a Copper Core

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As one type of power source, Weaveable supercapacitors are in high demand in wearable electronics such as biomedical monitoring and wearable communications[1]. Simple structure and flexibility are keys in order to make supercapacitors weavable. Although coaxial thread/fibre have been reported with good flexibilities, as the stainless steel micro wire and synthetic carbon thread were used as a core respectively[2, 3], the output power densities have been limited by the inherent high core resistance. Here, we report a highly flexible, low resistance and high volume power density thread supercapacitor fabricated using a core copper wire. A simple dip coating method was used.

(a) (b)

Figure 1 schematic of a coaxial thread supercapacitor (a) and a woven supercapcitor in cotton fabric (b)

Coaxial thread supercapacitors were finished by coating Chinese ink, PVA gel electrolyte, Chinese ink and silver paint layers onto a 50 μm copper wire sequentially (Fig. 1a). The devices were tested using cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy; high specific length capacitance of 1 mF cm^{-1} and low resistance of 0.2 Ω cm^{-1} were obtained. A volume power density of 220 mW cm^{-3} at a volume energy density of 0.17 mWh cm^{-3} was calculated, which is much higher than those of stainless steel and synthetic core supercapacitors[2, 3]. A woven supercapacitor (Fig 1b) showed good stability compared to the free case. The dip coating set up is easier to scale up for mass production.

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Development and Improvement of NiFe Batteries for Off-Grid Energy Storage

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Renewable sources (such as solar, wind power, etc.) are changing the energy market and they may displace significant amounts of energy that are currently produced by conventional means; this is, for example, an staggering 57% of the total demand of electricity in Denmark by 2025 [1], around 15% of the total UK energy demand by 2015 and almost 16% of China by 2020 [2]; however, due to the fact that energy produced from renewables is not always available on demand; energy experts have foreseen secondary batteries, such as lead-acid and nickel-iron, as an efficient way to overcome this problem [3].

NiFe cells are rechargeable energy storage devices that fell out of favour with the advent of lead-acid technology. There is a resurgence of interest on NiFe cells coming from their environmentally friendliness, longevity, tolerance to electrical abuse (such as overcharge, over-discharge, being idle for extended periods and short-circuit conditions) and of course, their potential to be a cost-effective energy storage solution for off-grid applications. However, challenges such as relatively low energy and power densities are still preventing a large scale utilization of these cells. Moreover, the charging efficiency of the iron electrode is drastically reduced by the wasteful evolution of hydrogen.

In this article, we evaluate the performance of different iron electrode formulations and try to find out whether or not meaningful differences between such formulations exist. Galvanostatic experiments of charge and discharge were conducted at room temperature on a 64 channel Arbin SCTS. Cells were cycled under concentrated KOH (28.5%) from 0.6 to 1.4 V vs. MMO at a C/5 rate for at least 40 cycles. In addition, we use the mixing rules in a three dimensional concentration space to develop cost-effective iron electrode formulations.

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ELECTROCHEM 2014

SPEAKER ABSTRACTS

ELECTROCHEMICAL ASPECTS OF FUEL CELLS

Direct Borohydride Fuel Cells

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During the last two decades, there has been increased interest in the development of direct borohydride fuel cells (DBFCs). Over this time, the fundamental aspects necessary to obtain a high performance operational cell have been investigated. The hydrolysis of borohydride ions and the choice of anode and cathode materials are still important factors that determine the number of electrons transferred and the energy and power densities that currently are far lower than the predicted values [1]. This presentation considers the choices of anodes and cathodes for the DBFC and outlines the role played by different surfactants in the kinetics of borohydride oxidation on gold and gold coated carbon electrodes together with their influence in the diffusion coefficient determined by cyclic voltammetry and rotating disc electrode techniques. Constant current and potential electrolysis of borohydride solutions in the absence and in the presence of surfactants was carried out by measuring the hydrogen generation rate in order to establish the surfactant's influence [2]. The electrolysis of borohydride ions was also evaluated at a Pd-Ir (1:1) alloy electrode supported on microfibrous carbon and the hydrogen generation measured [3]. Additional insights into the role of this electrode on the oxidation of borohydride ions were aided by density functional theory (DFT) at a PdIr surface.

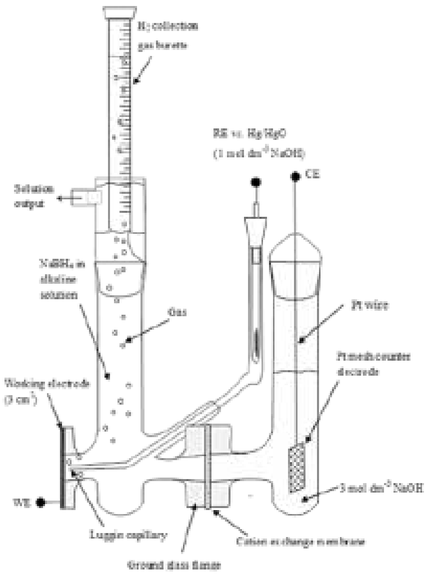

Figure 1. Glass cell used for volumetric rate of H_2 evolution.

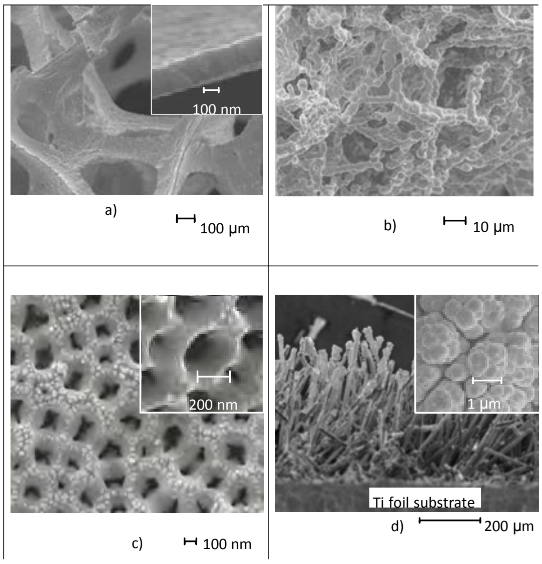

Figure 2.a) Au/RVC, b) Ag sponge, c) Au-coated TiO_2, d) Pd/Ir alloy coating on carbon fibres.

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Oxygen Reduction of Supported Platinum Nanoparticle Electrocatalysts: An *In situ* ATR-IR Spectroelectrochemical Study

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Reduction of oxygen gas to water is crucial in conversion of chemical to electrical energy (fuel cells and batteries), corrosion science and bio-catalysis. This seemingly simple reaction proceeds through a complex set of intermediates including superoxide, peroxide. The mechanism of the oxygen reduction reaction (ORR) is divided into either two electron (2 e^-) reduction or four electron (4 e^-) reduction by rotating ring disk electrode (RRDE) experiments based upon the end product obtained. However, traditional electrochemistry alone is not sufficient to give us a clear picture of the ORR mechanism and structural information is needed for the various intermediates involved at the electrode/electrolyte interface.

Second, development of efficient, inexpensive and environmentally friendly energy converting fuel cells is a major scientific concern. Platinum (Pt) is still one of the best available catalysts for the ORR at fuel cell cathodes but is unattractive because of its high cost, scarcity and the high loadings required to overcome its sluggish ORR kinetics [1]. Therefore the ORR remains a major obstacle for the development of fuel cells. Effort has been devoted to developing cheaper metal catalysts, transition metal oxides or nitrogen-doped graphene materials [2]. These exhibit activity close to Pt but suffer from poor stability in acidic and oxidizing media. Hence, most research is still focused on increasing the activity of Pt-based nanoparticles towards ORR. Despite various theoretical and electrochemical studies, *in situ* spectroscopic insight into nanoparticles as functioning ORR catalysts is still not well developed.

In this work, we couple infrared spectroscopy with electrochemical control in a new way to study ORR at the electrode/electrolyte interface. This work moves away from bulk metal surfaces [3] and addresses much more difficult Pt nanoparticles which are of greater relevance to real catalysts. Commercial Pt nanoparticles on carbon support are used for the study. In situ electrochemical Attenuated Total Reflection InfraRed (ATR-IR) experiments are carried out under oxygen and inert gas flow in acidic and alkaline media. These measurements are followed by isotope exchange measurements to confirm the band assignments of various surface adsorbed ORR intermediates. The work provides significant insight into understanding of ORR that will have broad applicability in nanoparticle catalysis.

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Infrared Spectroelectrochemistry of Supported Electrocatalysts – Observing Surface Species Beyond CO

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In situ spectroscopy, in particular infrared (IR) techniques, have played a crucial role in elucidating electrocatalytic reaction mechanisms at macroscopic metal surfaces.[1,2] A major gap in the techniques, however, is the ability to probe the type of supported nanoparticle surfaces used in the real world. On these systems, it is often only the most strongly absorbing or most prevalent adsorbed species that are observed, leaving other intermediates and their pathways out of reach.

We have developed an *in situ* IR spectroelectrochemical flow cell based around an attenuated total reflectance (ATR) geometry which can be used to study supported nanoparticle electrocatalysis under hydrodynamic conditions. The ATR-IR cell permits voltammetry similar to that on a rotating disc electrode to be performed, at the full range of scan rates commonly used in electrocatalysis, while simultaneously allowing the collection of IR spectra. The high sensitivity provided by the multi-bounce ATR geometry provides spectra of both adsorbed intermediates as well as desorbed solution products. These features enable us to probe the time-resolved responses to potential changes during turnover.

Here we demonstrate this approach by using electrocatalytic formic acid oxidation as a model system. We perform cyclic voltammetry on a commercially available carbon-supported Pt nanoparticle catalyst in perchloric acid electrolyte with and without formic acid present. By collecting spectra simultaneously with the cyclic voltammetry we can probe the intermediates giving rise to the distinctive voltammogram. We discuss the implications this has for understanding the mechanism as a whole and link these results to the oxidation of methanol and other small organic fuels.

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Application of Heteropolyacids in Bifunctional Air Electrodes

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Heteropolyacids (HPAs) are a subgroup of a wider class of chemicals called polyoxometalates. They exhibit high acidity, good thermal stability and stable redox behaviour [1]. Data is presented which shows that HPAs, complexed with Ni nano-particles, can be used to enhance both the oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR) in an alkaline environment. Two HPAs were initially chosen for investigation; molybdophosphoric acid ($H_3PMo_{12}O_{40}$) and phosphotungstic acid ($H_3PW_{12}O_{40}$). The catalyst was distributed within a supporting ink containing a Nafion® binder and was manually printed onto a Toray carbon paper gas diffusion substrate [2]. Cyclic voltammetry and constant current cycling between OER and ORR were used to characterise the electrodes. The use of HPAs in combination with nano-powder nickel showed enhanced performance when compared to nano-nickel alone. The overpotential associated with the OER, when HPA is mixed with nickel in the catalyst ink, is reduced when compared to the catalyst ink that includes only nickel. A slight reduction in overpotential for the ORR is also observed with the HPA containing electrodes. The voltage difference between OER and ORR for the Ni/HPA electrode is still relatively high for fuel cell and battery applications, however, it may be suitable for water electrolysers, since only oxygen evolution is required in these devices [3]. Further investigation on the catalyst ink composition, i.e. component concentration, HPA choice, has been made in order to optimise the performance further.

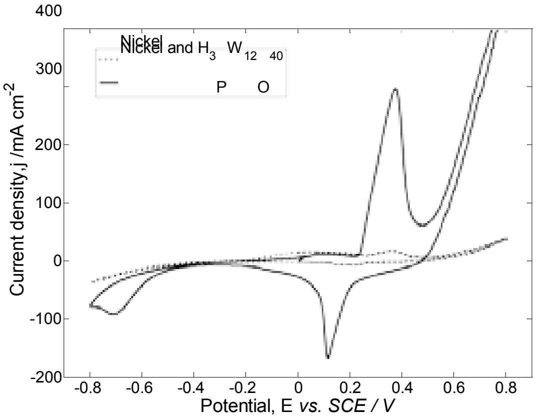

Figure 1: Cyclic voltammetry of gas diffusion electrodes with nickel and nickel with phosphtotungstic acid in 4.0 M KOH, fixed O_2 flow and 50 mV sec^{-1} scan rate

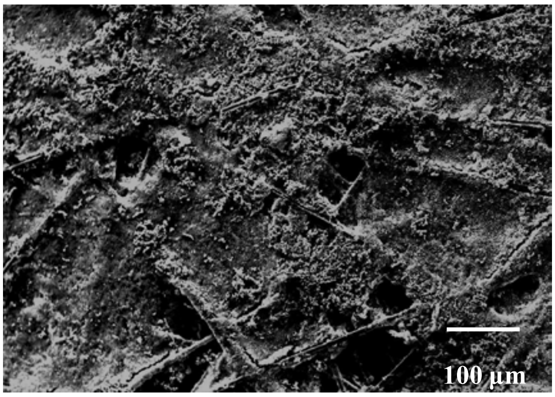

Figure 2: SEM picture of a gas diffusion electrode with nickel and phosphotungstic acid

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Using Reduced Graphene-Oxide as a Catalyst Support for Intermediate Temperature Polymer Electrolyte Fuel Cells

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It is widely accepted that the cost of platinum catalyst is the principle obstacle in the commercial application of Polymer Electrolyte Fuel Cells (PEFCs). In PEFCs, the overall performance is influenced by many properties of the catalyst layer, such as electrical and ionic conductivity, hydrophobicity and reactant diffusivity. Ideal support materials usually have four advantages, excellent electrical conductivity, large available surface area, mesoporous structure and good adhesion between catalyst particles and the support.

In this study, we focus on the electrode materials employed (Pt/C, Pt/RGO) and their fabrication, in order to reduce the platinum amount used in electrodes and improve electrochemical performance. The microwave-assisted polyol process (MWAPP) was used to fabricate catalysts in a quick way, involving only Pt precursor, support materials and polyol solution. MWAPP allows for simultaneous production of Pt nanocrystals deposited onto reduced graphene oxide (RGO) in the heating process.

The composition and structure of the synthesized catalysts were characterized via thermo-gravimetric analysis (TGA), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The electrochemical characterizations were tested by both ex-situ and in-situ electrochemical methods. Cyclic voltammetry indicated that the reproducible ECSA of the Pt/C catalyst was found to be ca. 80 m^2g^{-1} ($\pm$ 4 m^2 g^{-1}). The process applied to the fabrication of Pt/RGO catalyst, yielded an ECSA of ca. 32 m^2 g^{-1}. The ECSA of Pt/RGO is much smaller than the ideal calculation results. The most likely reason is the severe stacking of the RGO sheets which happens in the synthesis procedure. On the other hand, when Pt/RGO was tested for the ORR reaction, the water retention of the RGO may cause the excess water accumulating in the cathode as a severe flooding.

Focusing on these issues, an intense sonication on GO was added before MWAPP. Meanwhile, carbon black was added inside the Pt/RGO catalyst to prevent RGO from stacking and help the water management. The new catalyst (Pt/[80% RGO+20% C]) we made in-house is promising with an ECSA of ca. 69.4 m^2 g^{-1}. Throughout the in-situ testing, it showed a better performance than commercial catalyst TKK.

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Challenges in the Mass Manufacture of Alkaline Fuel Cells: Exploiting Existing and Novel Processes

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Hydrogen is a by-product of a number of industrial processes, including Chlor-alkali, municipal waste incineration and steam methane reforming. For the most part, hydrogen generated by these processes is treated as waste or used inefficiently. Significant opportunities exist for the conversion of waste hydrogen to electricity using fuel cells.

Alkaline fuel cells (AFCs) offer distinct cost benefits over other fuel cell technologies, owing to their high electrical efficiency and the ability to use non-precious metal catalysts. AFC Energy is the world’s leading developer of low-cost AFC systems for large-scale stationary power generation. The company will deploy its first commercial fuel cell platform in the coming year: a 250kW installation in Stade, Germany.

As AFC Energy enters a new phase in its development, there is a need to rapidly scale up fuel cell production capacity. The company has looked to exploit knowledge from other industries, employing high volume processes such as extrusion and robotic stacking and handling. Several innovative processes are also being developed to meet the unique needs of AFC technology. One such example has been the development of metallic electrode substrates using laser drilling and sintering techniques. As part of the European Union- funded Project LASER CELL[1], AFC Energy has worked in partnership with other organisations to develop novel electrode substrates with high porosity and electrical conductivity. These substrates have shown promising performance on both the small scale and AFC stack scale.

Acknowledgements
Project LASER-CELL is a three-year European collaborative R&D project, funded by the Fuel Cell and Hydrogen Joint Undertaking. AFC Energy would like to acknowledge the project partners: Air Products, Cencorp, VTT, Nanocyl and Universitat Duisburg-Essen.

Single Component Micro-Tubular Solid Oxide Fuel Cells: a New Electrochemical Aspect of Nano-Redox

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The high operating temperature and the three-layer construction of the conventional solid oxide fuel cells (SOFCs) usually cause the mismatch of thermal expansion as well as inter-diffusion and interaction between electrolytes and electrodes, bringing serious mechanical and chemical problems. To this end, considerable efforts have been devoted using novel component structures, e.g. adding an interlayer between the electrolyte and the electrode, which would increase the complexity and the fabricating cost at the same time. In this work, for the first time, we demonstrate a novel type of single component micro-tubular SOFC. With a reported nanocomposite mixture of samarium-doped ceria and nanoparticles of a LiNiCuZn-based oxide acting as ionic conductor and semiconductor phases [1-2], respectively, the single component micro-tube was manufactured by a single one-step extrusion. The final tubes with an inner diameter of 1.6 mm and a wall thickness of 0.4 mm (Fig 1a,b) were directly used as single-component SOFCs and tested with hydrogen and air. A power density of 264 mW cm^{-2} was achieved at 550 ºC.

The nanocomposite of the single homogenous layer consists of a mixture of semiconducting and ionic materials (Fig 1c) that provides the necessary electrochemical reaction sites and charge transport paths for a fuel cell. These can be accomplished through tailoring ionic and electronic conductivities and catalyst activities, which enable redox reactions to occur on nanoparticles and finally accomplish a fuel cell function. However, the stability test showed a fast degradation, and only 41% of the initial power remained after 15 hours. Although a high potential is expected for this technology in practical applications, a further understanding of the exact mechanism of the underlying electrochemical processes and the structure-property relationships for this single component device is necessary in our future work.

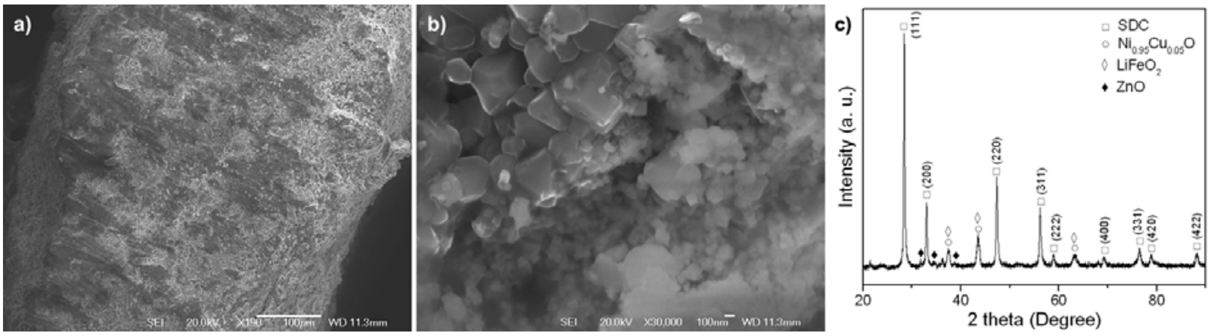

Fig. 1 a,b) SEM images of the cross section and XRD pattern of the single component micro-tubular SOFC

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Investigation into Redox Processes of Vanadium Substituted Heteropolyacids for Use in Energy Catalysis

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This presentation explores the redox process observed in vanadium substituted heteropolyacids. The presentation discusses the possible implication for catalytic processes within energy applications, specifically focusing on the use of the reduced polyanion of these acids.

The reduction of vanadium substituted heteropolyacids is discussed, focusing on vanadium substituted phosphomolybdic acid (phosphomolybdovanadic acid). The reduction processes are explored electrochemically when in an adsorbed layer form and when present in solution. Particular attention is drawn to the processes within aqueous environments and the effects that electrode surface has on the processes.

The redox processes observed are probed using cyclic voltammetry, allowing for the mechanism of reduction to be discussed. The formation of the adsorbed layer is investigated on different surfaces and under different conditions. Data is presented adding validity to previously discussed mechanisms. The effect of pH on the redox characteristics gives insight to the mechanism and experimental work is disseminated giving a view to the reaction pathways and their dependence on pH.

The work shown allows for a suggested mechanistic pathway to be suggested and further allows for the discussion of operating parameters in the use of vanadium substituted heteropolyacids. In particular application towards their use within energy catalysis and fuel cell operation is supported through experimental validation.

Electro-thermal Optimization of Air Cooled, Open Cathode, Proton Exchange Membrane Fuel Cells

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Proton Exchange Membrane Fuel Cells (PEMFCs) offer the possibility of zero-emission electricity generation. The technology has shown tremendous advances in terms of performance and durability and wide-scale commercialisation in a range of applications is imminent. In addition to current and voltage, temperature is the other key metric to be considered when selecting an optimal operation point, particularly in air-cooled, open cathode systems. As such, electro-thermal characterisation of fuel cells is required in order to understand the trade-off between these three parameters. In order to extend the *in-situ* understanding a novel current and temperature mapping sensor plate (S++, Simulation Services, Germany) was used to investigate the localised electro-thermal maps.

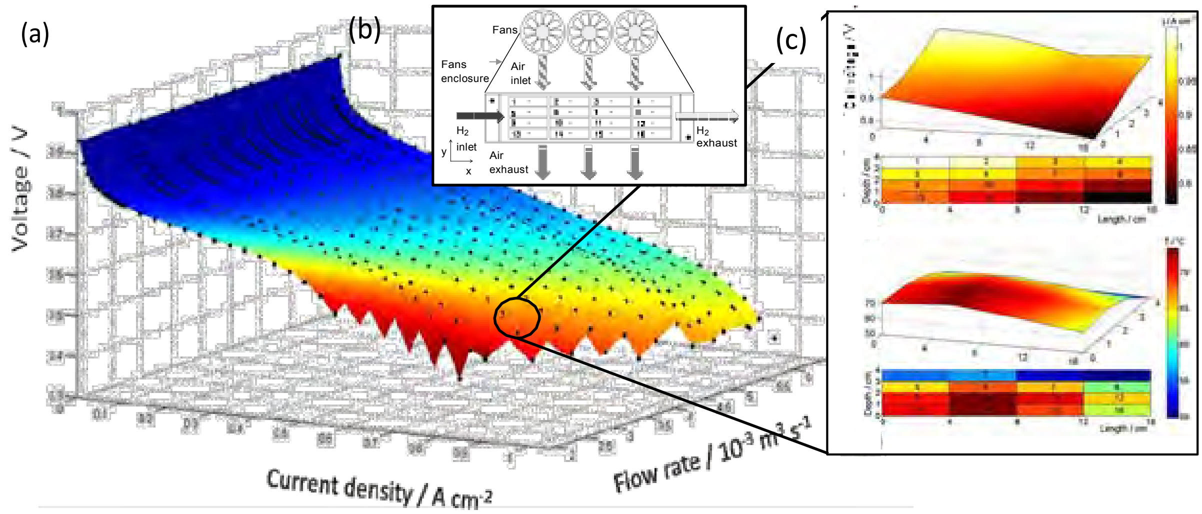

Figure 1. (a) Electro-thermal map as a function of the cooling flow rate. (b) Flow orientation on the sensor plate. (c) Localised electro-thermal map in the mass transport region

In this presentation, routes to generating an electro-thermal performance map for an air-cooled polymer electrolyte fuel cell stack are described, from a bulk device (stack) and localised current and temperature (cell) perspective (Figure 1). Also, the low frequency intercept with the real axis in the impedance measurement is used to locate the current of lowest resistance, which represents a trade-off between fuel cell efficiency and power density [1].

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Investigation of Electro-Catalytic Processes under HT-PEMFC Conditions by Differential Electrochemical Mass Spectrometry

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High temperature polymer electrolyte fuel cells have recently received a lot of interest as they are more suitable for use with reformed gases than NT-PEMFC and can thus be used for applications were pure hydrogen is not available and power demands are moderate. Beside the use of reformate also the direct use of alcohols like methanol or ethanol is investigated. Differential electrochemical mass spectrometry (DEMS) is a very suitable tool for the investigation of electrochemical processes like the alcohol oxidation. It can also be used to investigate corrosion processes of the electrode materials even under transient conditions [1]. So far the technique has, however, been limited to reactions taking place in liquid phase even if studies are performed at elevated temperatures [2].

A new set-up has been developed which allows for DEMS type measurements at a small gas diffusion electrode in the gas phase under HT-PEMFC conditions. With this cell the electro catalytic oxidation of ethanol in the vapour phase was studied at platinum and platinum rhodium catalyst. It could be shown that the platinum rhodium catalyst achieves a high CO_2 current efficiency (CCE) in the ethanol oxidation even at relatively high ethanol concentrations which in the liquid phase reduce the CCE.

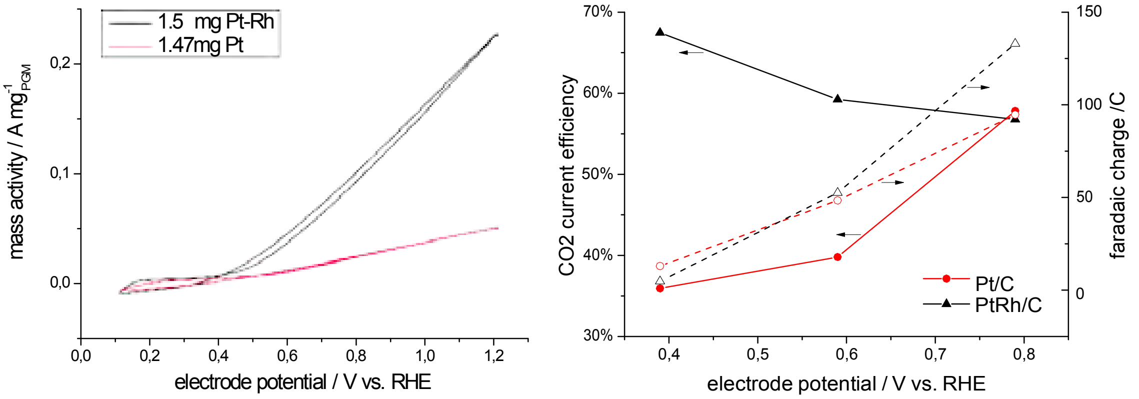

fig. 1: CV and integrated CCE values of the ethanol oxidation at electrodes with PtRh/C and Pt/C catalyst, respectively, measured at 160 °C in the vapour phase with a liquid feed concentration of 5 M ethanol.

In another study the oxidation of simulated reformate with a high content of H_2S was studied. A modification of the platinum catalyst was found that increases the H_2S tolerance significantly. Thereby also a significant conversion into SO_2 could be measured.

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Investigating Electrodes for Intermediate Temperature Polymer Electrolyte Fuel Cell (IT-PEFC): GDL Material Properties and their Influence

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Polymer Electrolyte Fuel Cells (PEFCs) are a key technology to secure the future of the automotive sector. PEFCs are advantageous due to their low operating temperature (60-80 ^{o}C), quick start up times and responsiveness to load change. However, the requirement for expensive platinum, difficulty of water management and heat dissipation means that further improvements are required [1]. One of the ways PEFCs can be improved is by increasing their operating temperature (>100 ^{o}C) [2], commonly known as the Intermediate Temperature PEFC (IT-PEFC) (120 ^{o}C). This allows for the generation of high temperature heat, which allows more facile heat rejection, while simplifying water management as water will exist solely in the vapour phase. In order to optimise these IT-PEFCs, further improvement in the cell components are necessary.

Comsol Multiphysics was used to create a model of a single cell unit in order to assess the importance of Gas Diffusion Layer (GDL) properties within the electrode. Specifically, their porosity, permeability, electrical conductivity and thermal conductivity were investigated. In addition to this, the modelling tool has been used to further improve the cell design by varying the cell materials and the cell configuration. Results have shown that the GDL porosity is a key factor of influence on the PEFC electrode. The balance between the mass transport capabilities and the electrical conductivity is very important to the success of the electrode. It was found that the cell performance was most sensitive to the GDL porosity when the cell was in the “standard operating” range of 0.7-0.5 V. It was found that a porosity between 40-60 % was best. It was also found that by replacing some of the conventional cell materials with novel component composite materials, the heat removal from the stack could be increased significantly as well as the electrical conductivity of the material. This could lead to a reduction in the requirement for the high gas flow rates specifically for cooling of the cell and therefore an increase in the air utilisation which lowers the parasitic losses from the system. In conclusion, the GDL is a very integral component of the PEFC, however, the effect of its properties on the MEA performance is not sufficiently understood. In the work presented, it is shown that the MEA performance is sensitive to changes in the GDL porosity and therefore electrical conductivity. It was also found that the materials used in the MEA and therefore the stack can influence the heat transfer properties of the stack and so the cost of novel materials to improve heat transfer must be carefully considered against the lifetime of the stack. Future work will involve the continuation of the study to gain a better understanding of the GDL permeability and the effect it has on the cell performance.

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ELECTROCHEM 2014

POSTER PRESENTATIONS

P1

Towards Biocompatible Conductive Gels Containing Gold Nanoparticles

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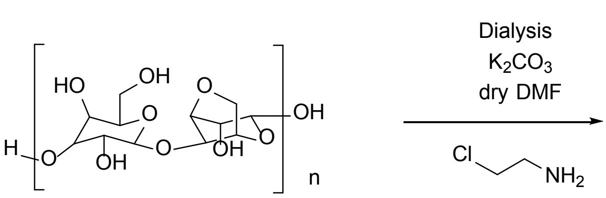
The synthesis of conductive and biocompatible gels containing gold nanoparticles is being investigated [1]. The gel to be used is functionalised agarose containing gold anchoring molecules such as NH_2 and SH [2].



The formed gels containing gold nanoparticles are stable for up to 6 months with no aggregation of nanoparticles being observed (Fig. 1). Their resistance is being studied to assess the feasibility of their use in biological applications.

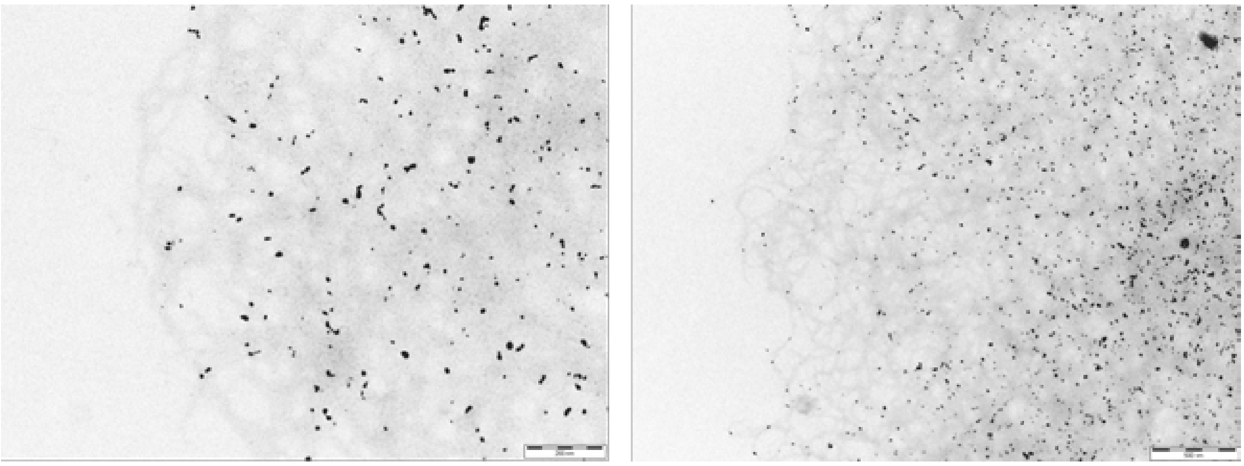


Figure 1: TEM of gels with nanoparticles, scale bar 200 nm and 500 nm

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P2

Emerging Concepts for Large Scale Graphene Synthesis towards Enhanced Electrochemical Applications

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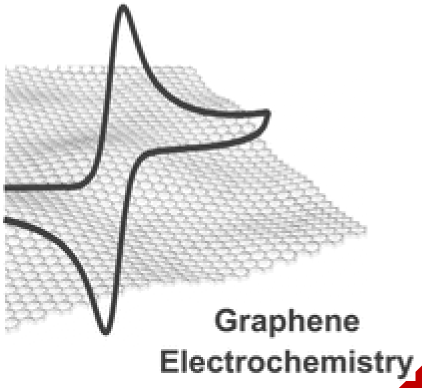
Graphene, a planar monolayer of carbon atoms that are densely packed into a 2D honeycomb lattice, has become one of the most intensively explored carbon allotropes in materials science due to its reported unique electronic and mechanical properties. One area that graphene has significantly impacted is in the field of electrochemistry where it is potentially the world's thinnest electrode material and has been applied in many areas, such as in sensing and energy storage/conversion.

We report the electrochemical properties of pristine monolayer, double layer and few-layer (termed quasi-) graphene grown via CVD and transferred using PMMA onto an insulating substrate (silicon dioxide wafers). The graphene response is compared to other available graphitic electrodes, namely that of basal- and edge- plane pyrolytic graphite electrodes constructed from Highly Ordered Pyrolytic Graphite (HOPG) and information on the respective heterogeneous electron transfer rate constant (k^o) is obtained. We observe, for the first time, a correlation in the structure of graphene, in terms of its 'number of layers' directly upon its macroscopic electrochemical performance, which in turn corresponds to the density of edge plane like-site/defects comprising its structure. Given that pristine monolayer graphene has a low degree of edge plane coverage compared to the multi-layered structures of quasi-graphene and HOPG, in comparison it possesses slow electrochemical properties and thus in scenarios when a large/favourable k^o is required, recourse to quasi-graphene and edge plane of HOPG is suggested.

It is evident that manipulation of the graphene structure, in terms of orientation (such as exposing more edge) or through the introduction of surface edge plane like-sites/defects, will result in beneficial alterations in the observed electrochemical properties, with the development of scalable production techniques also likely to further encourage graphene exploitation. Current work is focused on the fabrication of graphene through polymers, a concept first proven possible in 2011 (J. Phys. Chem. Lett., 2011, 2, 493). Through manipulating various parameters, including the polymers, heat treatment, substrate surfaces and the addition of additives, one has the possibility of tailoring graphene production and uncovering the technology for mass-production.



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P3

Fabrication and Photoelectrochemical studies of $Bi_2Ti_2O_7$ Pyrochlore Thin Films by Aerosol Assisted Chemical Vapour Deposition

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Phase pure thin film $Bi_2Ti_2O_7$ photoelectrodes were produced by aerosol assisted chemical vapour deposition at 600 °C for the first time. X-ray diffraction analysis showed that the as- deposited $Bi_2Ti_2O_7$ films were amorphous in nature, however post-deposition annealing at 600 °C for 12 h significantly increased the crystallinity to give phase pure $Bi_2Ti_2O_7$. Scanning electron microscopy revealed that the as-deposited film had a cauliflower-like structure with features ranging from 0.5-1.0 µm in size. It was found that the post-annealing step sintered the features together reducing the pores in the structure and giving rise to larger features 1.0-2.0 µm in size. Optical studies showed that the $Bi_2Ti_2O_7$ film had a direct band of 2.74 eV. For the first time, photoelectrochemical properties of $Bi_2Ti_2O_7$ were tested and it was found that the electrodes exhibited a photocurrent density of 1.8 µA cm^{-2} at 0.23 V vs. Ag|AgCl. Results showed that $Bi_2Ti_2O_7$ is an attractive material for photoelectrochemical water splitting.

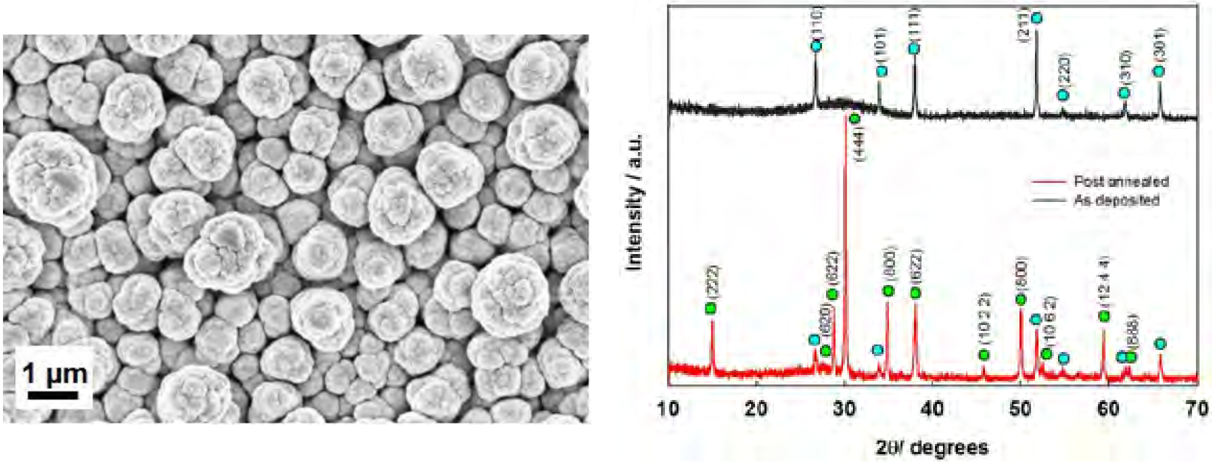

Figure 1. SEM image of as-deposited $Bi_2Ti_2O_7$ thin films by AACVD (left). XRD pattern for $Bi_2Ti_2O_7$ thin films before and after annealing step (right)[1].

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P4

$BiVO_4$ Thin Films for Photoelectrochemical Water Splitting

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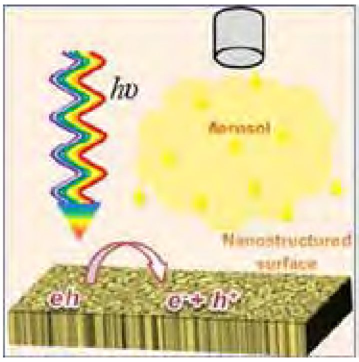
In recent years there has been considerable interest in developing materials capable of harvesting energy from sunlight to split water. These can be used as electrodes in photoelectrochemical (PEC) cells. PEC cells are typically made up of a photoanode (which drives the water oxidation reaction) and a photocathode (which drives the hydrogen evolution reaction). One of the most promising photoanode materials is monoclinic scheelite $BiVO_4$ which has a bandgap of 2.4 eV [1]. It possesses a conduction band edge almost sufficiently negative to evolve hydrogen, whilst the valence band edge is suitably placed to allow water oxidation [2]. In addition, $BiVO_4$ is one of the few photoanodic materials which is stable in mild, pH neutral conditions [3].

Previously we have reported on the fabrication of highly efficient thin film photoelectrode materials by the simple and readily scalable method of aerosol assisted chemical vapour deposition (AACVD) [4-6]. Use of AACVD has several advantages over conventional chemical vapour deposition (CVD) techniques. It allows the use of non-volatile and thermally unstable precursors, better control of deposit stoichiometry, a higher rate of deposition and a more flexible reaction environment than CVD (as it can be operated under atmospheric pressure in an open system). Herein we report the extension of this methodology to the deposition of highly performing $BiVO_4$ thin film photoelectrodes.



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P5

Development of Pt Bimetallic Electrocatalysts Using Electrochemical Methods

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Platinum (Pt) is very active fuel cell catalyst, but its cost is still high to be used commercially. Scientists in the field of electrocatalysis are working on development of various catalysts with lower amount of Pt, while maximising their catalytic activity. Development of bimetallic Pt surfaces is one of many approaches actively explored at the moment to achieve this. Many studies showed that nanoscale Pt such as Pt ultrathin layers, and clusters on different substrates X and PtX nano-alloys have different chemical and physical properties than those of Pt bulk [1]. These different bimetallic systems have low Pt content but they have high activity due to the combination of electronic and geometric configurations.

Pt-Pd is a promising system for fuel cells electrocatalysis. Pd has a unique ability to absorb hydrogen to its bulk [2] and its activity for hydrogen oxidation reaction is lower than of Pt, but it was shown that can obtain activity of pure Pt when a small amount (5 at %) of Pt is added to it [3].

Our research is focused on designing of Pt nanostructures on Pd thin films using electrochemical methods (SLRR, spontaneous deposition and galvanic displacement). Here we will show electrochemical examination of Pd thin films (up to 10 ML) hydrogen sorption behaviour and changes due to the Pt deposition. Epitaxial Pd films were electrodeposited on Au films [4] with a pronounced (111) crystallographic orientation. The hydrogen sorption characteristics have been analysed and compared in sulphuric and perchloric acid solutions of different pH.

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P6

Reversible Electrochemical Deposition of Metal Films for Light and Energy Modulation Applications

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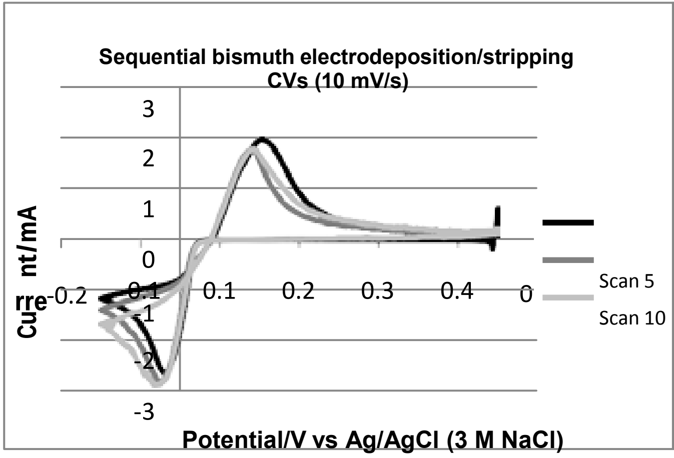
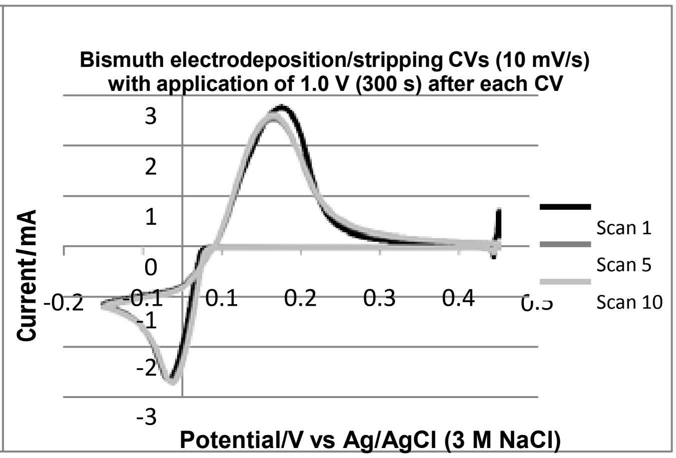
Reversible electrochemical deposition of metal films onto/from transparent conductive conductors offers a novel ‘electrochromic’ mechanism for light and energy modulation in ‘smart’ windows for architectural applications. Such a mechanism has seen little attention, with studies being restricted to bismuth [1], copper [2], lead [2] and silver [3]. In operation, reduction of dissolved metal cations results in metal deposition, the ‘electrochromism’ allowing light modulation from the opaque and/or optically reflective film. All ‘conventional’ electrochromic-based ‘smart’ windows [4] in operation involve modulation of light absorption. Systems based on metallic light reflection would be more efficient in preventing interior heating, with a reduction in energy demands from air-conditioning.

We here report cyclic voltammetric and chronoamperometric studies on the reversibility of the electrodeposition of bismuth, copper, iron, silver and zinc metal films onto glassy carbon, platinum and fluorine-doped tin oxide (FTO)/glass substrates. Reproducibility during multiple electrodeposition/stripping cycles/switches is assessed, together with the benefits of applying higher positive potential steps for the complete removal of metallic films. Of the metals studied, bismuth showed the best performance in terms of the formation of a uniform metallic film that can be reversibly electrodeposited/stripped over multiple switches.





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P7

Practical Implementation of Nano-Electrochemistry

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Many papers have been published on the use of nanoelectrodes fabricated by a wide range of techniques. However these electrodes have not been available to the wider electrochemical community (who do not necessarily have access to sophisticated fabrication facilities) until recently. As a result there are a number of preconceptions about the use and utility of nanoelectrodes. In our laboratory we have extensive experience of the practical use of nanoband array electrodes over a significant period of time and much of what we observe is at odds with the 'received wisdom' regarding their practical value. In this paper we describe the nanoband array structures we are using and discuss their performance in terms of repeatability, reproducibility, durability and longevity. We believe these observations have a material bearing on the future scope and practicality of such electrodes and provide examples which are germane to biosensing and environmental analysis.

Fig. 1 Photograph of a stainless steel NanoFlex™ electrode holder after being dropped from a 1st floor window. The electrode still gave high quality electrochemistry after drop.

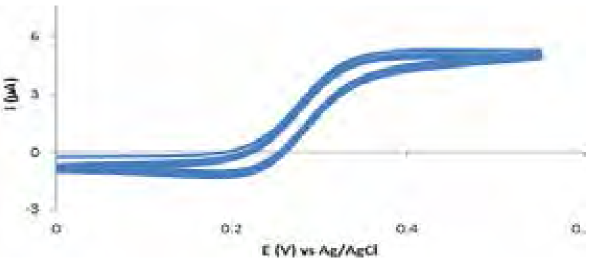

Fig. 2 Cyclic voltammograms (5 scans) recorded in 1 mmol dm^{-3} ferrocene carboxylic acid, 0.1 Mol dm^{-3} citrate buffer pH 7 at 500 mVs^{-1}. Pt electrode.

P8

Electrodeposition and Spectroelectrochemical Characterisation of a Polypyrrole Derivative Substituted with Dansyl Group

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In recent years, a great deal of interest has been focused on the synthesis of novel π-conjugated polymers because of their potential applications as materials for electrochromic devices, organic light emitting diodes (OLEDs), organic solar cells (OSCs) and energy storage. In this work an electrochromic and fluorescent pyrrole derivative bearing a 1-(dimethylamino)-naphthalene-5-sulfonyl group, also known as dansyl, substituent (Fig. 1) was prepared by a simple synthetic route and electropolymerised onto Indium Tin Oxide (ITO)/glass electrodes. The presence of the dansyl group in the monomer precursor prevents the electropolymerisation in usual systems, such as $(C_4H_9)_4NBF_4/CH_3CN$ (Fig. 2). For this reason, 20 % boron trifluoride diethyl etherate (BFEE) was added to this system, to achieve electropolymerisation (Fig. 3) [1]. The behaviour of poly(PyPDG) films upon doping and undoping was monitored by UV–vis-NIR spectroscopy in a 0.1 mol L^{-1} $LiClO_4/CH_3CN$ electrolyte. Reversible changes in the colour occur for poly(PyPDG) films from greenish-yellow in the reduced state to bluish-grey in the oxidised state. A solution of poly(PyPDG) in N-methylpyrrolidone is fluorescent with emission of green light. These features make these materials potential candidates for application as active layers in optoelectronic devices.

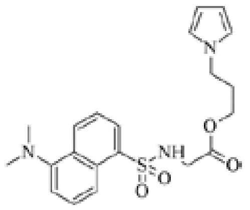

Fig. 1 Chemical structure of PyPDG.

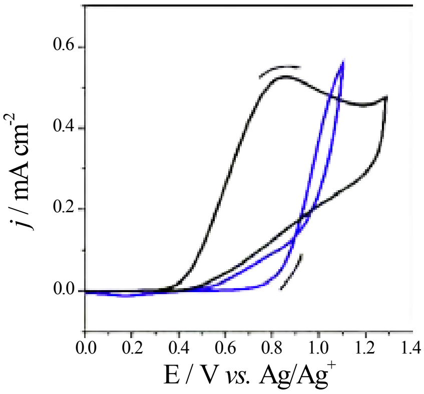

Fig. 2 Cyclic voltammograms of PyPDG in $(C_4H_9)_4NBF_4/CH_3CN$ (—) and in the same electrolyte with 20% BFEE (—), v = 0.02 V s^{-1}.

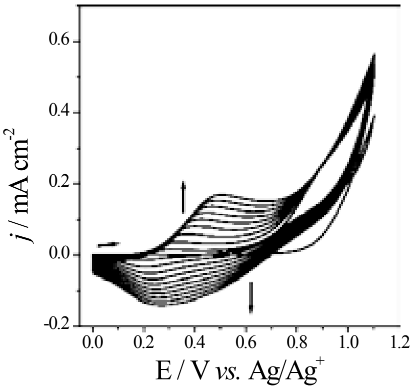

Fig. 3 Cyclic voltammograms recorded during the electropolymerisation of PyPDG in $(C_4H_9)_4NBF_4/CH_3CN$ with 20% BFEE, v = 0.02 V s^{-1}.

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P9

Electrochromic Nickel Hydroxide Thin Films

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Well-established for its superior electrochemical properties in rechargeable batteries [1] and supercapacitors [2], nickel hydroxide ($Ni(OH)_2$) films are also studied for their anodically- colouring electrochromic properties towards applications in energy saving 'smart' windows and displays [3]. Shown below are photographs of the 'bleached' (fig. 1a) and coloured (fig. 1b) electrochromic states, the cyclic voltammogram for the electrochromic process (fig. 2) and the in situ spectra (fig. 3) of the electrochromic states. The electrochromic performance of nickel hydroxide decreases on repeated electrochemical cycling in aqueous alkaline electrolyte. In addition, the anodic colouration peak lies close to the oxygen evolution reaction (OER), and undesirable gassing can occur. The cause of the thin-film degradation and electrochromic performance decrease is the phase transition of the 'as deposited' hydrated nickel oxide, from the unstable but high performance, turbostratic α-$Ni(OH)_2$ / γ- NiOOH redox couple to the stable but less performing β-$Ni(OH)_2$ / β-NiOOH redox couple. The relationship between the phases and their charged counterparts are demonstrated by the Bode reaction scheme [4]. Different metal additives can impact on the structure of the thin film and thus electrochemical response [5]. Presented here are un-doped and doped $Ni(OH)_2$ thin films electroprecipitated on fluorine-doped tin oxide (FTO)/glass substrates with the aim to improve electrochromic performance. Also presented are designs for an in-situ electrochemical cell to be used at the Diamond Light Source Synchrotron facility to study X- ray diffraction (XRD), and X-ray absorption spectroscopy (XAS) of thin films during deposition and colour-switching cycles.

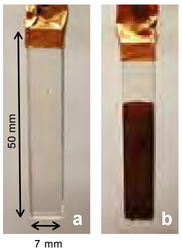

Figure 1

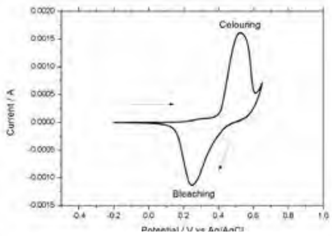

Figure 2

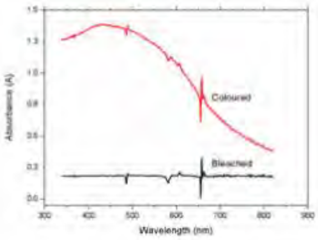

Figure 3

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P10

Preparation and Characterisation of Nanoporous-Nanocrystalline Tungsten Oxide/Viologen Electrochromic Films

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Electrochromic materials have long been investigated for potential commercial application in displays, ‘smart’ windows, anti-glare car mirrors, and eyewear [1]. A prominent example of an electrochromic material is thin-film tungsten oxide (WO_3) which on electrochemical reduction switches from colourless to blue [2]. We here describe the characterisation and properties of electrochromic thin-film WO_3 modified with a viologen monolayer. The nanostructured films were deposited by a unique Electrophoretic Deposition (EPD) process onto ITO/glass substrates. The viologen bis-(2-phosphonopropyl)-4-4’-bipyridinium dichloride (fig. 1) was used as chromophore to enhance the electrochromic properties of the WO_3. Electrochemical reduction of the colourless viologen di-cation forms the intensely coloured viologen radical cation. Cyclic voltammetry and chronoamperometry experiments were carried out using PC-$LiClO_4$ as electrolyte. During spectroelectrochemical experiments the WO_3 films undergo typical reversible colour change from colourless to blue. When modified with a viologen monolayer there is an increase in both the optical density change and the coloration efficiency (fig. 2). Using CIE principles, chromaticity coordinates were calculated from visible region absorbance-wavelength spectra [3]. The quantification of colour for both the WO_3 and viologen reduction processes showed changes in hue and luminance, with colour contributions from both materials being detected.

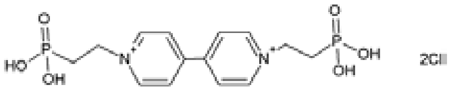

Fig. 1: Viologen structure.

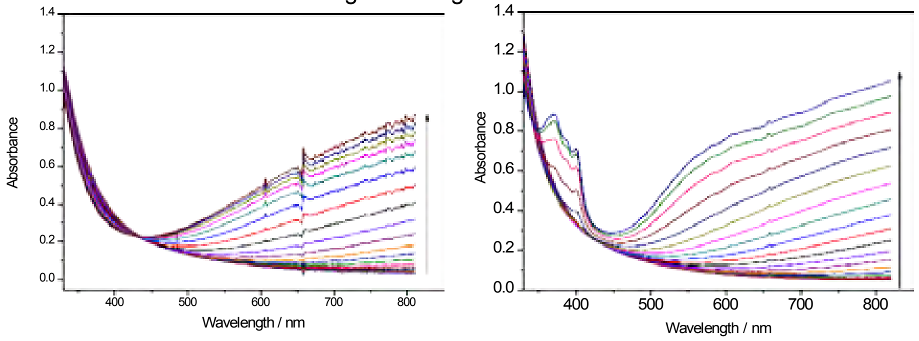

Fig. 2: Dynamic Visible Region Absorption Spectra for the Reduction of WO_3 and WO_3/viologen films.

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Electrodeposition and Characterisation of Novel Ni-NbO$_x$ Composite Coatings as a Diffusion Barrier for High Temperature Electronics Packaging

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The control of interfacial microstructural stability is of utmost importance to the reliability of liquid solder interconnects in high temperature electronic assemblies. This is primarily due to excessive intermetallic compounds (IMCs) that can form and continuously grow during high temperature operation, which practically renders conventional barrier metallisations inadequate. With the intention of reducing such excessive IMC growth, electrically conducting, NbO$_x$ containing Ni coatings were developed using electrodeposition.

The present work adopts a novel electrochemical route [1] to produce Ni-NbO$_x$ composite coatings of good uniformity, compactness and purity, from non-aqueous glycol-based electrolytes consisting of $NiCl_2$ and $NbCl_5$ as metal precursors. The effects of cathodic current density and $NaBH_4$ concentrations on the surface morphology, composition and thickness of the coatings were examined. A combined study of Scanning Transmission Electron Microscopy (STEM) and Electrochemical Quartz Crystal Microbalance (EQCM) was conducted to understand the fundamental aspects of this novel electrodeposition process. The reaction behaviour between a molten 52In-48Sn solder and Ni-NbO$_x$, with Nb contents up to 6 at.%, were studied at 200ºC. The results indicate that, Ni-NbO$_x$ with sufficient layer thickness and higher Nb content, offered longer service lifetime. Nb enrichment was generally observed close to the reaction front after high temperature storage (Figure 1), which suggests evident effectiveness of the enhanced diffusion barrier characteristics [2].

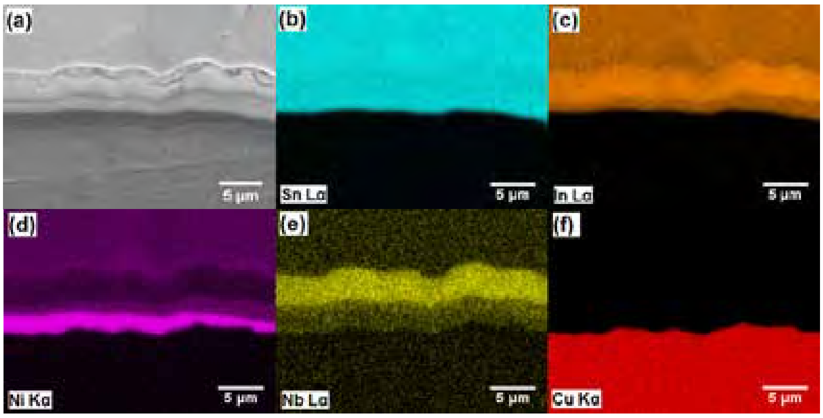

Figure 1. SEM image showing the interfacial microstructure of a 96.8Ni-3.2Nb after reaction with Sn-In solder at 200ºC and its corresponding X-ray maps

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P12

Commercial Ionic Liquids for Tin Deposition and Whisker Mitigation

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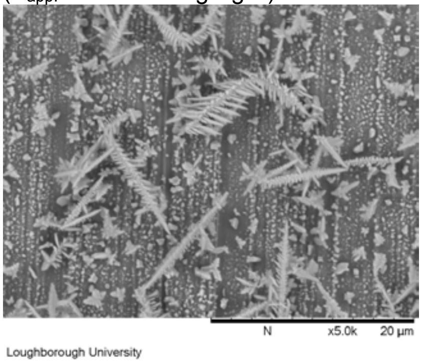
Tin coatings are used in the electronics industry for their inherent high solderability, high corrosion resistance and low toxicity. A draw back to the use of pure tin coatings is the growth of whiskers, which are conductive protruding growths which form post-electrodeposition in a variety of geometries. Techniques such as alternating thermal treatment and use of conformal coatings have produced no definitive whisker mitigation strategy [1]. Electrolytically-absorbed hydrogen on the cathode may have a role in initial whisker growth, so the use of non-aqueous electrolyte may assist mitigation. The use of choline chloride-derived ionic liquids has been investigated for zinc-tin [2] and zinc–manganese alloy coatings [3]. The development of new generations of ionic liquids and their industrial production, e.g., imidazolium compounds [4], has here prompted their investigation as alternatives to aqueous electrolytic media.

Cyclic voltammetry of 4 commercial ionic liquids* (no electrolyte added) at room temperature showed very large potential ‘windows’ compared with aqueous solutions for Pt and Cu electrodes (table), despite their lower conductivity and in one case high viscosity (CYPHOS 101). Sn^{2+} voltammograms in LQ01 and VS03 showed a one-step two-electron reduction for $SnCl_2$ and two-step one-electron reductions for $SnSO_4$. Potentiostatic and galvanostatic deposition from $SnCl_2$ dissolved in ionic liquids revealed crystalline deposits (figure).

Table: Electrochemical windows for ionic liquids. (E/VvsAg/AgCl)

Electrode	Electrolyte	E_{cath}	E_{anod}	Δ E
Pt	Water/H_2SO_4 7%	-0.5	1.2	1.7
Pt	LQ01	-2.1	2.2	4.3
Pt	VS03	-1.4	2.4	3.8
Pt	Cyphos-IL101	-3	2	>5
Pt	Cyphos-IL105	-3	2	>5
Cu	Water/H_2SO_4 7%	-1.0	-0.2	-0.8
Cu	LQ01	-2.13	-0.43	1.7
Cu	VS03	-1.81	-0.41	1.4
Cu	Cyphos-IL101	-3	0	>3
Cu	Cyphos-IL105	-2.30	-0.30	2.0

Figure: SEM of tin deposition on Cu in VS03 ($E_{app.}$= -1.5V vs. Ag/AgCl)



*Ionic liquids: LQ01 (1-Ethyl-3-methylimidazolium ethyl sulfate), VS03 (1-Ethyl-3-methylimidazolium dicyanamide), CYPHOS 105 [Tetradecyl(trihexyl)phosphonium dicinamide] and CYPHOS 101 [Trihexyl(tetradecyl)phosphonium chloride]. Samples kindly furnished by Basf/Germany and Cytec/Canada.

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Adsorption of Carbon Nanotubes at the Electrified Liquid-liquid Interface

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There is much interest in the electrical and optical properties of carbon nanotubes (CNTs). Processing and formation of stable assemblies of CNTs is a topic of importance. CNTs can be readily dispersed in polar organic solvents: addition of an aqueous phase to the system, leads to the spontaneous adsorption of the CNTs at the resultant liquid-liquid interface [1]. The liquid-liquid interface can be polarised and charge (ion, electron) transfer across the interface followed using electrochemical means. Polarised interfaces can be "modified" with adsorbed solids [2], hence the object of this work is to use electrochemical methods to probe the adsorption of nanotubes at the liquid-liquid interface.

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The Effect of Low Frequency Ultrasound on the Long Term Stability of an Electroless Nickel Plating Solution

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Introduction

Previous studies have shown that when low frequency ultrasound (US) is applied to an Electroless Ni process benefits such as increased plating rate (1), grain structure modification and improved mechanical properties (2) can be achieved. However for such benefits to be realised commercially it is necessary to understand the long term effects of applying low frequency US to an catalysed electroless Ni plating process. The study was carried out over a 6 month time period and was compared with plating using conventional agitation (or “silent” conditions). In brief, copper clad epoxy laminated coupons, were cleaned and dried at 120°C and then weighed. Prior to plating, the coupons were cleaned again in a mild detergent solution, rinsed, placed in the activator (catalyst) solution for 4 minutes, and rinsed. The coupons were then placed in the Ni plating solution for 30 minutes at 75 ºC. The coupons in the US bath had a 3 minute delay, before the US was turned on. Thickness and deposition rate could then be determined gravimetrically, alongside gloss, hardness, XRF and surface characteristics. Before and after each plating process, the solutions were analysed for Ni, Hypophosphite and orthophosphite concentration and replenished when concentrations went below optimal levels. Initial results indicate that the stability of an Electroless Ni bath over the long term can be maintained when US is used during the plating process. Thickness measurements determined gravimetrically appears to show no detrimental effect on Ni thickness and may show some improvement in gloss when compared with plating under silent conditions.

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P15

TD-DFT Spectrometry of Phenylamine-Functionalized Doped with Particles of Ni, Pt, and Co for Photocatalytic Hydrogen Production

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Abstract:

This study aims to show that the phenylamine-functionalized graphene doped with particles of Ni, Pt, or Co, can be used as catalyst in photocatalytic hydrogen production. To reach this results, was calculate the DOS using Density Functional Theory (DFT). The Ultraviolet visible and Raman absorption spectra was calculated by the spectroscopy method of Time-Dependent Density Functional Theory (TD-DFT), with the application of the Effective Core Potential method using pseudopotentials and the basis Lanl2dz for transitions metals, and the general basis 6-31g(d) for other elements. Through the comparative of the Ultraviolet visible spectra of different impurities we will demonstrate the variation of absorption. Raman spectra gave several information about thermodynamics behavior of this molecules. Also, it was observed the transference of the electrons from phenylamine to the graphene sheets an thermodynamic properties under influence of temperature and electric field. These results show that the phenylamine-functionalized graphene doped with particles of Ni, Pt, or Co, have strong potential to be used in the photocatalytic hydrogen production.

Keywords:

Phenylamine-functionalized. Graphene. Photocatalytic hydrogen production, UV-vis. Raman spectra. TD-DFT. DFT, Thermodynamic properties.

P16

Oxygen Evolution During Water Splitting at Hydrous Iron Oxide Electrodes in Alkaline Solution and the Effects of Surfactants.

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Finding alternative ways to access clean energy has become a major issue recently, and alkaline water splitting is one of the emerging electrochemical solutions. [1, 2] A major barrier to the widespread use of this technology is in the large anodic overpotential associated with the oxygen evolution reaction (OER). Currently the most effective OER catalysts are based on platinum group metals, but due to the high cost of production their use is limited. Therefore, we propose the use of less noble, lower cost metal oxides based on transition meals such as Fe or Ni. These oxides show relatively good catalytic behaviour for the OER but at a significantly lower cost and hence can make this process more economically viable In the present study we examine and evaluate the electrocatalytic behaviour of iron oxide Fe_2O_3 anode materials for OER in aqueous base.

Fe_2O_3 electrodes were prepared via the thermal decomposition of a simple precursor salt on an inert Ti substrate [3]. The material is very inexpensive and exhibits reasonable electro-catalytic activity for electrolytic water oxidation, but remain unstable and require the presence of surfactants to be stable for prolonged periods of time. The electrocatalytic behaviour of Fe_2O_3 films in the absence and presence of surfactant was examined via cyclic voltammetry and Tafel plot analysis (fig.1) and for the morphology via SEM. We have also examined the turnover frequency (TOF) as a function of the surfactant..

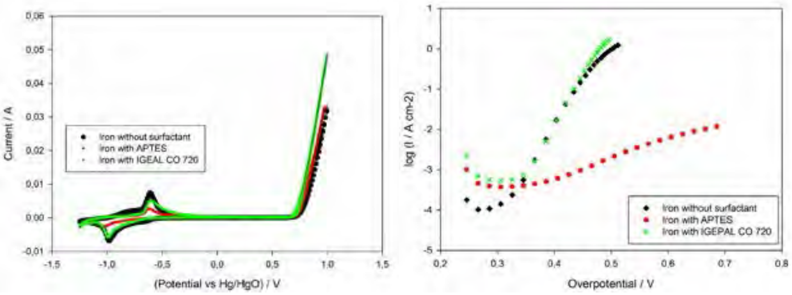

Fig.1. (a) Cyclic voltammogram in 1M NaOH at 50mV/s for iron oxides, from $Fe(NO_3)_3$ 98%, with and without the presence of surfactant (b) Tafel plots at 1mV/s in 1M NaOH for iron oxides, from $Fe(NO_3)_3$ 99.99%, with and without the presence of surfactant

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P17

Studies of Decorated Macroporous Fluorinated Tin Oxide (mac- FTO) Photoelectrodes for Water Splitting

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Photoelectrochemical water splitting is an attractive method to produce storable energy (solar fuels). Photoactive materials and co-catalysts are typically supported by planar transparent conducting oxides, such as FTO (fluorine doped tin oxide). In order to increase efficiency, porous electrodes are often required, but this can lead to complex methods of fabricating structured photoactive materials.

We have structured FTO via a simple and cheap method [1] to form macroporous FTO (macFTO) with regular monodisperse holes (fig 1). This inverse opal structure results in increased surface area and may gain additional benefits from the photonic effect [2, 3]. Furthermore, this structure can support conventional morphologies of photoactive materials (i.e. nanoparticles and films), negating the need for complex fabrication methods.

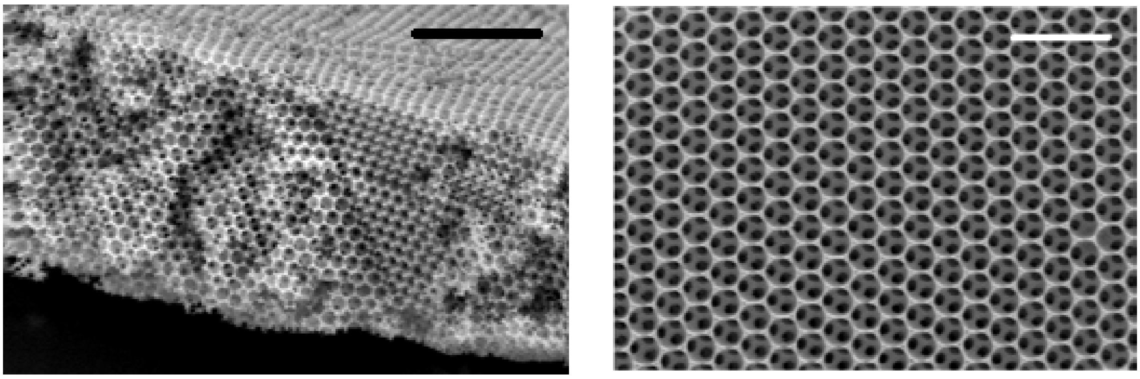

Fig 1. SEM images of macFTO, side (scale bar = 2 µm) and top views (scale bar = 1 µm)

In this work, macFTO has been shown to support high photocurrents from photoactive materials of up to 10 mA cm^{-2} compared to <1 mA cm^{-2} for planar electrodes of the same material. These high currents can be converted into fuels by addition of a co-catalyst for either the oxygen evolution reaction (OER) or the hydrogen evolution reaction (HER).

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Photoelectrochemistry of Arrays of 1D $In_xGa_{1-x}N$

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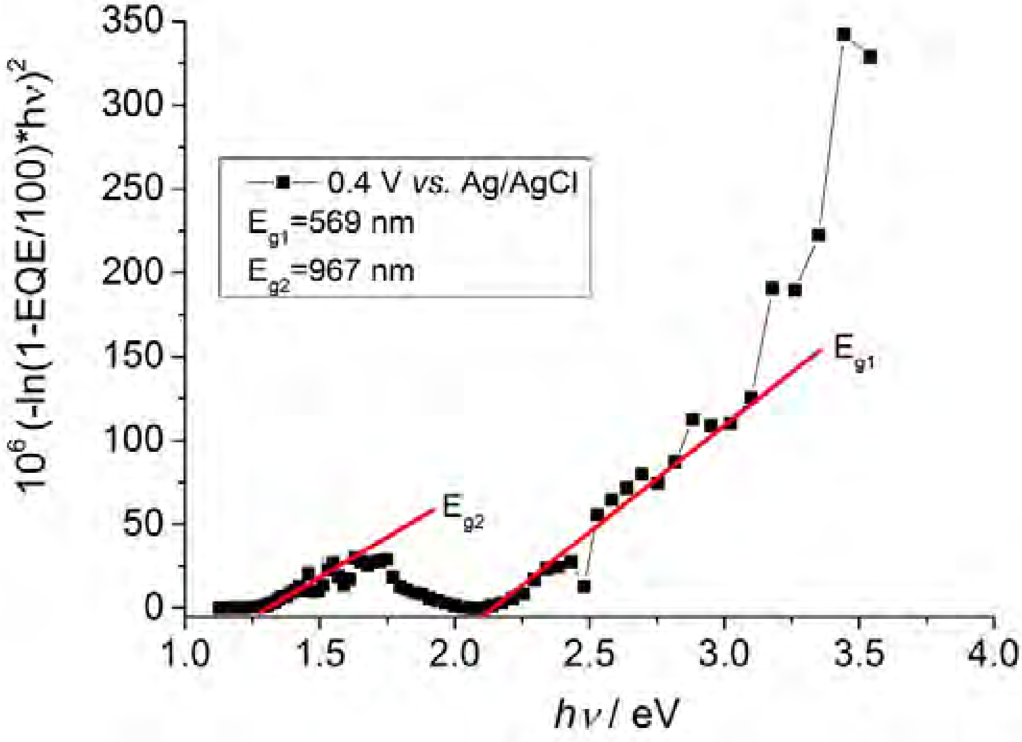
$In_xGa_{1-x}N$ materials potentially have tuneable bandgaps by variation of their composition. Pure InN has E_g of 0.7 eV, GaN E_g=3.4 eV. Between the two extremes it should be possible to provide any bandgap required. For example a 1.1 eV absorber for a single junction solar cell or ~1.3 eV for water splitting applications. Unfortunately it is not thermodynamically favourable to get pure mixtures; spinodal decomposition leads to multiple phases of differing In and Ga compositions. One method of growth is molecular beam epitaxy (MBE), it was hoped that it could avoid decomposition by using lower temperatures than other common growth techniques. From TEM data it has been shown to decompose whilst forming submicron rods such that a Ga rich sheel is formed on top of an In rich core. There are also indications of further Ga rich radial layers within the In rich core. This material is likely to have more than one band gap leading to a rather complex band structure. This work is a photoelectrochemical study of the material; taking action spectra of different compositions at various bias potentials and with different electrolytes can allow for the determination of photoelectrochemcially active optical band gaps and suggest the feasibility for use in solar devices.



P19

The Effect of ZnO Seed Layer Thickness on the Performance of Flexible ZnO Dye-Sensitised Solar Cells

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The synthesis of numerous ZnO nanostructures has recently attracted significant interest due to their promising energy-related applications. In particular, ZnO nanorods have received extensive attention in the electrochemical devices due to the ease of fabrication at ambient conditions. Unlike glass based substrates, the deposition of ZnO nanorods on plastic substrates is quite challenging due to the poor thermal stability of these organic based polymer substrates. Fabrication of ZnO nanorods on various substrates and using such electrodes to construct different energy conversion devices is one of the key research interests in material processing. [1]

ZnO seed layers, at different thickness, were coated on ITO-PEN substrates using sputtering technique, followed by the growth of ZnO nanorods using chemical bath deposition. [1],[2] These were characterized by X-ray diffraction and scanning electron microscope for evaluating the structural and morphological proves of successful growth of ZnO nanorods at various seed layer thickness. The effect of seed layer thickness on the DSC performance was evaluated using ZnO as photoanodes. (fig.1).

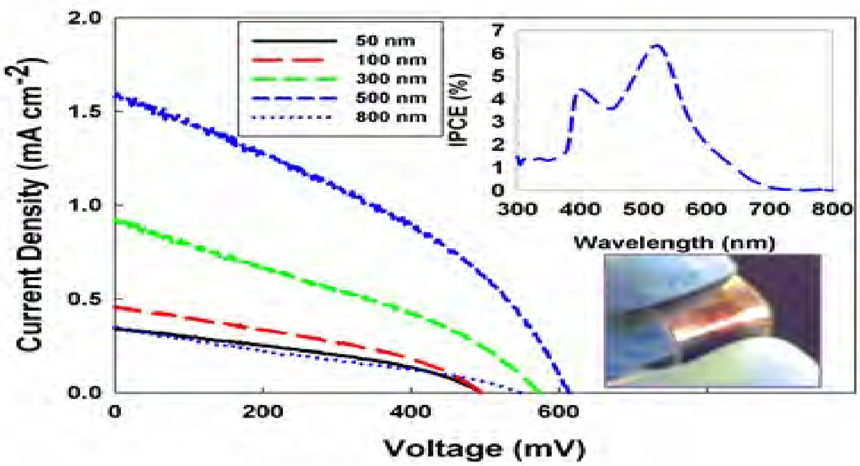

Figure 1: J-V characteristics of flexible ZnO DSCs (under 1 sun illumination) at different seed layer thicknesses. Top-right inset shows the IPCE spectrum of the best performing electrode (500 nm seed layer); bottom-right inset shows an image of the constructed flexible ZnO DSC.

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In situ Characterisation of PEM Water Electrolysers Using a Novel Reference Electrode

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Polymer electrolyte membrane water electrolysers (PEMWE) are a promising technology for hydrogen production, with the advantages of higher power density and wider partial load range compared to incumbent alkaline electrolysis technologies. This means they are well suited to coupling with intermittent renewable electricity sources such as wind or solar. A major barrier to widespread commercialisation of PEMWEs is the relatively high cost of the catalysts required for water oxidation at the anode and hydrogen evolution at the cathode, typical materials being based on iridium/ruthenium oxide and platinum respectively. Furthermore, degradation mechanisms of these catalysts are poorly understood, hindering informed catalyst design for extended lifetimes and more economical loadings. In this study, an innovative reference electrode is demonstrated for *in situ* electrochemical characterisation of a PEMWE. This approach enables separation of the relative contributions of anode and cathode to the overall reaction. During power cycling of the cell – thought to be a cause of catalyst degradation – it was observed that, during shut-down periods, the cathode contributes more to changes in open circuit voltage than the anode. This implies that degradation of the platinum cathode plays a more significant role than conventionally assumed by the electrolyser community, which has tended to focus more on the iridium oxide anode as it dominates the performance of the cell. Changes in the electrochemically active surface area (ECSA) of the platinum cathode as a result of potential cycling were determined in situ via hydrogen underpotential (H_{upd}) cyclic voltammetry. Scanning electron microscopy and X-ray tomography were used to correlate changes in catalyst morphology with performance degradation of both carbon-supported and unsupported platinum catalysts.

P21

Towards a Hydrogen Economy: A Study into the Oxygen Evolution Reaction (OER) using Manganese and Ruthenium Oxide Electrocatalysts

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Alkaline water electrolysis has been proposed as an environmentally inoffensive route to the production of the large volumes of hydrogen gas required by a possible hydrogen economy [1-5]. In practice, the efficiency of water electrolysis is limited by the large anodic over- potential of the oxygen evolution reaction (OER) [5]. Over the past thirty years, considerable research effort has been devoted to the design, synthesis and characterization of OER anode materials, with the aim of achieving useful rates of active oxygen evolution at the lowest possible over-potential, in order to optimize the overall electrolysis process. Currently, the optimal OER anode materials are Ruthenium and Iridium oxides, since these oxides exhibit the lowest overpotentials for the OER at practical current densities [6]. However, the high cost of these materials compared to other metals and their poor long term stability in alkaline solution renders their widespread commercial utilisation uneconomical [7]. For these reasons, the oxides of the first row transition metals (e.g. manganese, iron, cobalt and nickel) offer a compromise solution. Even though they are not as electrocatalytically active, their relatively low cost and long term corrosion resistance in alkaline solution makes them attractive OER anode materials [7-11].

In the present work, we focus on the redox properties and electrocatalytic behaviour with respect to anodic oxygen evolution of manganese and ruthenium oxide electrodes prepared at different molar ratios in aqueous alkaline solution. These films can be prepared simply via thermal decomposition of a metal salt [12]. The structure and morphology of the thermally decomposed oxide materials are examined using thin film XRD, high resolution SEM and FTIR.

The redox behaviour of the resulting oxide films is investigated as a function of molar ratio and annealing temperature using cyclic voltammetry. The kinetics of the OER at these films have been studied using a range of electrochemical techniques including steady-state polarization. In particular, Tafel slopes and reaction orders with respect to hydroxide ion activity are determined. Interestingly, the electrochemical performance for the films is strongly dependent on the molar ratio used. The electrocatalysts will be compared and contrasted under a number of Key Performance Indicators (KPI's) including Turnover Frequency (TOF) number, stability, cost and initial oxygen evolution overpotential.

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P22

Nickel Based Alloy Nanoparticles as Reduction Electrocatalysts for Fuel Production

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Fuel production via reduction of protons and/or carbon dioxide is an important process for clean-energy technologies. Developing catalysts that utilise relatively cheap, abundant and readily available materials is of great interest. Ni/NiO core/shell nanoparticles have been shown to be effective proton reduction catalysts on photocatalytic semiconductors, however there are longevity issues with this material [1].

Alloying nickel with other metals, could improve both the corrosion resistance and activity. Many electrodeposited nickel alloys, including NiCo, NiCu, and NiMoZn, have been investigated for their relevant electrocatalytic activity. However, due to corrosion and leaching, the exact composition and structure of the active catalyst is often unknown [2]. Nanoparticles offer an alternative with greater control of composition and structure as well as a large surface area.

There are many methods for synthesising alloy nanoparticles; using preformed, ligand stabilised nanoparticles allows for good control of size and distribution [3]. Alloy nanoparticles of nickel with other inexpensive and abundant metals are being synthesised and their compositions analysed using powder x-ray diffraction, x-ray fluorescence, transmission electron microscopy and energy dispersive x-ray spectroscopy.

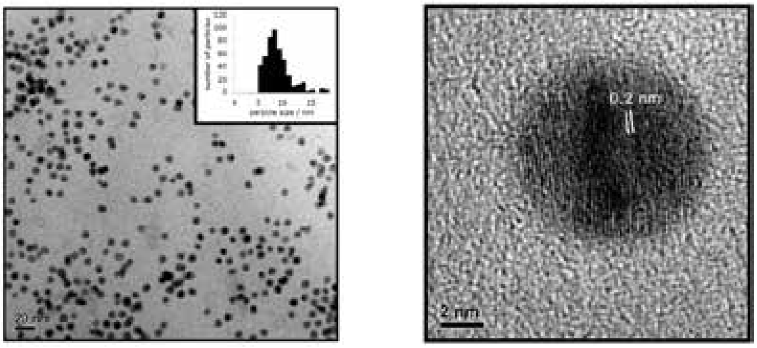

Figure 1. TEM images of $Ni_{0.5}Cu_{0.5}$ alloy nanoparticles at magnifications of 50,000 (left) and 800,000 (right) and histogram of size distribution (inset).

Electrocatalytic activity of the nickel alloy nanoparticles will be described.

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P23

The Effect of Electrodeposited $Mg(OH)_2$ Layer on Flexible and Glass based Solar Cells

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Exploration of lightweight and flexible renewable energy conversion devices is highly important in the modern world because of their unique advantages for various advanced mobile applications and power devices. Applying flexible-device technologies to dye-sensitized solar cells (DSCs) have attracted great interest in academic research owing to the potential of fabricating flexible solar cells at low-cost by roll-to-roll mass production. However, compared to glass based DSCs, the flexible solar cells are far away behind in the device performance due to the poor inter-particle and particle-substrate connection of plastic based electrodes fabricated at low temperatures. Therefore, finding low temperature routes to improve the performance of flexible solar cells is one of the key research interests in this field.[1]

Nanocrystalline TiO_2 films were prepared on a conductive indium-tin oxide coated polyethylene naphthalate plastic substrate to fabricate flexible dye-sensitised photoanode. The surface of the photoanode was coated with a thin overlayer of $Mg(OH)_2$ by Electro-deposition (ED).[2] The effect of the ED time on the performance of flexible DSC was evaluated on the basis of their photoelectrochemical properties. Among the ED times, 2 min showed the best performance in open-circuit voltage (Voc) on a treated flexible DSC, with resulting 847 mV and a photocurrent density of 7.13 mA/cm^2, providing an overall light-to-electricity conversion efficiency of 4.01%. This photovoltage is among the highest attained for a flexible DSC to date. The Impedance analysis for DSCs made using TiO_2 electrodes with and without $Mg(OH)_2$ coating and compression for the full range of operating conditions provides a detailed explanation about the effect of this electrodeposited $Mg(OH)_2$ conformal layer.[3] Impedance analysis confirmed that $Mg(OH)_2$ coating decrease the recombination along the whole voltage range both under light and dark which agreed well with the OCVD measurements. Reduction of the recombination path ways and hence upward shift of the Fermi level is the main reason behind the enhancement of the photovoltage by the $Mg(OH)_2$ coating. Currently, we are working on developing Perovskite based flexible and glass based solar cells by incorporating $Mg(OH)_2$ as a passive layer.

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P24

Atmospheric Pressure Radio Frequency Plasma for the Detection of Gaseous Species

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The poster outlines preliminary work in the use of an atmospheric pressure radio frequency plasma for the detection of gaseous species. Emission spectroscopy has been used as a method to investigate the identity and distribution of ions in an argon radio frequency plasma before and after the addition of methane. Length profiles of the undoped plasma show a decay in argon intensity whilst width profiles show increased intensity at the channel edges. On addition of methane, argon intensity is seen to decrease in the emission spectra; whether this is due to reactions or dilution effects is still to be deduced. Two different methane inlet geometries have been investigated - these are seen to affect argon distribution and plasma stability, comparison of which has allowed us to form conclusions regarding optimum positioning of the methane inlet: upstream from the plasma.

This research will ultimately help in our understanding of ionisation phenomena in a radio frequency plasma jet. By characterisation through various techniques, including analytical electrochemistry in the gas phase, we hope to produce a novel sensing technology for the detection of gaseous species in the environment.

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Edge-carboxylated Graphene Nanoflakes and the Ferri/ferrocyanide Redox couple

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The ferri/ferrocyanide redox couple is often used as a standard probe, even though it has been shown to be inner-sphere in nature and very sensitive to the electrode surface [1]. It is known that ferri-/ferrocyanide can be unstable in solution, particularly at low ionic strength and low pH. The very high density of carboxylic acid groups of the edge-carboxylated graphene nanoflakes (c-GNF) and the absence of other oxygen-containing functionalities allow us to specifically investigate the effect of these highly charged and acidic groups on the electron transfer kinetics of $[Fe(CN)_6]^{3-/4-}$.

In this poster presentation we report the characterisation c-GNF and their use in electrochemical and FTIR studies of ferri/ferrocyanide. STM [2] and TEM images show that c-GNF have average lateral dimensions of 30 nm. XPS spectrum of the C 1s region is dominated by C=C and COOH functionalities [2] (Fig. 1). The voltammetric response of $[Fe(CN)_6]^{3-/4-}$ is very inhibited by the presence of c-GNF at pH < 8. This pH range coincides with partial protonation of the carboxylic acid groups as determined by titration (Fig. 2). When D_2O is used as solvent, COOH groups are replaced by COOD groups and the response becomes near reversible within a few consecutive scans. In H_2O, response remains very inhibited. c-GNF are also found to promote instability of aqueous $[Fe(CN)_6]^{3-/4-}$ through the formation of a precipitate.

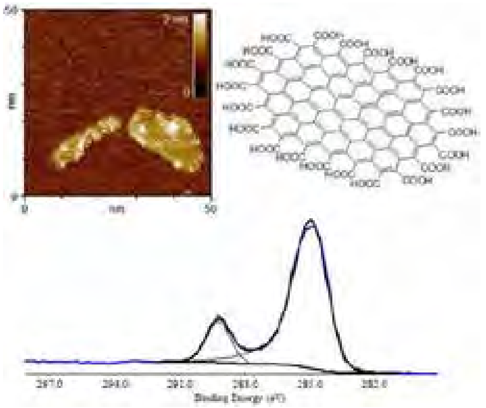

Figure 1. STM image, idealised chemical structure and XPS spectrum of the C 1s region of c-GNF.

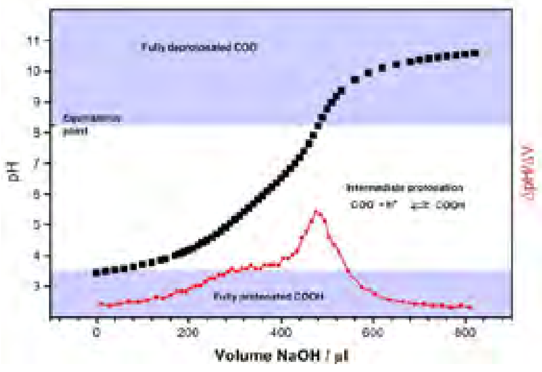

Figure 2. pH titration curve (black) and first derivative (red) of c-GNF.

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P26

A Preliminary Comparison of the Critical Fractal Values of a Chemical Sensor to predicted Chemical Shift Values for Inorganic Polymers to indicate different Swelling Mechanisms.

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Introduction

It is interesting to consider the aqueous arrangement of inorganic polymers.

Spherical Bodies. Spherical bodies resting on a floor or wall, etc.

1. If spheres are placed together in a pile there appear to be a maximum of five spheres. Thus if the volume, (V) of the sphere is $(4/3\pi r^3)$, then the volume(v) occupied by each small identical sphere is $-(4/5.3\ \pi r^3)$ or $(0.24\ \pi r^3)$**(1&2).**
Where r = radius of the sphere.
Another view is – $(0.2\kappa D/(1/E_{min})\pi r^3)$, which also includes a gamma integral, namely,$((\kappa D)/\pi^4)(\kappa D/E_{min})\ \pi r^3)$,
If $c^2 = 0.1\kappa D$,
Where c = concentration , Then $v = (c^2/\pi^2.E_{min})R^3$
For unit measure $v = (0.1c^2/E_{min})$
And if $(\kappa D = 4.0)$, v = 1.3 units and $(2^2)/(3^{1/2})^2$ The fractal measure = 1/v**(3)** = 0.75
1 = 0.75v

Conclusion

The different comparable values for the fractal functions compared to the predicted chemical shift values**(4)**, indicate different various swelling mechanisms for different vermiculite modifications. For example for hydrogen vermiculite, swelling ratio = 1.22 and the predicted chemical shift = 0.5.(1.22) / 0.5 = 1.22,(fractal function value = 0.82) and for butyl ammonium vermiculite, (100a), the swelling ratio = 1.25(0.8) and the predicted chemical shift = 2.0 (1.15) / 0.5 = 4.6. If the HLB ratio is 2:1 and a super structure is considered, (if delta = 1and the decision factor R= 1/2δ), then the predicted ratio is 2.3.It can be noted that the typical loose bulk density of superfine exfoliated vermiculite =850-1050 kg/m^3

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P27

Formal Synthesis of Kingianin A Based Upon a Novel Electrochemically-Induced Radical Cation Diels-Alder Reaction

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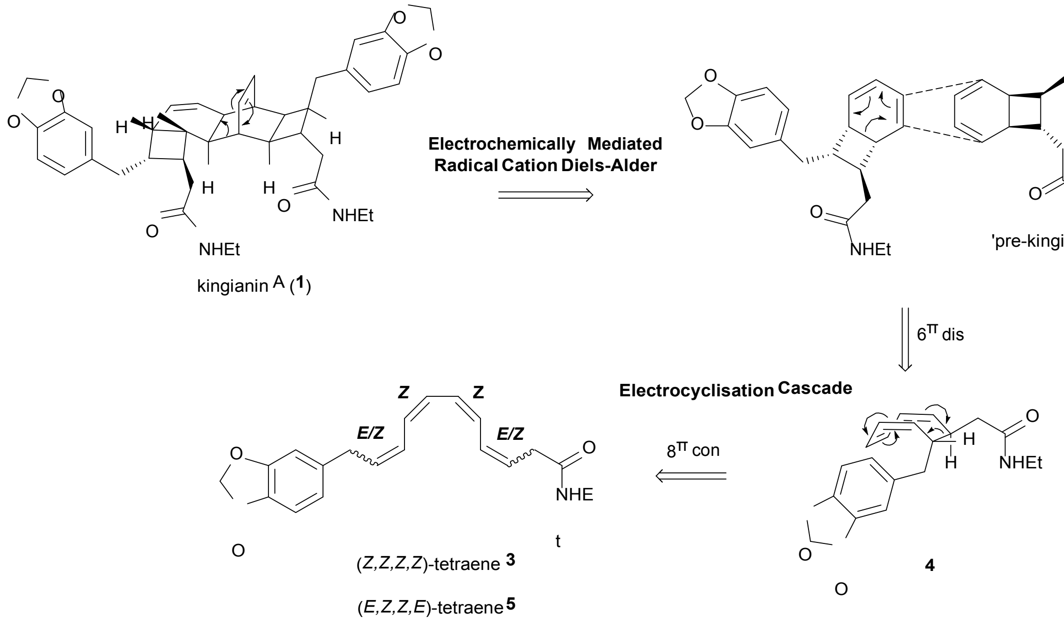
The application of electrochemical reactions in natural product synthesis has burgeoned in recent years. We herein report a formal synthesis of the complex and dimeric natural product kingianin A, which employs an electrochemically-mediated radical cation Diels-Alder cycloaddition as the key step.

The kingianin family of natural products (A-N) isolated by Leverrier *et al.,*[1,2] from the bark of the Malaysian *Endiandra kingiana* Gamble, characteristically comprise a unique, complex and stereochemically rich pentacyclic core framework. A plausible biogenesis of kingianin A (**1**), involving a key Diels-Alder dimerisation of the bicyclo[4.2.0]octadiene monomer pre-kingianin A (**2**) was proposed by the isolation group.[1] Pre-kingianin A (**2**) is most likely formed *via* a tandem 8π/6π thermal electrocyclisation sequence from the tetraene (**3** or **5**).



We would like to report a formal synthesis of kingianin A which utilises the described previously described electrocyclisation cascade. The key step in this synthesis is an electrochemically mediated radical cation Diels-Alder reaction.

This work further demonstrates the potential of electrochemical transformations in organic synthesis and represents the first example of an electrochemically mediated Diels-Alder dimerisation in the field of total synthesis.

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P28

Exploring Electrochemical Processes in Poly(ethylene glycol)

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Polymer solvents are widely used due to their environmentally benign and non-volatile properties. In particular poly(ethylene glycol) (PEG) [1] has been used in electrochemistry [2] and become a solvent of choice, for example in energy storage applications [3]. PEG is known to absorb CO_2 effectively from the atmosphere, and is therefore also a candidate solvent for electrochemical CO_2 reduction.

In this study, an electrochemical cell suitable for experiments under reduced pressure is designed (figure 1) and used to investigate the electrochemical properties of several redox systems. A novel high viscosity hydrodynamic system is developed to enhance currents.

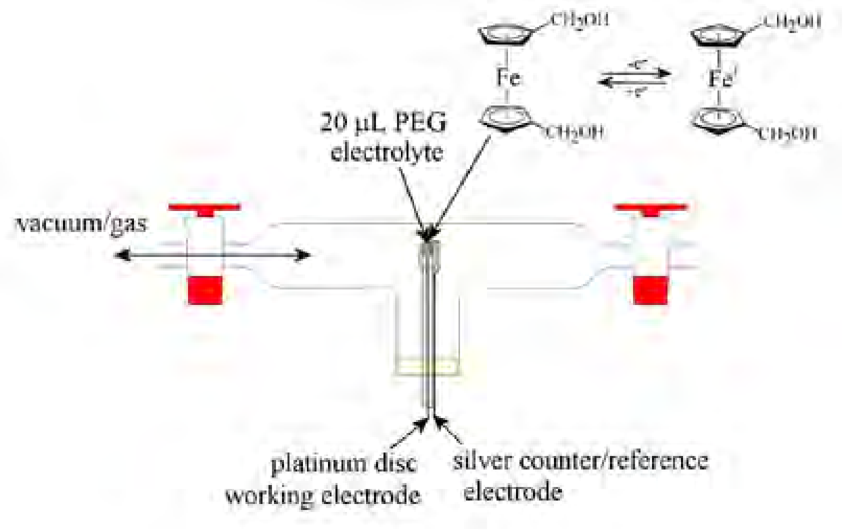

Figure 1. Schematic drawing of the 2-electrode electrochemical cell for measurements in 20 µl polymer solvent after vacuum-degassing.

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P29

Exploring Ionic Strength Effects with Microwire Electrode Voltammetry

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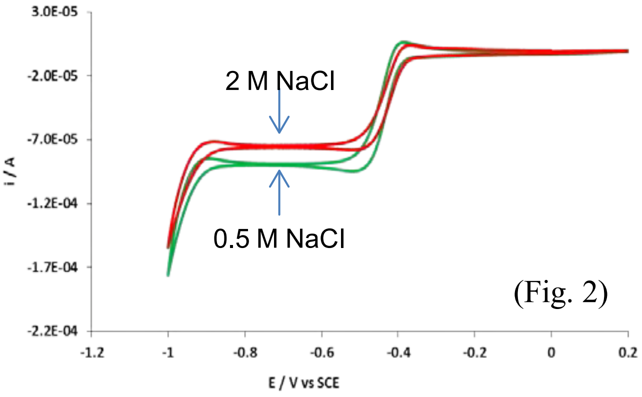
A microwire electrode was fabricated by laminating a 25 μm diameter Pt wire with an exposed length of approximately 3 cm as an electrode (Fig. 1) [1]. The microwire length was calibrated using the potassium ferricyanide redox system before being used to simultaneously quantify the concentration of protons (c_{H+}) and the diffusion coefficient (D_{H+}) in various concentrations of acidified NaCl solutions (Fig. 2). Data analysis was based on digital simulation.

The methodology developed was also employed in determining the concentration (c_{o2}) and diffusion coefficient (D_{O2}) of oxygen dissolved in the acidified saline solutions. Results showed that the microwire electrode demonstrated good stability with good resolution of c_{O2} and D_{O2}.

(Fig. 1)



(Fig. 2)

References:
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Anodic Grafting of Poly(ethylene glycol) on Glassy Carbon and Boron Doped Diamond Electrodes

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Low molecular weight poly(ethylene glycol)s (PEGs) are environmentally benign solvents well known to have anti-fouling and anti-corrosion properties.[1, 2, 3] PEGs are frequently added to electroplating baths to improve the uniformity and quality of film.[4] This study focusses on the electrochemical changes observed after grafting PEGs of various molecular weights to glassy carbon (GC) and boron doped diamond (BDD) surfaces.

The presence of PEG films on the electrode surface dramatically affected the rate of electron transfer for the potassium ferricyanide redox system, which was determined using electrochemical impedance spectroscopy (EIS). The change in electron transfer agreed with cyclic voltammograms in which increased peak to peak separation was seen.

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Using DPV to Study Immobilised Redox Species – Studies of Anthraquinone Covalently Attached to Gold and Glassy Carbon Electrodes

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Principally, the basis of all pulse techniques used for the study of electroactive species in homogeneous solution is the difference in the rate of decay of the charging and the faradaic currents following a potential step. The charging current decays exponentially, whereas the faradaic current associated with the rate of solution-phase diffusion decays as a function of 1/ $(\text{time})_{1/2}$. Thus, the rate of decay of the charging current is considerably fast than the rate of decay of the faradaic current [1]. As a result, by measuring the current at the end of the potential pulse it is possible to discriminate in favour of the faradaic current over the charging current1. However, in case of surface-bound reactants (immobilised electroactive species) this is no longer the case. Now, the Faradaic current for the attached reactant decays faster following the potential step than in the homogeneous solution case [2]. Despite this DPV still remains a more sensitive technique than cyclic voltammetry for the study of low coverages of immobilised species.

In order to increase the sensitivity of DPV for immobilised redox species a suitable additional external uncompensated resistance (R_u) can be added to the working electrode [3]. Anthraquinone was covalently immobilisation at gold and glassy carbon electrodes using linkers based on the electrochemical reduction of a BOC protected diazonium salt [4] or the electrochemical oxidation of mono-BOC protected ethylenediamine [5] followed by deprotection and coupling with anthraquinone carboxylic acid. Different amounts of external uncompensated resistance were employed by using a resistance box and DPV measurements were carried out. The rate of decay of the current following the application of each potential pulse decreases as R_u increases. As long as the R_u is not too large, the magnitude of the current sampled near at the end of each pulse is correspondingly greater and the more R_U amounts, so the larger the value of charging and faradaic currents. Hence, adding a suitable external uncompensated resistance to the working electrodes can lead to larger differential pulse voltammetric peak currents [3]. In the near future, a model for the determination of surface coverage for the attached anthraquinone by using DPV technique with a suitable external uncompensated resistance will be developed.

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Yielding Improvements in Electroanalytical Performance Through Surface Area Enhancement

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Screen-printed electrodes (SPEs) are an innovation in electrochemistry and particularly electroanalysis given their low cost to manufacture and disposable nature whilst also offering a competitive alternative to conventional solid electrodes. SPEs offer real potential for applications in-the-field and have attracted the interest of researches worldwide (1-4). This research addresses the modification of both screen-printed graphite and single-walled carbon nanotubes electrodes surface with solvent to try to assess whether an increase in the surface area results. These electrodes are explored using outer-sphere electron transfer probes and in the electroanalytical detection of important analytes**.** This poster presentation will reveal the results of this study which has generic implications in the field of electroanalysis where screen-printed electrodes are used.

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An Automated System for the Measurement and Identification of Organophosphate Pesticides in Food Extracts Based on a Disposable Screen-printed Biosensor Array.

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Organophosphate pesticides (OPs) are widely used throughout the world in agriculture and veterinary medicine due to their high efficiency as insecticides. Unfortunately, they have been shown to exhibit high acute toxicity primarily caused by acetylcholinesterase (AChE) inhibition which can result in severe neuronal dysfunction and possibly death. Consequently, there has been increased regulation and control of exposure by these compounds from contaminated food and the environment.

An automated analytical device has been developed and optimised for the rapid identification and quantification of specific OP residues in food samples using a simple extraction technique capable of use *in situ*. The instrument incorporates an electrochemical biosensor array based on screen-printing technology allowing mass production at low cost[1]. The biosensors are comprised of a layer of AChE obtained from *D. melanogaster* and immobilised onto the surface of the screen-printed carbon electrodes modified with the electrocatalyst cobalt phthalocyanine. AChE is inhibited by the OPs leading to a reduction in the anodic current[2], forming the basis of the measurement. The array was composed of 12 individual biosensors representing two replicate sensors containing the wild-type or one of five additional modified forms of AChE. Inhibition studies performed using the biosensor array provided training data for a neural network program (NN). The NN was then used to analyse the inhibition profiles created from the analysis of each sample to provide an interpretation of the quantity and identity of any OPs present. The automated system was demonstrated to be capable of identifying and quantifying target OPs in a range of food samples; there were no false positive or negative results for the samples investigated. Interestingly, the extract matrix improved the biosensor responses and the detection limits included concentrations of interest to food protection agencies. Following development, the components of this system have since become commercially available.

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P34

Designing Electrochemically Efficient Screen-printed Sensors: Explaining the Effect of Electrochemical Performance on Electrode Distance

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Screen-printed electrodes have been a key area of research for many years within electrochemistry due to their ability to be mass produced, giving a high reproducibility and low costs which allow for one-shot sensors. Along with these attributes, they have the ability to be produced with many different geometries and designs, which can be suited for the application at hand. Creating a design can prove difficult as fundamental electrochemistry states that the Ohmic drop can lead to a reduced signal due to the distance between the reference and working electrode [1].

Recent literature by Tangkuaram [2] has explored the difference between six different electrode configurations, testing many scenarios for the three electrode system. In this work we elaborate upon this and test extreme distances between the electrodes and the overall effect upon their electrochemical capabilities, towards analytes such as potassium ferrocyanide and hexaammine-ruthenium chloride, with some staggering results, in terms of peak height, over potential and heterogeneous rate constants.

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Electrochemical Detection of Kidney Problems

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The detection of creatinine *via* an enzymeless electrochemical method is reported through an indirect electrochemical system in which the picrate anion consumed upon the reaction with creatinine is electrochemically measured. Such an electrochemical system has the potential to monitor the filtration efficiency of kidneys. This electrochemical protocol is successfully applied to the detection of urinary creatinine and compared to other clinical techniques. The detailed work serves as a novel creatinine detection method and adds to the ever-expanding field of medicinal electrochemistry through use of portable electrochemical sensors. Critically, our system possesses the ability to differentiate between both healthy and unhealthy creatinine levels, demonstrated through use of standard additions, and could replace old and outdated methods such as the colourimetric Jaffe procedure for kidney disease diagnosis.

P36

Atmospheric Pressure Radio Frequency Plasma for the Detection of Gaseous Species

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The poster outlines preliminary work in the use of an atmospheric pressure radio frequency plasma for the detection of gaseous species. Emission spectroscopy has been used as a method to investigate the identity and distribution of ions in an argon radio frequency plasma before and after the addition of methane. Length profiles of the undoped plasma show a decay in argon intensity whilst width profiles show increased intensity at the channel edges. On addition of methane, argon intensity is seen to decrease in the emission spectra; whether this is due to reactions or dilution effects is still to be deduced. Two different methane inlet geometries have been investigated - these are seen to affect argon distribution and plasma stability, comparison of which has allowed us to form conclusions regarding optimum positioning of the methane inlet: upstream from the plasma.

This research will ultimately help in our understanding of ionisation phenomena in a radio frequency plasma jet. By characterisation through various techniques, including analytical electrochemistry in the gas phase, we hope to produce a novel sensing technology for the detection of gaseous species in the environment.

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P37

Forensic Electrochemistry: the Electroanalytical Sensing of Synthetic Cathinone-derivatives and their Accompanying Adulterants in “Legal High” Products

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The production and abuse of new psychoactive substances, known as “legal highs” which mimic traditional drugs of abuse is becoming a global epidemic. Traditional analytical methodologies exist which can provide confirmatory analysis but there is a requirement for an on-the-spot analytical screening tool that could be used to determine whether a substance, or sample matrix contains such legal, or formally “legal highs”.

In this work, the electrochemical sensing of synthetic cathinones is explored and we demonstrate for the first time that this class of “legal highs” are electrochemically active providing a novel sensing protocol based upon their electrochemical activity. Screen-printed electrochemical sensors (SPES) as platforms are favoured due to their proven ability to be mass-produced providing large numbers of reliable and reproducible electrode sensing platforms that preclude the requirement of surface pre-treatment such as mechanical polishing as is the case in the use of solid/re-usable electrode substrates. Additionally they hold potential to be used on-site potentially being the basis of an on-site legal high screening device.

The use of metallic (Bi, Hg) in-situ modified SPES is also explored and it is found that no significant electrochemical enhancement is evident through the use of *in-situ* bismuth or mercury film modified SPS compared to the bare underlying electrodes substrate. In fact, the direct electrochemical *reduction* of the cathinone derivatives is found to be possible for the first time to give rise to useful voltammetric electroanalytical signatures. Additionally adulterants that are commonly incorporated into “legal high” products are electrochemically explored.

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ZnO Nanoparticles Bound to Multi-Walled Carbon Nanotubes for the Electrocatalytical Oxidation of Phenolic Compounds and their Amperometric Detection

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ZnO nanoparticles attached to carboxylic acid functionalized multi-walled carbon nanotubes (MWCNTs) was investigated as a potential amperometric sensor for phenolic compounds. The incorporation of ZnO nanoparticles into MWCNTs showed great evidence of synergistic effect towards the electrocatalytical oxidation of phenolic compounds, including dopamine, hydroquinone, and tert-butylhydroquinone. Cyclic voltammetry of these compounds in Percloric Acid showed great increase in current for ZnO-MWCNT modified glassy-carbon electrode (GCE) and decrease in peak-to-peak separation for the three phenolic compounds investigated in comparison with the bare GCE, ZnO modified GCE, and MWCNT modified GCE. Amperometric recordings were performed using a homemade batch-injection cell [1]. Batch injection analysis (BIA) is an alternative to flow-injection analysis (FIA) with the advantages of simple operation, due to elimination of pumps and valves (easily adapted for portable applications) and reduced volume of carrier solutions [2]. In the BIA system, a sample plug is injected directly onto the working electrode surface in a wall-jet configuration, which is immersed in a large-volume blank solution [3]. Amperometric detection of the three phenolic compounds was attained at 0.6 V (vs. Ag/AgCl), using an injection volume of 150µL and a dispensing rate of 193 µL s^{-1}. Linear range between 2 and 1000 µmol L^{-1} was verified at the ZnO-MWCNT modified electrode. Moreover, high sample frequency (85 h^{-1}) and precision (RSD values lower than 1.64%) were obtained for BIA amperometric measurements for the three compounds. ZnO nanoparticles were hydrothermally synthetized and attached to carboxylic acid functionalized MWCNTs under high-power sonication in acetone. An aliquot of 10 µL of the suspension was dropped on inverted glassy-carbon electrode. The electrode was covered using clamped sample tube and the solvent was evaporated by exposure at 50 °C for 30 minutes.

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Development of a Disposable Screen-printed Amperometric Biosensor Based on Glutamate Dehydrogenase, for the Determination of Glutamate in Clinical and Food Applications

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The purpose of the present investigation was to develop an amperometric glutamate biosensor for application in both clinical and food analysis. A screen printed carbon ink electrode was modified by the addition of Meldola's Blue (MB) [1] [2] to act as an electro- catalyst for NADH oxidation. The resulting screen-printed electrodes act as the base transducer for biosensor construction. Initial voltammetric studies were performed with these devices in the presence and absence of NADH to characterise their redox behaviour under various solution conditions. In order to fabricate a glutamate biosensor, this transducer was coated with glutamate dehydrogenase and chitosan, a binding agent. The optimum conditions, such as temperature, pH, cofactor concentration, were fully optimized. The amperometric biosensor was successfully applied to the measurement of glutamate in serum and OXO cubes, using the method of standard addition.

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"Back-to-Back" Screen-Printed Electrodes: New Advances in Screen Printed Sensor Design for Electrochemical Applications

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With an ever intensifying prerequisite for newly developed sensors to be not only highly reliable and cost effective whilst allowing ultra-low limits of detection, but also easily utilised away from the laboratory at a given site, it is easy to understand why so few viable sensing solutions have been proposed. Electrochemical sensors fabricated via screen-printing technologies can provide a potential solution to such problems.

This work demonstrates for the first time that improvements in the analytical sensitivity of screen-printed electrochemical sensing platforms can be readily obtained through the use of back-to-back screen-printed sensors. In this configuration screen-printed electrodes are printed back-to-back with a common electrical connection to the two working electrodes with the counter and reference electrodes for each connected in the same manner. This approach utilises the usually redundant back of the screen-printed sensors, converting this "dead-space" into a further electrochemical sensor which results in the doubling of the observed analytical sensitivity.

Such work is generic in nature and can be facilely applied to a plethora of screen-printed (and related) sensors utilising the commonly overlooked redundant back of the electrode providing facile improvements in the electroanalytical sensitivity.

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Probing the Redox Activity of Baker's Yeast Using Ferrocenemethanol

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Cell activity is significantly influenced by chemical and physical stimulation[1], various methods are employed to monitor physiological changes in cell, such as monitoring the uptake rate of glucose/oxygen or enzymatic activity. The mediated electrochemical method based on the interaction of an artificial electron acceptor with microbial catabolism provides a rapid approach to probing intracellular redox acitivity[2]. The mediator is chosen for its ability to pass through the cell membrane into the intracellular space. Once there, it can interact with metabolic pathways by participating in redox reactions with biological redox components such as NAD, flavoproteins, iron-sulfur proteins and cytochromes by accepting electrons (fig 1). The amount of bioconversion (i.e. metabolic status of the cells) is reflected in the amount of the reduced mediator generated by the cells.

Here we report the use of a lipophilic mediator, ferrocenemethanol to probe the redox activity of Baker's yeast. The cultured yeast cells are immobilized onto a boron doped diamond (BDD) electrode and the cyclic voltammograms of ferrocenemethanol are collected at the yeast-modified electrode in the presence of different substrate and/or inhibitors. We present results distinguishing between respiratory and fermentative metabolism, the influence of external pressure on yeast fermentation and the effects of catabolic inhibitors.

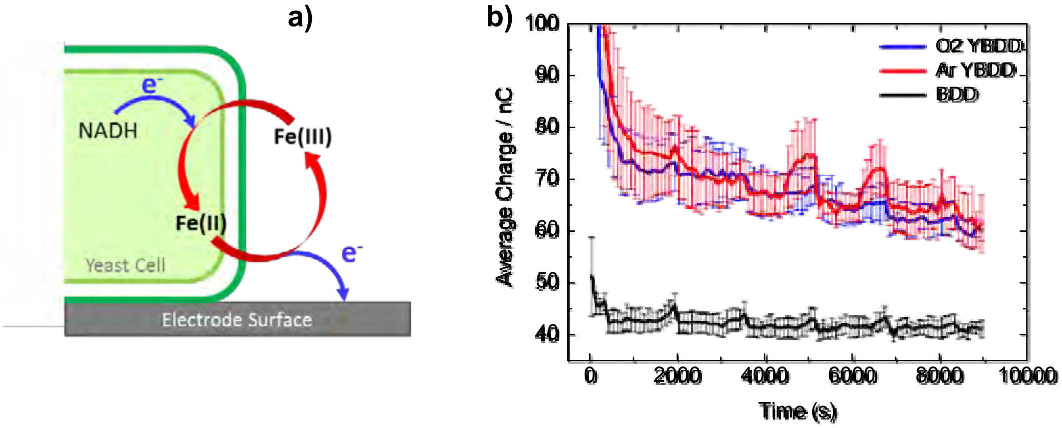

Figure 1. a) Interaction of redox mediators with yeast cells, b) average charge of 1 µM ferrocenemethanol passed at BDD and yeast-modified BDD (YBDD) in the presence of 0.1 M glucose (fermentative metabolism), with and without oxygen present.

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Tin(IV) Iodide Complexes: A Novel Group of Semiconductors

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Semiconductor devices play key role in performance of many electronic devices like solar cells, transistors or diodes. The new semiconducting materials might have a significant impact on development or improvement of the functionality of electronic devices. Tin(IV) iodide based complexes with diphenyl sulfoxide and triphenylphosphine oxide have been synthesized (Fig.1). This two compounds are semiconductors with estimated bandgap around 1.7 and 1.9 eV respectively. The solid-state absorption spectra correlate with the range of photovoltage response.

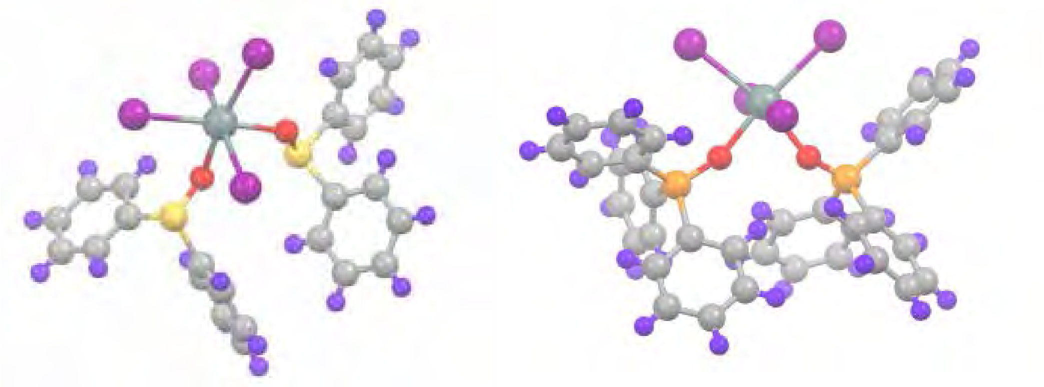

Fig.1. Structures of complexes **1** -$[(C_6H_5)_2SO]_2SnI_4$, **2** - $[(C_6H_5)_3PO]_2SnI_4$,

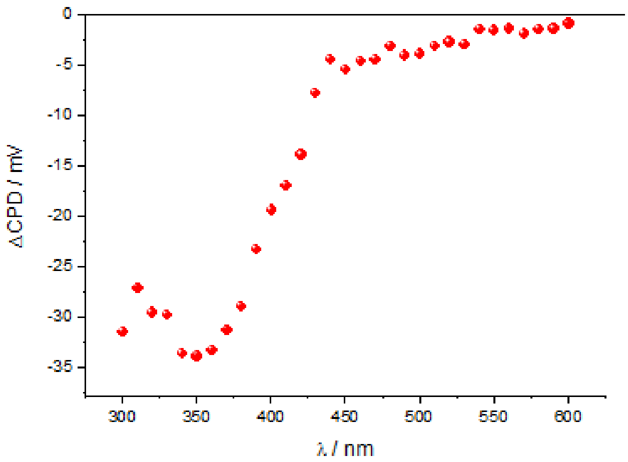

Fig.2. Differential surface photovoltage spectrum of $[(C_6H_5)_2SO]_2SnI_4$,

Photovoltage spectrum (Fig.2) suggests that compound **1** is n-type semiconductor. The relatively narrow band gap and absorption of the visible light, make this compound a candidate for photosensibilization of wide gap semiconductors like TiO_2 or CuI.

Presented materials were characterised by ultraviolet-visible spectro-photometry, cyclic and differential pulse voltammetry, chronoamperometry and Kelvin probe spectroscopy.

Acknowledgements

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Facile Electro-crystallization of Ferricenyl materials from Coordination-driven Self-assembled Ferrocenyls

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New neutral tetra-ferrocenyl-ethynylpyridinyl copper complexes have been formed by the coordination-driven self-assembly of the ferrocenylethynyl-pyridine Ligand (L) and the copper(I) halides (I^-, Br^- and Cl^-) forming cubic $L_4(CuI)_4$ (**2**), and rhomboid $L_4(CuBr)_2$ (**3**), $L_4(CuCl)_2$ (**4**). However, in the presence of triphenylphosphine (PPh_3) under similar conditions, the reactions gave new neutral di-ferrocenyl-ethynylpyridinyl copper complexes, $L_2(CuI)_2(PPh_3)_2$ (**5**),$L_2(CuBr)_2(PPh_3)_2$ (**6**), and $L_2(CuCl)_2(PPh_3)_2$ (**7**). Ferrocenylethynyl functionalized pyridine ligand provided the coordination site to connect ferrocenyl units through the copper clusters [1].

The ferrocenylethynyl-copper cluster materials oxidize under mild condition giving electro- crystallization of oxidized products. EDX analysis indicated formation of partially- and fully- oxidized products. These results were complimented by Raman analysis. SEM showed oxidation products having distinct morphologies. Some of these morphologies of the electrodeposited Cu-based microstructure are of high recent interest for fundamental studies and for potential applications in catalysis and other fields [2].

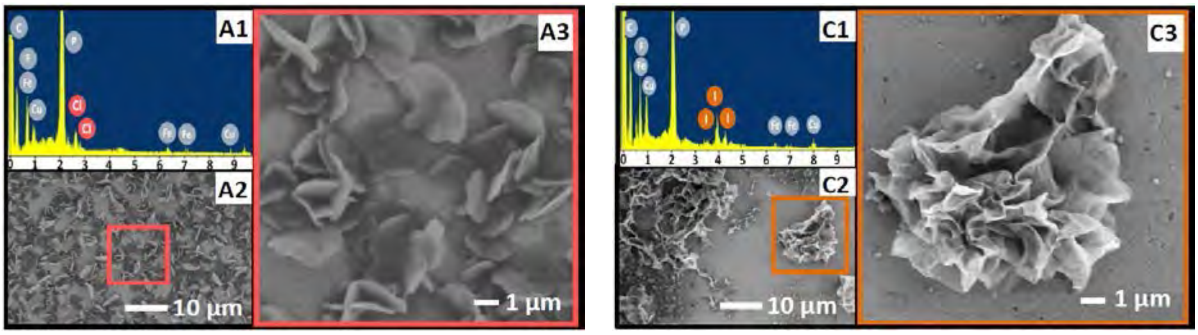

Figure 1 EDX spectra shown in panels : (A1) & (C1) while; (A2) & (C2) show low magnification and (A3) & (C3) show high-magnification SEM images

Herein, we will present the convenient synthesis, electrochemistry, SEM, EDX, etc. and future prospect of the electro-crystallized multi-ferricenyl materials.

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A Practical Electrocatalytic Approach for the Synthesis of E-Stilbene Oxide

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Stilbene derivatives are small molecular weight naturally occurring compounds and are found in a wide range of plant sources, aromatherapy products, and dietary supplements. Stilbenes act as natural protective agents to defend the plant against viral and microbial attack, excessive ultraviolet exposure and disease. For example, resveratrol has been extensively studied and shown to possess potent anti-cancer, anti inflammatory and anti-oxidant activities [1].

Over the past recent years a great attention has been paid to the synthesis of stilbenes oxides involving biomimitic catalysis approaches [2]. In this domain of research, metalsalens and porphyrins complexes have been considered for a long time as prototypes of cytochrome p-450 which play a key role as enzyme in many biochemical oxidation reactions such as olefin epoxidation and hydroxylation. We report in this study a practical electrochemical method for the synthesis of E-stilbene oxide using Manganese Schiff base complex as electrocatalyst [3].

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Investigate the Effect of Some Additives on the Electrochemical Performance of NiFe Batteries

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The quest for low-cost, high-efficiency, battery energy storage is critical to renewable energy integration and smart-grid energy infrastructure. Renewable energy sources have the potential to drastically reduce greenhouse gas emissions. Energy storage (ES) batteries are key to integrating renewable resources like wind and solar into the power grid. ES can provide energy when it is needed. The low cost-materials, robustness, non-toxic materials, and eco-friendliness make iron-based electrodes such as Nickel/Iron battery the ideal for large-scale electrical energy storage. Iron-based cells devices are limited by poor charge efficiency and low discharging capability related to hydrogen evolutions (HOR) that occur during the charge reaction, however, improving the performance and lowering the cost of these components is necessary if such devices are to be considered viable alternatives rechargeable battery for large-scale ESS. The influences of additives in the iron electrode for the hydrogen evolution reaction in 28.5w/w% KOH at 25°C during the electrode preparation are considered. In this work we investigate the effect of some additives on the electrochemical performance of NiFe batteries. Pasted-type electrode been used which iron powder used as the main active material on a grid nickel foam as a current collector. The electrochemical characteristics of these electrodes were investigated by galvanostatic charge/discharge, X-ray diffraction methods (XRD) high-resolution transmission electron microscopy (HRTEM), together with X-ray energy dispersive spectroscopy (EDS). It is shown, that the addition of bismuth sulfide significantly improves the performance of the iron electrode. The discharge capacity of iron electrodes gets better with addition of 4.5 wt. % to 10 wt.% Bi_2S_3 additives, with optimum percentage of 4.5wt% Bi_2S_3 additive. Currently we explore the effect of the Iron/copper composites as Anodic additives on the performance of Nickel/Iron cell.

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P46

Identifying an Efficient and Cost-Effective Battery Storage System for PV Energy

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In this project existing solar data is used to identify the local resource profile and model a photovoltaic system that incorporates electrical energy storage and supplies electricity directly to an off-grid load. The project seeks to identify the best battery system for PV energy storage, in response to the demand created by the EU's support for energy storage [1, 2]. In Germany, which is a world leader in PV installations, the demand is driven by government's funding of battery storage for rooftop PV systems [3]. Other governments around the world have introduced initiatives that support energy storage [2: Table 7].

To address this demand, impedance spectroscopy is used to characterise different battery chemistries and assess them against the solar input profile. The methodology developed in [4] is used. The battery systems are also evaluated on cost, environmental factors and capacity for off-grid applications. Through the project, an optimum battery system for storage of the particular solar resource is established and matched to the load.

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N-doped Graphene Used as an Electrode for Supercapacitors

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Electrochemical capacitors, which are also termed supercapacitors and ultracapacitors, have attracted increasing attention because of their high power density, high energy density, fast response and long cycle life. Graphene has been extensively used as an electrode material in supercapacitors, and researchers have recently developed many modification techniques to further increase its supercapacitive performance. It has been reported that nitrogen doping (or other heteroatom doping) could enhance the capacitance of graphene due to the modified electronic properties and the induced pseudo-capacitance, in addition to the electrical double layer capacitance. In this work, we used a simple thermal expansion method at low temperature, and then dope nitrogen into graphene oxide by a hydrothermal process. Capacitive properties of the resultant electrodes will be reported.

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Growth of Carbon Nanotubes on to Steel Substrates by Aerosol-Assisted Chemical Vapour Deposition for Application in Supercapacitors

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A supercapacitor is a device which is capable of accumulating, storing and delivering thousands of more times more charge than a conventional parallel plate capacitor. These supercapacitors are capable of providing large power peaks that are necessary for fast acceleration in electric vehicles, for example.[1] However; there is much need for improvement if these electric vehicles are to match the performance of their petrol or diesel counterparts. Carbon nanotubes (CNTs) have attracted much attention for use as a supercapacitor electrode material, due to their high surface area, good conductivity and good stability at large voltage ranges. Also, as steel is cheap, versatile and widely available, it is the ideal choice for use as a substrate for CNT growth and current collector in supercapacitors. The steel substrate can also act as a catalyst for CNT growth as it contains Fe which is known to catalyse CNT growth. Development of high performance supercapacitors from cheap and widely available materials is of great importance. We have utilized a continuous and simple aerosol assisted chemical vapour deposition (AACVD) method of growing CNTs on steel substrates using a single source precursor containing an Fe catalyst in ethanol.[2] AACVD is a method which is suitable for large scale production of CNTs.[3] The SEM and TEM images of the CNTs are shown in Fig. 1. The CNTs produced using this method were very long (many µm) and adopted an entangled morphology on the steel. TEM images confirmed that the CNTs were multi-walled and had small crystals of Fe encapsulated inside the tubes. The CNT/Steel electrodes produced in this way showed high areal capacitances of 34 $mFcm^{-2}$ but low specific capacitances of around 3.4 Fg^{-1}.

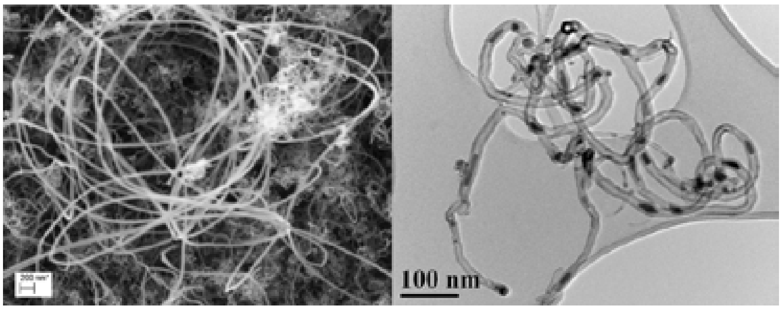

Figure 1. Showing SEM (left) and TEM (right) images of CNTs grown on steel substrates by AACVD.

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Development of Efficient Electrocatalysts for Direct Alcohol Fuel Cells Applications

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Direct alcohol fuel cells (DAFCs) are very attractive as power sources for mobile and portable applications. Beyond methanol and ethanol, other higher alcohols/ oxygenates with higher energy density are proposed as alternate attractive fuels for 3rd generation direct fuel cells. The key challenge here is to develop efficient electrocatalysts which are able to break C-C bonds and to fully oxidise the fuels under fuel cell operating conditions to release maximum energy. The ultimate goal is to evaluate the fuel cell performance utilising bio-derived higher alcohols in fuel cell mode and model the performance under a range of operating conditions.

An efficient alcohol electrooxidation catalyst should be able to facilitate (i) dehydrogenation, (ii) C-C bond cleavage, (iii) COad oxidation and (iv)water activation at a low potential. Various bimetallic electrocatalysts have been developed at QUB and evaluated for the electrooxidation of a range of higher alcohols, and electrooxidation mechanisms are elucidated using electrochemical and in-situ FTIRS techniques. New insight into electrocatalysis at molecular level has been obtained and will be reported.

Acknowledgements

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Alcohol Oxidation at Palladium Alloy Catalyst in Alkaline Solution

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Because of the high energy density and easy handling of the liquid direct alcohols fuel cells are very suitable as portable power supply solution or back-up power solution. Today direct methanol fuel cells using proton exchange membranes have achieved a high maturity and are entering first high price markets. An increase of the market share as well as an increase of power of the single units is, however, hampered by the high price of the used platinum catalyst. To overcome this issue the use of alkaline anion exchange membrane technology instead of acidic PEMs may become a solution.

In former studies it has been found that palladium has a very high activity for the ethanol oxidation in alkaline media [1]. It was further shown that using palladium based commercial catalyst a direct ethylene glycol fuel cell can be realised that achieves peak power of up to 45 mW cm^{-2} at CO_2 current efficiencies between 40 and 60 % [2]. In order to further improve the catalyst performance and to reduce the use of palladium, palladium binary alloys with silver and nickel were studied [3] and recently palladium nickel ternary alloys with tin and ruthenium. The palladium nickel catalysts showed high performance for the methanol oxidation both in an electrochemical cell and a fuel cell configuration. It will be shown, that this high performance is further enhanced by the ternary catalysts.

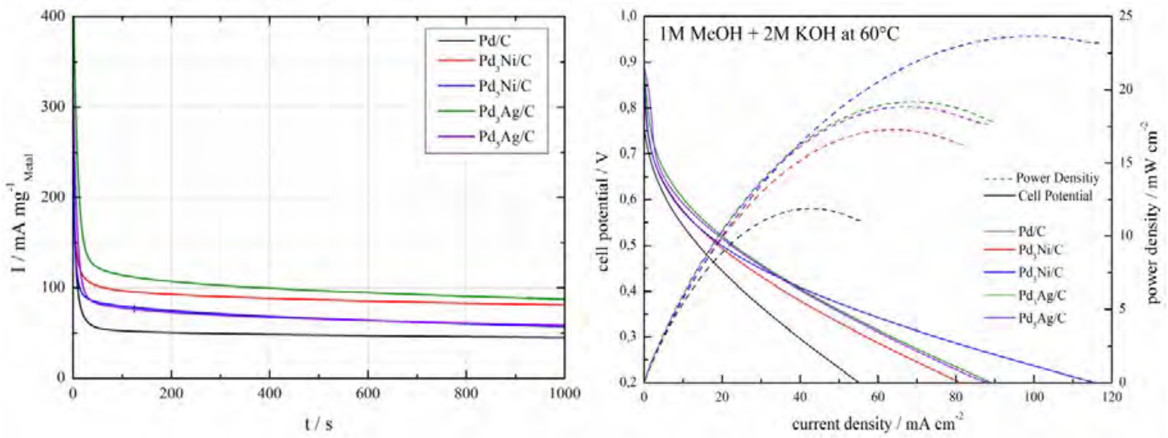

fig. 1: Methanol oxidation at different Pd_xM catalysts measured by chronoamperometry at ambient temperature (left) and in a single cell at 2 mg/cm^2 anode loading with 4 mg/cm^2 Acta 4020 cathode loading, Sigracet 10 AA GDL and FumaPEM FAA3 electrolyte membrane (right).

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Synthesis and Activity of AuCu-C Core-Shell Catalysts for Direct Formic Acid Fuel Cell Applications

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Immense interest has been generated in the field of catalysis for gold nanoparticles anchored on a porous support, due to their high reactivity and selectivity. It is reported for the first time that a carbon-supported Au and AuCu core-shell catalyst for the anodic catalyst in a direct formic acid fuel cell (DFAFC) was prepared using a polyvinylpyrrolodone (PVP) protected method. The morphology and structure of as-prepared particles were examined by high resolution transmission microscopy (HRTEM) and X-ray diffraction analyses. The energy-dispersive X-ray spectroscopy (EDS) analysis confirms the particles to be composed of a copper-core and a gold-shell. The electrooxidation behaviour of formic acid on as-prepared Au-C, AuCu-C and commercial gold nanoparticles were compared. From the XRD patterns, the superlattice reflections of 001 and 110, and the splitting reflections of 200/002 and 220/202 evidently confirm the absence of intermetallic bonding between Au and Cu. Results suggest that the core-shell controlled morphologies/nanostructures of Au shell Cu-core anodic catalysts will play a significant role in low cost economics for practical DFAFCs technology.

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In situ Characterisation of PEM Water Electrolysers Using a Novel Reference Electrode

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Polymer electrolyte membrane water electrolysers (PEMWE) are a promising technology for hydrogen production, with the advantages of higher power density and wider partial load range compared to incumbent alkaline electrolysis technologies. This means they are well suited to coupling with intermittent renewable electricity sources such as wind or solar. A major barrier to widespread commercialisation of PEMWEs is the relatively high cost of the catalysts required for water oxidation at the anode and hydrogen evolution at the cathode, typical materials being based on iridium/ruthenium oxide and platinum respectively. Furthermore, degradation mechanisms of these catalysts are poorly understood, hindering informed catalyst design for extended lifetimes and more economical loadings. In this study, an innovative reference electrode is demonstrated for *in situ* electrochemical characterisation of a PEMWE. This approach enables separation of the relative contributions of anode and cathode to the overall reaction. During power cycling of the cell – thought to be a cause of catalyst degradation – it was observed that, during shut-down periods, the cathode contributes more to changes in open circuit voltage than the anode. This implies that degradation of the platinum cathode plays a more significant role than conventionally assumed by the electrolyser community, which has tended to focus more on the iridium oxide anode as it dominates the performance of the cell. Changes in the electrochemically active surface area (ECSA) of the platinum cathode as a result of potential cycling were determined in situ via hydrogen underpotential (H_{upd}) cyclic voltammetry. Scanning electron microscopy and X-ray tomography were used to correlate changes in catalyst morphology with performance degradation of both carbon-supported and unsupported platinum catalysts.

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Optimizing the Synthesis Conditions of Radiation Grafted Polyethylene-based Alkaline Anion Exchange Membrane for Fuel Cell Applications

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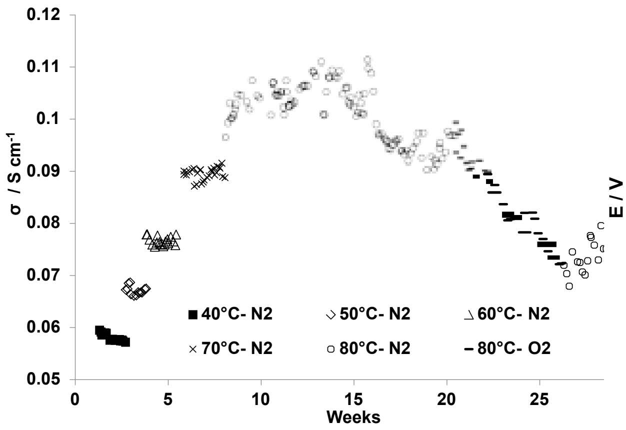
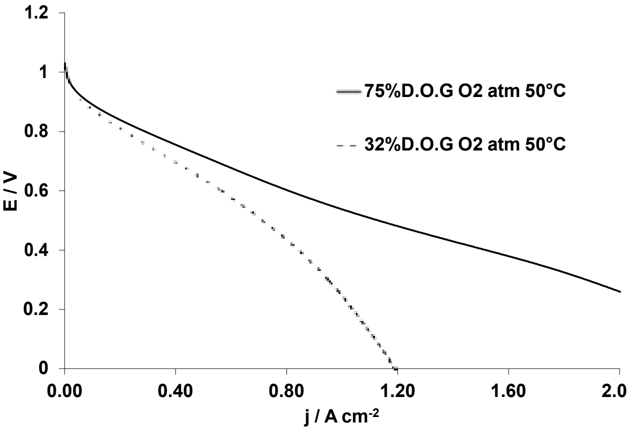
Alkaline electrolyte membranes (AEMs) are solid polymer electrolyte membranes that contain positive ionic groups such as poly—$N^+(CH_3)_3$ and mobile negatively charged anions (e.g., OH^-). These solid (cation-free) OH^- ion conducting polymer could hold the key answer to many of the limitations of Proton Electrolyte Membrane Fuel Cell (PEMFC): faster oxygen reduction reaction (ORR) under alkaline conditions than in acidic conditions providing therefore lower activation losses [1], non-precious metal catalysts (NPMCs) can be used quite effectively achieving the same power density as Pt [2, 3], increased number of inexpensive materials for cell components due to less corrosive environment [4]. Our TMA functionalized vinylbezyl chloride (radiation) grafted on Polyethylene backbone (LDPE-*g*- VBC-TMA) showed low activation energy of 12 kJ mol^{-1} for OH^- ionic conductivity close to the reported value for H^+ conductivity in Nafion [5] with OH^- through plane conductivity of 0.13 S cm^{-1} at 80 ºC and 100% RH[1]. These (LDPE-*g*-VBC-TMA) AEMs have superior fuel cell peak power densities, at a high potential of 500 mV, the highest reported yet in the literature for alkaline anion exchange membrane fuel cell (AAEMFC) of 823 mW cm^{-2} under oxygen (atm) and 506 mW cm^{-2} under air (1 bar gauge) at 60 ºC [6]. Optimizing the synthesis conditions of these (LDPE-*g*-VBC-TMA) is paramount to achieve superior fuel cell performance. Among of the studied conditions: initial polymer film thickness, degree of grafting (D.O.G), radiation dosage & monomer concentration. The membranes were evaluated in terms of ionic conductivity, ion exchange capacity, fuel cell performance and stability.





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P54

Nanotubular PtNi Alloys as Superior Catalysts for the Oxygen Reduction Reaction in Fuel Cells

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This work describes the design of 1D Pt-alloy catalysts in *nanotubular* format for the oxygen reduction reaction in fuel cells. These high surface area metal alloys are becoming a more common approach in the development of stable, active and low cost ORR catalyst layers for PEMFC [1-3]. One of the main challenges in the development of these catalysts is the formation of nanoscale catalysts to be cost effective, yet with a high enough Pt surface area and mass activity for higher performance capabilities.

We have developed a high performance ORR catalyst by forming a nanotubular PtNi alloy with an extremely high surface area and mass activity. These were formed by depositing a sacrificial core within an anodized alumina template having a pore diameter of 200 to 250 nm. The sacrificial core-containing alumina templates were pore widened in NaOH prior to PtNi electrodeposition and the sacrificial material and the alumina template were etched away resulting in hollow PtNi nanotubes. The PtNi nanotubes have an atomic ratio of 40% Pt and 60% Ni; with a length of approximately 4 µm and an inner diameter of 200 nm, with a wall thickness of 20-45 nm. The catalytic activity of the PtNi nanotubes has been assessed for the ORR by drop casting onto a glassy carbon electrode and using cyclic voltammetry in 0.05 M sulphuric acid.

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P55

Development and Characterisation of Mild Steel as a Bipolar Plate Material for PEM Fuel Cells

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The total cost of a fuel cell system is an aggregate of the costs of membranes, catalyst and electrodes, peripherals, assembly processes and the bipolar plates (BPPs). In order to accelerate the widespread commercialisation of fuel cell technologies, there is significant research in cost reduction[1]. In particular, BPPs contribute significantly towards the cost and volume of a fuel cell stack.

The primary aim of the project is to study the feasibilities of mild steel and low carbon steel to be applied as BPPs in Polymer Electrolyte Membrane Fuel Cells (PEMFC). The project is undertaken in collaboration with one of the largest steel producers, Tata Steel to develop a novel coating solution that would be applicable to the selected substrates and would withstand the harsh PEMFC environment. As compared to stainless steel, low carbon steel is low cost, but has poor chemical properties. Mild steel or low carbon steel substrate by itself has a high tendency to corrode and does not contain a protective passive layer as in case of stainless steel. Mild steel substrate without an additional protective coating would not be able to withstand PEMFC environment. Conventional low carbon steel with a corrosion resistant coating or a surface treatment has been analysed as a BPP material. An alloy coated mild steel sample is tested and compared to a standard SS 316L sample using ex-situ tests including, interfacial contact resistance (ICR) measurement, corrosion rate measurements at varying electrolyte concentrations, temperatures and purging conditions. The alloy coated material had an ICR of 33 $m\Omega\ cm^2$ as compared to 300 $m\Omega\ cm^2$ that of SS 316L. The cathode current densities in 0.1 M sulphuric acid with 2 ppm F^- ions for the alloy coated mild steel was 28.9 $\mu A\ cm^{-2}$ at 80 °C. Long term accelerated corrosion tests have been devised to examine the change in the electrochemical impedance data over long periods of operation and have been conducted on these materials; subsequently they have been analysed using a suite of surface analysis techniques. A single cell prototype fuel cell has been designed to incorporate flat metal samples without flow fields as a BPP on one side of the cell with a graphite plate on the other in order to compare their performance.

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P56

Duel Layer Catalyst Coated Substrates in Polymer Electrolyte Fuel Cells

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Polymer Electrolyte Membrane (PEM) Fuel Cells (FCs), have been a topic of interest for many years now, holding out the hope of a viable alternative to the internal combustion engine. The F.U.T.U.R.E. project assesses a variety of hybrid vehicles; including PEMFC systems. However the manufacturing cost and durability of PEMFCs is still a significant stumbling block. In this current research we seek to tackle both issues simultaneously by reducing the overall requirement for platinum catalysts and then monitoring the behaviour of said catalyst over time.

Traditionally catalyst have been deposited as a single concentration layer on either the membrane or on the Gas Diffusion Layer (GDL). Several authors have tackled this issue numerically[1,2,3] and with some focus on the experimental validation of these models: All assumed uniform catalyst layer, and have not factored in the impact of degradation on these systems. For example Xie etal [2] model the system as several very simple geometric bands with uniform size (in the 100nm scale) adjacent to other surfaces; and have apparently verified this experimentally. These models have assumed the dispersion of catalyst material deeper into the GDL is not significant.

Attempting to replicate a similar distribution with our own inks as a ‘Duel Layer’ system has proven impossible. We instead find several layers of concentrated Platinum have ‘tracked’ deeper into the body of the GDL regardless of the type of GDL used. So much so that platinum presence has been detected an overall depth into the carbon paper several orders of magnitude greater than that taken into account in the models of previous authors (100μm scale).

These discrepancies may be due to any one of several factors, and this work seeks to investigate this effect on several GDL materials.

This work is on-going, but initial results have been promising: Peak power performance for both a single layer 0.40mg.cm^{-2} (total Platinum loading) and duel layer 0.20mg.cm^{-2} (total Platinum loading) perform equally well. Assessment of the longevity of the test cells is underway under a variety of load cycles, and this poster presents some of the results achieved to date.

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P57

Kinetic Enhancement of water Oxidation Using Graphitic Carbon Nitride Support in Proton Exchange Membrane Water Electrolysers

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Proton exchange membrane water electrolysis (PEMWE) technology can be made more attractive if production costs, which is dominated by the cost of the membrane and the precious metal electrocatalysts, can be reduced. This can be achieved through improvements in performance and durability of the technology [1]. Graphitic Carbon Nitride (gCN) has been identified as a highly durable Pt catalyst support for PEM fuel cells (FCs) [2] and the current study focuses on integrating gCN technology with PEMWEs to reduce the metal loading on the anode electrocatalyst.

The electrochemical performance of gCN supported IrO_2 with metal loadings of 0.8, 1.6 and 2.8 mg cm^{-2} was studied on the anode (oxidation) side of a PEMWE operating at 80 °C and ambient pressure. Linear polarisation sweeps and electrochemical impedance spectroscopy (EIS) measurements made on the PEMWE and were compared with the performance of baseline electrocatalysts. It was observed that the charge transfer resistances of the electrolysis cell were significantly reduced in the gCN supported catalysts, this enhancement can be attributed to the improved electrocatalatic activity of the electrocatalyst layer.

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Electrochemical and Spectroscopic Studies of Carbon Dioxide Reduction at Copper Oxide Catalysts

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In recent years, components of the global carbon balance have changed substantially with major increases in anthropogenic emissions [1], causing growing concerns about global warming and extreme climate issues. Therefore, there is a need to overcome the barriers between the environment, economy, human society and sustainable development [2]. Electrochemical reduction is one theoretical prospect method to convert CO_2 to hydrocarbons and alcohols [3]. In this case, a potential catalyst material is needed to make the reduction process energetically viable.

The focus of our investigation is to study the electrochemical behaviour of copper oxides catalyst in CO_2 reduction. The project aims to evaluate the reaction process; determine the reaction products; and eventually identify the optimum reduction conditions. In order to study the effect of CuO catalyst, a series of electrochemical methods are used, such as cyclic voltammetry and step-by-step chrono amperometry. Besides, In-situ FTIR, Raman spectroscopy and NMR are introduced to analyse the reduction process and after reaction electrode and electrolyte, respectively. It may be concluded that selection of appropriate operating conditions is essential to the reduction process. The lowest reducing potential is likely to be limited by the stability of catalyst.

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Electrochemistry and Spectroscopic studies of Iron-Nickel Sulphides for CO_2 reduction

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Catalytic or functional roles of minerals have been cited in a number of origins of life models. Iron and iron-nickel sulphide minerals, in particular, have been proposed to play roles in two origins of life theories: the Iron Sulphur World[1] and Iron-Sulphide Membrane[2] theories. In both theories, iron sulphides are proposed to interact with carbon dioxide, electrochemically reducing the carbon dioxide and producing small molecule products which may be the first building blocks of life.

Another motivation for the study is the similarity in structure and property of iron sulphide minerals to ferredoxin and found in enzymes suggests that they may have the potential to perform the same chemistry as carbon monoxide dehydrogenase (CODH). CODH is an enzyme with an iron-nickel sulphide reactive centre, which catalyses the conversion between carbon monoxide and carbon dioxide in nature. Thus if these concepts are plausible, iron sulphides may be the next catalyst to consider for the electrochemical reduction of CO_2.

Successful CO_2 reduction on iron sulphides to formate via electrochemical methods has been reported only once.[3] The reaction mechanism however is not fully understood. This is associated with the complex electrochemical behaviour of the minerals, rich in iron and sulphur chemistry. Hence to understand CO_2 reduction on these minerals, we must first understand the redox mechanism of the mineral surface itself. It is thus the main aim of this project to obtain a firm understanding of the surface reactions on these minerals.

In-situ electrochemical and spectroscopic techniques are employed in our study on synthetic iron and iron-nickel sulphide nanoparticles. Preliminary results showed differences in their electrochemical behaviour in the presence and absence of CO_2 and spectroscopic evidence of the dominance of sulphur chemistry over iron chemistry.

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2) Russell, M. J.; Daniel, R. M.; Hall, A. J.; Sherringham, J. A. J. Mol. Evol. **1994**, *39*, 231- 243
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DEVELOPMENTS IN ELECTROCHEMISTRY:

Science Inspired by Martin Fleischmann

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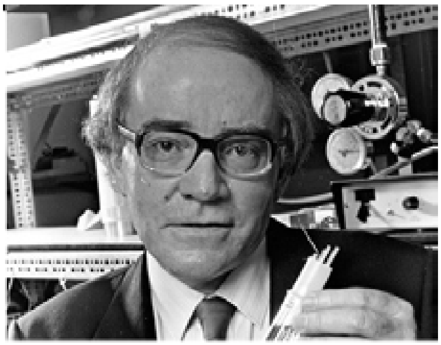
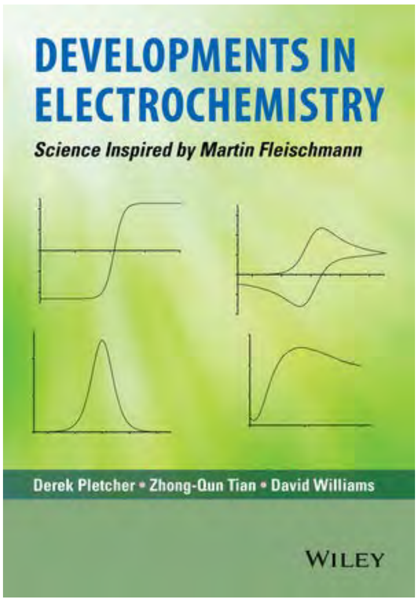


While this book was written as a tribute to Martin Fleischmann to mark his many contributions to electrochemical science particularly related to the development of techniques for understanding electrode reactions, it is not a historical document. Rather it is intended to reflect the state of electrochemical research in 2014. Each of the chapters highlights a topic of current importance, setting out the contribution of Martin Fleischmann and reviewing the literature to the present time. The chapters are all written by one-time associates of Martin Fleischmann, now established experts within their fields. Topics covered include:



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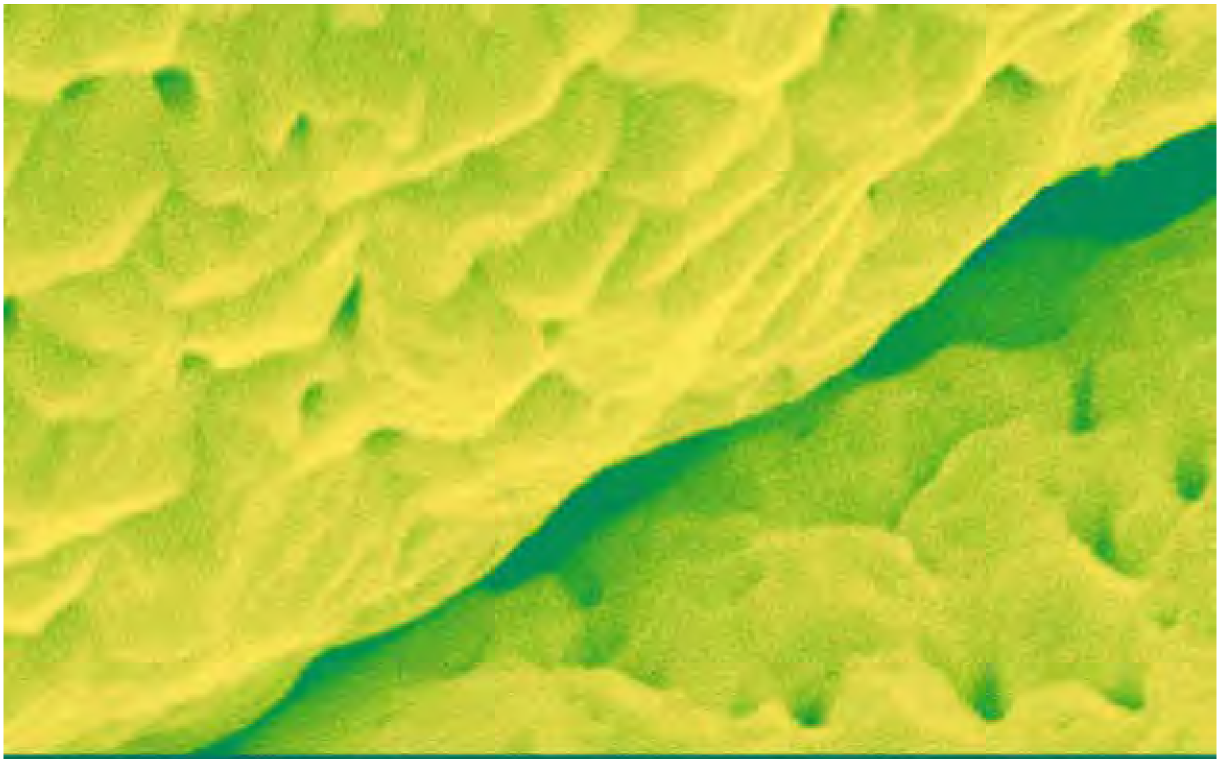

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