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NEWSLETTER

Electrochem 2013: Electrochemistry: an interdisciplinary science

Special Issue

September 1-3, 2013
Southampton University

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Serving Electrochemical Science, Technology and Engineering
within the catchment of
The Royal Society of Chemistry
and
The Society of Chemical Industry

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an environment to advance knowledge exchange

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Editorial

Electrochem conferences have a 20 year history (with the 20th full meeting now approaching in September 2014 in Loughborough) and have emerged as an annual UK & Ireland event, where a cross-disciplinary spectrum of electrochemistry, fundamental and applied, is on show with a particular view on broadening exchange of knowledge, providing information about the latest research developments, linking academia to industry and suppliers, and engaging with the next generation of electochemsits and electrochemical entrepreneurs.

This very special edition of *The Electrochemistry Newsletter* features the programme and abstracts for the ***Electrochem 2013*** at Southampton University held 1st to 3rd September. The theme of this meeting is ***Electrochemistry: an interdisciplinary science*** and the location promises a full programme of exciting talks and presentations. Highlights of this meeting include the award of the RSC Electrochemistry Group ***Faraday Medal to Professor N. M. Markovic*** (Argonne national Laboratory, USA), the SCI Electrochemical Technology Group ***Castner Medal award for Professor Derek Pletcher*** (Southampton University), the ***Institute for Corrosion Evans Medal for Professor John R. Scully*** (University of Virginia, Charlottesville, USA), and the first Fleischmann Lecture given in memory of Professor Martin Fleischmann by ***Professor Alexander Kuhn*** (University of Bordeaux, ENSCBP, France).

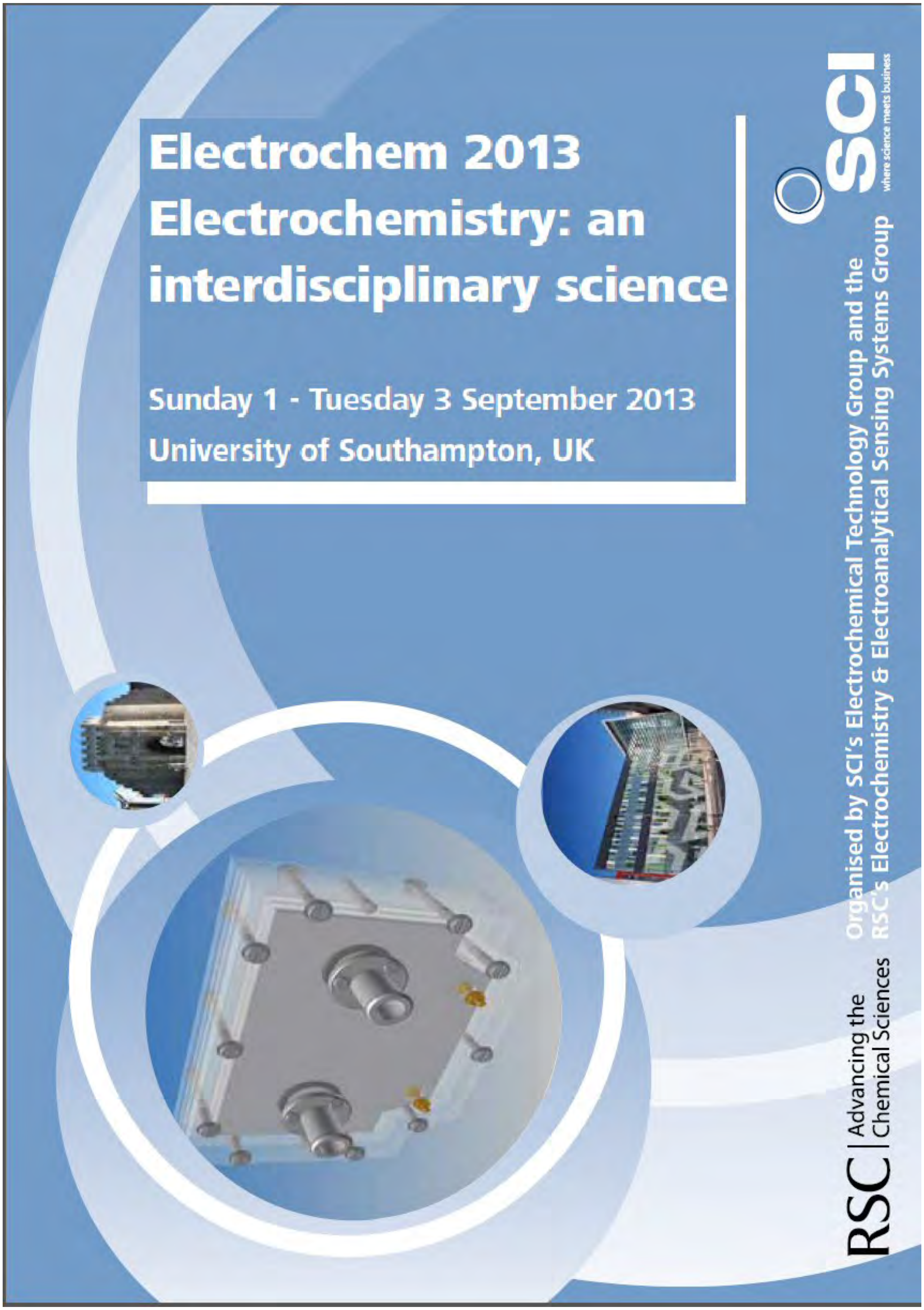
University of Southampton

September 1, 2013 – September 3, 2013

The international nature of the meeting was reflected in the excellent participation (more than 220 attendees) and the presence of industry sponsors and exhibitors, without whom Electrochem would not be what they are.

A big thank you to Dr. Carlos Ponce de León Albarrán and the local organising team, to Patricia Cornell and her SCI team for master-minindg this event, and to the supporting bodies: the ***RSC Electroanalaytical and Sensing Systems Group***, the ***SCI Electrochemical Technology Group***, and the ***RSC Electrochemistry Group***, and particularly thank all of those who have generously sponsored the meetings, in particular the ***International Society of Electrochemistry***.

Frank Marken
Editor-in-Chief



Electrochem 2013
Electrochemistry: an interdisciplinary science

Sunday 1 - Tuesday 3 September 2013
University of Southampton, UK

Organised by SCI's Electrochemical Technology Group and the
RSC's Electrochemistry & Electroanalytical Sensing Systems Group

SCI where science meets business

RSC | Advancing the Chemical Sciences

Symposia Key and Lecture Venues

Scientific Committee

Chair of Scientific Committee	Carlos Ponce de León Albarrán
1: Fundamental electrochemistry Building 46, Lecture Theatre A3001	Frank Marken, Andrea Russell and Jay Wadhawan
2: Materials and nanomaterials Building 46, Lecture Theatre B2003	Stephen Fletcher and Natasa Vasiljevic
3: Electrochemical engineering and technology, industrial developments Building 46, Lecture Theatre C2005	Frank Walsh, Geoffrey Kelsall and Richard Wills
4: 54th Corrosion science symposium Building 2, Lecture Theatre 1089	Julian Wharton
5: Energy storage: batteries, redox flow cells, supercapacitors Building 44, Lecture Theatre 1057	John Owen and Laurence Hardwick
6: Energy conversion, fuel cells, biofuel cells, solar cells Building 44, Lecture Theatre 1041	Denis Kramer and Paul Shearing
7: Applications of electrochemistry in sensors, medicine, biology Building 46, Lecture Theatre C2005	Peter Fielden, John Hart and Petra Cameron

Staff and Student Helpers

The organisers would like to thank the following staff and students of the University of Southampton for their assistance:

Nawal Al Abass
Badr Alshammary
Dmitry Bavykin
Charlie Cummings
Hannah Goode
Gabriela Kissing
Maria Kourasi
Xiaohong Li
Rachel McKerracher
Irene Merino Jimenez
Michael Parkes
Sam Perry
Peter Richardson

PROGRAMME AT A GLANCE

Sunday 1 September

17:00	Registration and welcome reception
Room	*Building 38, Garden Court*
19:00	Dinner for those staying at University of Southampton halls of residence
Room	*Building 38, Terrace Restaurant*

PROGRAMME AT A GLANCE

Monday 2 September

08:00	Registration					
	Building 38, Garden Court					
09:00	**Welcome:** Carlos Ponce de León Albarrán					
09:10	**Chair:** Andrea Russell **Plenary Lecture:** Philip Bartlett					
Room	*Building 46, Lecture Theatre A3001*					
10:00	Refreshments, Posters and Exhibition *Building 38, Garden Court*					
Symposia	**Symposium1: Fundamental electrochemistry**	**Symposium 2: Materials and nanomaterials**	**Symposium 3: Electrochemical engineering and technology, industrial developments**	**Symposium 4: 54th Corrosion Science Symposium**	**Symposium 5: Energy storage - batteries, redox flow cells, supercapacitors**	**Symposium 6: Energy conversion, fuel cells, biofuel cells, solar cells**
Room	*Building 46 Lecture Theatre A3001*	*Building 46 Lecture Theatre B2003*	*Building 46 Lecture Theatre C2005*	*Building 2 Lecture Theatre 1089*	*Building 44 Lecture Theatre 1057*	*Building 44 Room 1041*
	Chair: Andrea Russell	**Chair:** Natasa Vasiljevic	**Chair:** Geoffrey Kelsall	**Chair:** Julian Wharton	**Chair:** Denis Kramer	**Chair:** Richard Wills
10:30	**Keynote** Laurence Peter	**Keynote** Karl Ryder	**Keynote** Manuel Rodrigo	Steven Geary	**Keynote** Kisuk Kang	**Keynote** Nicholas van Dijk
10:50				Rob Burrows		
11:10	Daniela Plana	Stephen Fletcher	María Martín de Vidales	Chike Oduoza	Lee Johnson	Kieren Bradley
11.30	Daniel López-Sauri	Laura Mais	Javier Llanos	Andrew King	Andrew Lodge	Christopher Zalitis
11:50	Esperanza Mena	Yvonne Gründer	Maarten Biesheuvel	Matthew Kitchen	John Owen	Anna Hankin
12:10	Frank Marken	Charlie Cummings	Gregory Forrest	Yikun Wang	Laurence Hardwick	Jagdeep Sagu
12:30	Lunch, Posters and Exhibition *Building 38, Garden Court*					
13:30	**Chair:** Robert Dryfe **RSC Faraday Medal Award Plenary Lecture:** Nenad Markovic					
Room	*Building 46, Lecture Theatre A3001*					
	Chair: Charlie Cummings	**Chair:** Stephen Fletcher	**Chair:** Manuel Rodrigo	**Chair:** Julian Wharton	**Chair:** Laurence Hardwick	**Chair:** Paul Shearing
14:30	**Keynote** Alexei Kornyshev	Adam Cooper	**Keynote** Sudipta Roy	Andrew Pidcock	**Keynote** Clare Grey	**Keynote** Hubert Girault
14:50		Katherine Holt		Weichen Xu		
15:10	Samuel Perry	Nawal Al Abass	Christiane de Arruda Rodrigues	Steven Street	Ann Cornell	Micheál Scanlon
15:30	Her Shuang Toh	Matěj Velický	Shengzhong (Frank) Liu	Haval Mohammed Ali	Kathryn Toghill	Thomas Chen
15:50	Refreshments, Posters and Exhibition *Building 38, Garden Court*					
16:20	**Chair:** Derek Pletcher **Martin Fleischmann Plenary Lecture:** Alexander Kuhn					
Room	*Building 46, Lecture Theatre A3001*					
19:30	Conference dinner					
Room	*Building 38, Garden Court*					

PROGRAMME AT A GLANCE

Tuesday 3 September

09:00	**Chair:** Pauline Allen **SCI Castner Medal Award Plenary Lecture:** Derek Pletcher					
Room	*Building 46, Room A3001*					
Symposia	**Symposium 1: Fundamental electrochemistry**	**Symposium 2: Materials and nanomaterials**	**Symposium 4: 54th Corrosion Science Symposium**	**Symposium 5: Energy storage - batteries, redox flow cells, supercapacitors**	**Symposium 6: Energy conversion, fuel cells, biofuel cells, solar cells**	**Symposium 7: Applications of electrochemistry in sensors, medicine, biology**
Room	*Building 46* *Room A3001*	*Building 46* *Room B2003*	*Building 2* *Room 1089*	*Building 44* *Room 1057*	*Building 44* *Room 1041*	*Building 46* *Room C2005*
	Chair: Frank Marken	**Chair:** Karl Ryder	**Chair:** Julian Wharton	**Chair:** John Owen	**Chair:** Dmitry Bavykin	**Chair:** Peter Fielden, John Hart, Petra Cameron
10:00	Keynote Matteo Duca	Keynote Christopher Lucas	Ricardo Souto	Hannah Goode	Talge Anton Nirmal Peiris	Amélie Wahl
10:20			Susanne Holmin	Rachel McKerracher	James McQuillan	Seán Barry
10:40	Simon Higgins	Michael O'Connell	Stephen Cockerell	James Donoghue	Rakesh Kumar	Victor Costa Bassetto
11:00	Refreshments, Posters and Exhibition *Building 38, Garden Court*					
11:30	Tomas Bystron	Sarah Horswell	Yuanfeng Yang	Keynote Yang-Shao Horn	Graham Smith	Kevin Honeychurch
11:50	Jack Branch	Michael Mercer	Ikechukwu Ivonye		Ian Godwin	Hazel McArdle
12:10	Rui Qiao	Veronica Celorrio	Mengyan Nie	Cristina Flox	Irene Merino-Jiminez	Elaine Spain
12:30	Richard Doyle	Andrew Rodgers	Fei Yu	Julian Kalhoff	Ehsan Ahmad	Alasdair Stewart
12:50	Lunch, Posters and Exhibition *Building 38, Garden Court*					
13:50	**Chair:** Julian Wharton **ICorr Evans Award Plenary Lecture:** John Scully					
Room	*Building 46, Room A3001*					
14:40	Refreshments, Posters and Exhibition *Building 38, Garden Court*					
15:10	**Chair:** Carlos Ponce de León Albarrán **Plenary Lecture:** Mark Meyerhoff					
Room	*Building 46, Lecture Theatre A3001*					
	Symposium 3 continued	Symposium 2 continued	Symposium 4 continued	Symosium 5 continued	Symposium 6 continued	Symposium 7 continued
	Chair: Richard Wills	**Chair:** Christopher Lucas	**Chair:** Julian Wharton	**Chair:** Nuria Garcia-Araez	**Chair:** Xiaohong Li	**Chair:** Peter Fielden, John Hart, Petra Cameron
16:00	Arjan Hovestad	Roger Mortimer	Andrew du Plessis	Chin Teng Goh	Geoffrey Kelsall	Ronan Baron
16:20	Peter Richardson	Gabriela Kissling	Olusegun Fatoba	Asa Noofeli	Rhodri Jervis	Damian Corrigan
16:40	Gopal Keerthiga	Andrew Naylor		Nicola Kay	Quentin Meyer	Mun'delanji Vestergaard
17:00	K. S. Rajmohan	James Rohan		Syed Imran Ullah Shah	Dmitry Bavykin	Jennifer Halliwell
17:20	Close					

Programme: Sunday 1 September

17:00	Registration and welcome reception (*Building 38, Garden Court*)
19:00	Dinner for those staying at University of Southampton halls of residence (*Building 38, Terrace Restaurant*)

Programme: Monday 2 September

08:00	Registration (*Building 38, Garden Court*)
	Plenary lectures all take place in Building 46, Lecture Theatre A3001
09:00	**Welcome:** Carlos Ponce de León Albarrán, University of Southampton, UK
09:10	**Chair:** Andrea Russell, University of Southampton, UK
	Plenary: Templated electrodeposition of nanostructured materials Philip Bartlett, University of Southampton, UK
10:00	Refreshments, posters and exhibition (*Building 38, Garden Court*)
10:30	**Symposia** (*see symposium timetables below*)
12:30	Lunch, posters and exhibition (*Building 38, Garden Court*)
	Chair: Robert Dryfe, University of Manchester, UK
13:30	RSC Faraday Medal Award Plenary Lecture: Building the energy highway Nenad Markovic, Argonne National Laboratory, USA
14:30	**Symposia** (*see symposium timetables below*)
15:50	Refreshments, posters and exhibition (*Building 38, Garden Court*)
	Chair: Derek Pletcher, University of Southampton, UK
16:20	Martin Fleischmann Plenary Lecture: Recent advances in bipolar electrochemistry Alexander Kuhn, University of Bordeaux, France
19:30	Conference dinner (*Building 38, Garden Court*)

Symposium 1: Fundamental Electrochemistry

Building 46, Lecture Theatre A3001

	Chair: Andrea Russell, University of Southampton, UK
10:30	Keynote: Kinetics of light-driven water splitting at semiconductor electrodes Laurence Peter, University of Bath, UK
11:10	Charge transport and reactivity of metal/diamond nanocomposites Daniela Plana, University of Bristol, UK
11:30	Study of the potential oscillations during electrodeposition of Ag-Cd alloys Daniel López-Sauri, Centre for Investigation and Advanced Studies, México
11:50	A laboratory study of the feasibility of applying electrobioremediation for the treatment of diesel-polluted soils Esperanza Mena, University of Castilla-La Mancha, Spain
12:10	Photoelectrochemistry at liquid | liquid | electrode triple phase boundary interfaces Frank Marken, University of Bath, UK
	Chair: Charlie Cummings, University of Southampton, UK
14:30	Keynote: Towards electrochemical artificial muscle: electroactuation with single charge carrier ionomers. Alexei Kornyshev, Imperial College London, UK
15:10	Sampled current voltammetry as a means for probing the oxygen reduction reaction on the sub-second time scale Samuel Perry, University of Southampton, UK
15:30	Electrochemical oxidation of silver nanoparticles Her Shuang Toh, University of Oxford, UK

Symposium 2: Advanced design of materials and nanomaterials

Building 46, Lecture Theatre B2003

Chair: Natasa Vasiljevic, University of Bristol, UK

10:30 Keynote: Advanced applications of deep eutectic solvent-type ionic liquids in materials finishing for high performance manufacturing in electronics and aerospace
Karl Ryder, University of Leicester, UK

11:10 Quantum design of ionic liquids for extreme chemical inertness, and a new theory of the glass transition
Stephen Fletcher, Loughborough University, UK

11:30 On the electrodeposition of niobium and copper in a ionic liquid for multilayer preparation
Laura Mais, University of Cagliari, Italy

11:50 Electrochemistry of nanoparticles at the liquid-liquid interface
Yvonne Gründer, University of Manchester, UK

12:10 Progress in the supercritical fluid electrodeposition of germanium nanowires
Charlie Cummings, University of Southampton, UK

Chair: Stephen Fletcher, Loughborough University, UK

14:30 An electrochemical cathodic route to the production of few layer graphene
Adam Cooper, University of Manchester, UK

14:50 Redox chemistry of insulators: voltammetry of polystyrene nanospheres
Katherine Holt, University College London, UK

15:10 Nucleation and growth of Pd nanodeposits in lyotropic liquid crystal mixtures
Nawal Al Abass, University of Southampton, UK

15:30 Electrochemical behaviour of mono- and multi-layer graphene on various substrates
Matěj Velický, University of Manchester, UK

Symposium 3: Electrochemical engineering and technology, industrial developments

Building 46, Lecture Theatre C2005

Chair: Geoffrey Kelsall, Imperial College London, UK

10:30 Keynote: Treatment of dimethyl phthalate by sonoelectrolysis
Manuel Rodrigo, University of Castilla - La Mancha, Spain

11:10 Degradation of triclosan by means of sono-photoelectrochemical oxidation processes with con- ductive-diamond electrodes
María Martín de Vidales, University of Castilla - La Mancha, Spain

11:30 Wastewater regeneration by means of a sono-electrodisinfection process with BDD anodes
Javier Llanos, University of Castilla - La Mancha, Spain

11:50 Capacitive deionization
Maarten Biesheuvel, Wetsus and Wageningen University, The Netherlands

12:10 Immersion coatings from deep eutectic solvents, precious metal coatings of copper
Gregory Forrest, University of Leicester, UK

Chair: Manuel Rodrigo, University of Castilla - La Mancha, Spain

14:30 Keynote: Electrochemically fabricated of TiO2 layer on Ti-6Al-4V cylinders
Sudipta Roy, Newcastle University, UK

15:10 Fabrication, characterization and photocatalytic activity of oriented oxide nanotube arrays on TiW alloy
Christiane de Arruda Rodrigues, Federal University of São Paulo, Brazil

15:30 High deposition rate, high electronic quality, low cost electrochemical ZnO deposition
Shengzhong (Frank) Liu, Shaanxi Normal University and Dalian Institute of Chemical Physics, China

Symposium 4: 54th Corrosion science symposium

Building 2, Lecture Theatre 1089

Chair: Julian Wharton, University of Southampton, UK

10:30 A novel environmental SVET for the study of tin based coatings
Steven Geary, Sustainable Product Engineering Centre for Innovative Functional Industrial Coatings (SPECIFIC), UK

10:50 Multiscale insights into the passive and localised corrosion behaviour of magnesium
Rob Burrows, National Nuclear Laboratory, UK

11:10 Chromium electroplating of selected aluminium alloys
Chike Oduoza, University of Wolverhampton, UK

11:30 Environmental degradation of a Mg-rich primer: comparison of selected field environments with laboratory exposures
Andrew King, University of Virginia, USA

11:50 A study into the formation of patina on copper-containing antifouling marine coatings
Matthew Kitchen, Sheffield Hallam University, UK

12:10 Influence of localised pit distribution and bench-shape pits on the ultimate compressive strength of steel plating for shipping
Yikun Wang, University of Southampton, UK

Chair: Julian Wharton, University of Southampton, UK

14:30 Galvanic interactions in the corrosion of AZ91 Mg alloy and its implications for the use of Mg-Al intermetallic coatings
Andrew Pidcock, Cranfield University, UK

14:50 In-situ synchrotron and electrochemistry studies of Fe artificial pits
Weichen Xu, University of Birmingham, UK

15:10 Synchrotron X-ray diffraction study of the effect of nitrate on salt films in pitting corrosion of 304 stainless steel
Steven Street, University of Birmingham, UK

15:30 Synchrotron microtomography studies of atmospheric pitting corrosion of stainless steel
Haval Mohammed Ali, University of Birmingham, UK

Symposium 5: Energy storage - batteries, redox flow cells, supercapacitors

Building 44, Lecture Theatre 1057

Chair: Denis Kramer, University of Southampton, UK

10:30 Keynote: Atomic and nano-scale design of electrode materials for lithium rechargeable batteries
Kisuk Kang, Seoul National University, Republic of Korea

11:10 Is there life in the Li-air battery?
Lee Johnson, University of St Andrews, UK

11:30 The study of oxygen reduction in room temperature ionic liquids for use in a lithium-air battery
Andrew Lodge, University of Southampton, UK

11:50 Redox shuttles to relocate oxygen reduction in the lithium-air battery
John Owen, University of Southampton, UK

12:10 The electrochemistry of dioxygen in Li-O_2 cell electrolytes
Laurence Hardwick, University of Liverpool, UK

Chair: Laurence Hardwick, University of Liverpool, UK

14:30 Keynote: Following function in real time - new NMR and MRI methods for studying structure and dynamics in batteries and supercapacitors
Clare Grey, University of Cambridge, UK and Stony Brook University, USA

15:10 Flexible Li-ion batteries based on nanocellulose
Ann Cornell, KTH Royal Institute of Technology, Sweden

Symposium 5: Energy storage - batteries, redox flow cells, supercapacitors

Building 44, Lecture Theatre 1057

15:30 Indirect water electrolysis at a Ce-V redox flow battery
Kathryn Toghill, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

Symposium 6: Energy conversion, fuel cells, biofuel cells, solar cells

Building 44, Lecture Theatre 1041

Chair: Richard Wills, University of Southampton, UK

10:30 Keynote: The development of novel superpowerful PEM electrolyser membranes
Nicholas van Dijk, ITM Power Plc, UK

11:10 Zinc oxide: An illuminating photocurrent response
Kieren Bradley, University of Bristol, UK

11:30 Pt nano-particle performance for PEFC reactions at low catalyst loading and high reactant mass transport
Christopher Zalitis, Imperial College London, UK

11:50 Implementation of hematite (α-Fe_2O_3) photo-anodes in photo-electrochemical reactors for water splitting
Anna Hankin, Imperial College London, UK

12:10 Spinel ferrites as an emerging class of semiconductor for solar energy conversion
Jagdeep Sagu, Loughborough University, UK

Chair: Paul Shearing, University College London, UK

14:30 Keynote: Electrochemistry at soft interfaces
Hubert Girault, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

15:10 Energy conversion at soft interfaces using floating nano-catalytic rafts
Micheál Scanlon, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

15:30 Aluminium can battery
Thomas Chen, Imperial College London, UK

Programme: Tuesday 4 September

Plenary lectures all take place in Building 46, Lecture Theatre A3001

Chair: Pauline Allen, UK

09:00 SCI Castner Medal Award Plenary Lecture: The oxygen electrode in strongly alkaline solutions
Derek Pletcher, University of Southampton, UK

10:00 **Symposia** (*see symposium timetables below*)

11:00 Refreshments, posters and exhibition (*Building 38, Garden Court*)

11:30 **Symposia** (*see symposium timetables below*)

12:50 Lunch, posters and exhibition (*Building 38, Garden Court*)

Chair: Julian Wharton, University of Southampton, UK

13:50 Institute of Corrosion U. R. Evans Award Plenary Lecture: Some advances and challenges in understanding the influence of microstructural heterogeneity on corrosion
John Scully, University of Virginia, USA

14:40 Refreshments, posters and exhibition (*Building 38, Garden Court*)

Chair: Carlos Ponce de León Albarrán, University of Southampton, UK

15:10 Plenary: Electrochemical sensors in medicine - meeting needs for the 21st century
Mark Meyerhoff, University of Michigan, USA

16:00 **Symposia** (*see symposium timetables below*)

17:20 Close of conference

Symposium 1: Fundamental electrochemistry

Building 46, Lecture Theatre A3001

Chair: Frank Marken, University of Bath, UK

10:00 Keynote: Electrochemical study of a tyrosine radical in an asymmetric three-stranded coiled coil peptide
Matteo Duca, Université Paris Diderot, France

10:40 A new family of oligomeric, redox-active metal complexes as 'molecular wires'
Simon Higgins, University of Liverpool, UK

11:30 Electrochemical formation/reduction of PtO on bulk Pt electrode at elevated temperature in concentrated H_3PO_4
Tomas Bystron, Institute of Chemical Technology Prague, Czech Republic

11:50 The use of metallocenes as redox probes in supercritical fluids
Jack Branch, University of Southampton, UK

12:10 From double layer properties to charge storage in nanostructured supercapacitors with ionic liquids
Rui Qiao, Clemson University, USA

12:30 Electrocatalytic properties of nafion and carbon nanotube/hydrous oxide composite electrodes: oxygen evolution & reduction
Richard Doyle, Trinity College Dublin, Ireland

Symposium 3: Electrochemical engineering and technology, industrial developments

Building 46, Lecture Theatre A3001

Chair: Richard Wills, University of Southampton, UK

16:00 Direct Cu electrodeposition on sputtered Mo films for thin film $Cu(InGa)Se_2$ solar cells
Arjan Hovestad, TNO, The Netherlands

16:20 Supported oxygen evolution electrocatalysts for proton exchange membrane water electrolysis
Peter Richardson, University of Southampton, UK

16:40 Electrochemical reduction of CO2 on electrodeposited Cu and Zn electrodes
Gopal Keerthiga, Indian Institute of Technology Madras, India

17:00 Electrochemical reduction of nitrate at Cu/Cu Cathode
K. S. Rajmohan, Indian Institute of Technology Madras, India

Symposium 2: Advanced design of materials and nanomaterials

Building 46, Lecture Theatre B2003

Chair: Karl Ryder, University of Leicester, UK

10:00 Keynote: Understanding the link between atomic structure and reactivity at the electrochemical interface
Christopher Lucas, University of Liverpool, UK

10:40 Probing electrocatalysis at nanostructured materials using combined scanning electrochemical– scanning ion conductance microscopy (SECM-SICM)
Michael O'Connell, National Physical Laboratory, UK

11:30 Electrocatalysis at Au-Pt and Au-Rh nanoalloys
Sarah Horswell, University of Birmingham, UK

11:50 Pt-Pb bimetallic thin film electrocatalysts
Michael Mercer, University of Bristol, UK

Symposium 2: Advanced design of materials and nanomaterials

Building 46, Lecture Theatre B2003

12:10 Effect of iron-doping on oxygen electrocatalysis at barium strontium colbatite
Veronica Celorrio, University of Bristol, UK

12:30 Dispersion and assembly of graphitic particles at the liquid|liquid interface and their catalysis of reduction reactions
Andrew Rodgers, University of Manchester, UK

Chair: Christopher Lucas, University of Liverpool, UK

16:00 Electrochromic and colorimetric properties of nickel(II) oxide thin films prepared by aerosol-as- sisted CVD
Roger Mortimer, Loughborough University, UK

16:20 Electrodeposition of ternary alloys for phase change random access memory applications
Gabriela Kissling, University of Southampton, UK

16:40 Electrodeposition of n-type bismuth telluride alloys for highly efficiency thermoelectric energy conversion
Andrew Naylor, University of Southampton, UK

17:00 Electroless processing for nanoscale interconnect technology
James Rohan, University College Cork, Ireland

Symposium 4: 54th Corrosion science symposium

Building 2, Lecture Theatre 1089

Chair: Julian Wharton, University of Southampton, UK

10:00 Uses of scanning electrochemical microscopy in corrosion research – an update
Ricardo Souto, University La Laguna, Spain

10:20 Why ruthenium oxide-based cathodes in alkaline media are sensitive to reverse currents
Susanne Holmin, Permascand AB, Sweden

10:40 The involvement of stress in uranium corrosion phenomena
Stephen Cockerell, University of Manchester, UK

11:30 Electrochemical investigation of the corrosion of different microstructural phases of X65 pipeline steel under saturated carbon dioxide conditions
Yuanfeng Yang, University of Manchester, UK

11:50 The corrosion of carbon steel in the presence of monoethylene glycol and iron carbonate scale
Ikechukwu Ivonye, University of Leeds, UK

12:10 Corrosion behaviour of ultrafine-grained titanium alloys processed by high-pressure torsion
Mengyan Nie, University of Southampton, UK

12:30 Corrosion of titanium for biomedical applications
Fei Yu, University of Birmingham, UK

Chair: Julian Wharton, University of Southampton, UK

16:00 In-situ tomography studies of atmospheric corrosion of AA2024
Andrew du Plessis, University of Birmingham, UK

16:20 Evaluation of inhibitor performance against localised corrosion in welded pipelines using the mi- crocell technique
Olusegun Fatoba, University of Manchester, UK

Symposium 5: Energy storage - batteries, redox flow cells, supercapacitors

Building 44, Lecture Theatre 1057

Chair: John Owen, University of Southampton, UK

10:00 The design, construction and characterisation of an iron-air battery for use in automotive vehicles
Hannah Goode, University of Southampton, UK

10:20 Novel nanostructured materials for an air-breathing electrode: A comparison with state-of-the- art commercial electrodes
Rachel McKerracher, University of Southampton, UK

10:40 Aggregated use of vehicle battery technology for electricity grid support applications (V2G) and the effect on lifespan
James Donoghue, University of Southampton, UK

11:30 Keynote: Title to be confirmed
Yang-Shao Horn, Massachusetts Institute of Technology, USA

12.10 Advances vanadium redox flow battery using flexible nano-structured carbon-based electrodes materials
Cristina Flox, Catalonia Institute for Energy Research (IREC), Spain

12:30 The next step towards safer lithium-ion batteries: replacing LiPF6 by LiTFSI using fluorinated carbonates
Julian Kalhoff, University of Münster, Germany

Chair: Nuria Garcia-Araez, University of Southampton, UK

16:00 Large signal impedance analysis for the characterisation of supercapacitors
Chin Teng Goh, University of Southampton, UK

16:20 Self-discharge in ionic liquid supercapacitors
Asa Noofeli, University of Sheffield, UK

16:40 Investigation of the electrochemical behaviour of a vanadium species using a nanoelectrode Structure
Nicola Kay, The Innovation Centre, UK

17:00 Molybdenum nitrides as electrochemical capacitors
Syed Imran Ullah Shah, University of Southampton, UK

Symposium 6: Energy conversion, fuel cells, biofuel cells, solar cells

Building 44, Lecture Theatre 1041

Chair: Dmitry Bavykin, University of Southampton, UK

10:00 Electrochemical analysis of the effect of electrodeposited Mg(OH)2 layer on the performance of mechanically compressed flexible dye sensitized solar cells
Talge Anton Nirmal Peiris, Loughborough University, UK

10:20 Infrared spectroscopic study of anatase TiO2 photocatalysis. Formate adsorption, hole scaveng- ing, electron trapping with proton intercalation
James McQuillan, University of Otago, New Zealand

10:40 Tailoring carbon electrodes, redox complexes and polymer supports for glucose oxidase bioelectrocatalysis of glucose
Rakesh Kumar, National University of Ireland Galway, Ireland

11:30 The development and characterisation of silver electrodes for alkaline membrane fuel cells
Graham Smith, Imperial College London, UK

11:50 Enhanced oxygen evolution at 'aged' hydrous nickel oxide electrodes in alkaline solution: kinetics and mechanism
Ian Godwin, Trinity College Dublin, Ireland

12:10 The design and characterization of a standalone hydrogen generator operating via catalytic boro- hydride decomposition
Irene Merino-Jimenez, University of Southampton, UK

12:30 The stability of LaMnO3 surfaces: a hybrid exchange density functional theory study of an alka- line fuel cell catalyst
Ehsan Ahmad, Imperial College London, UK

Chair: Xiaohong Li, University of Southampton, UK

16:00 Kinetics of solid oxide fuel cells with molten tin anodes
Geoffrey Kelsall, Imperial College London, UK

16:20 Development of a non-Pt anode catalyst for alkaline anion exchange membrane fuel cells
Rhodri Jervis, University College London, UK

16:40 Advanced diagnosis for proton exchange membrane fuel cell stacks
Quentin Meyer, University College London, UK

17:00 Applications of metal oxide nanotubes for solar cells
Dmitry Bavykin, University of Southampton, UK

Symposium 7: Application of electrochemistry in sensors, medicince, biology

Building 46, Lecture Theatre C2005

Chair: Peter Fielden, Lancaster University; John Hart, University of the West of England; Petra Cameron, University of Bath

10:00 Electroanalysis at gold nanowire electrode arrays: assessment of required inter-electrode distance towards sensing applicability enhancement
Amélie Wahl, University College Cork, Ireland

10:20 Electrochemical detection of TNT at gold nanowire arrays
Seán Barry, University College Cork, Ireland

10:40 Copper alloy for direct detection of amino acids in ion chromatography
Victor Costa Bassetto, Unicamp, Brazil and University of Southampton, UK

11:30 The redox behaviour of Diazepam (Valium®) using a disposable screen-printed sensor and its de- termination in drinks using a novel adsorptive stripping voltammetric assay
Kevin Honeychurch, University of the West of England, UK

11:50 Detection of sub-femtomolar DNA based on double potential electrodeposition of electrocatalytic platinum nanoparticles
Hazel McArdle, Dublin City University, Ireland

12.10 DNA mediated immobilisation of electrocatalytic nanoparticles in gold nanocavity arrays
Elaine Spain, Dublin City University, Ireland

12:30 A cholesterol biosensor based on the NIR electrogenerated - chemiluminescence (ECL) of water- soluble CdSe/ZnS quantum dots
Alasdair Stewart, University of Strathclyde, UK and Dublin City University, Ireland

Chair: Peter Fielden, Lancaster University; John Hart, University of the West of England; Petra Cameron, University of Bath

16:00 Amperometric gas sensors: the challenge of low concentrations
Ronan Baron, Alphasense Ltd, UK

16:20 An electrochemical assay for the detection of methicillin resistant staphylococcus aureus (MRSA)
Damion Corrigan, University of Edinburgh, UK

16:40 A label-free impedimetric Au-NPs immunosensor for amyloid beta peptides
Mun'delanji Vestergaard, Japan Advanced Institute of Science and Technology, Japan

17:00 An activity assay for the detection and quantification of botulinum toxin
Jennifer Halliwell, Bangor University, UK

ELECTROCHEM

2013
Plenary Speaker Abstracts

Templated Electrodeposition of Nanostructured Materials

Philip N. Bartlett
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Electrochemical deposition is a powerful method for the deposition of thin, conformal, usually metallic coatings on objects. Think for example of the chrome plated bumpers of 1950s American cars or the deposition of silver onto electroplated nickel cutlery; less well known is that electrodeposition is an essential process in the fabrication of magnetic read/write heads for hard disc drives and in the process used to make the interconnects in the latest generations of microprocessor chips. Beyond that electrodeposition, when combined with the use of self-assembled templates, is a practical bottom-up approach to the fabrication of regular nanostructures with dimensions between 2 and 1000 nanometres with a high degree of control. The resulting nanostructured metallic or semiconducting films can have unusual magnetic, superconducting, optical or catalytic properties which can be tuned by varying the dimensions of the structure.

In Southampton we have particularly used two sorts of template to control the nanostructure; lyotropic liquid crystalline phases for the smallest structures [1], and arrays of colloidal polystyrene particles for the larger structures [2]. In this talk I will review these approaches and the properties and applications of the resulting nanostructures.

Looking forward we believe that electrodeposition can be pushed even further and in the future could be used to fabricate nanometre scale transistors and other electronic components. To this end we are working with colleagues in Southampton, Nottingham and Warwick Universities to develop electrodeposition of phase change memory alloys for data storage applications [3] and electrodeposition from the supercritical fluid phase [4] – essentially a highly compressed gas which can fill even the smallest pores yet still dissolves the ions we need to carry out electrochemistry. This novel approach should allow us to deposit metals and semiconductors in nanoscale structures just a few nanometres in size.

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The Oxygen Electrode in Strongly Alkaline Solution

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UK

The pressure to develop technology for large scale energy storage is ever increasing as we move towards an energy economy where a major fraction of our energy requirements is met from renewable sources (solar, wind, wave etc). Oxygen evolution and oxygen reduction are critical reactions in water electrolysis, fuel cells and secondary batteries, technologies promoted for this important role. They are, however, reactions that are associated with large overpotentials and improved electrocatalysts would enhance the possibility of their implementation. In addition, the catalysts must be incorporated into electrode structures that allow rapid supply/removal of oxygen gas to/from the catalyst centres. This lecture will discuss two recent programmes related to oxygen electrode technology in alkaline media. The use of alkaline media decreases corrosion problems and introduces the possibility of non-precious metal electrocatalysts.

The first concerns the development of a zero gap, alkaline water electrolyser. The performance of a number of transition metal based coatings on steel meshes will be compared as anodes in the electrolyser. The preferred coating is a mixed Ni/Fe oxide produced by cathodic precipitation of the mixed hydroxides. It will be shown that such coatings allow oxygen evolution at current densities of > 1 A cm^{-2} for periods of many days and the cell voltage remains at below 2.1 V.

The second relates to the development of a secondary zinc/air flow battery. The positive electrode in such an energy storage device is required to evolve O_2 during charge and reduce O_2 during discharge. Hence, a bifunctional catalyst capable of current densities of the order of 0.1 A cm^{-2} is needed. In addition, the electrode must release gas during charge but allow a high flux of O_2 to the catalyst sites during discharge. Moreover, this must be achieved without carbon components in the electrode since carbon oxidises at the potential for O_2 evolution. The spinel, $NiCo_2O_4$, is one appropriate catalyst and the preparation and performance of a 'gas diffusion electrode' based on all nickel materials will be described.

Recent Advances in Bipolar Electrochemistry

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The idea of applying bipolar electrochemistry to microsystems has been pioneered by Fleischmann almost thirty years ago [1]. Since then the concept has been adapted to many different experimental situations. The field undergoes currently a renaissance in various scientific domains, with applications ranging from analytical chemistry to materials science [2, 3]. In this contribution we'll illustrate some of the most recent advances [4], either concerning the highly controlled wireless electrochemical modification of micro- and nanoobjects [5-8], or with respect to the design of dynamic systems [9- 12], that are able to show analytical or other functionalities [13-15].

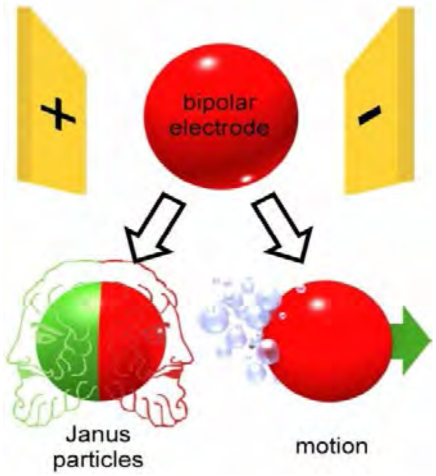

Fig.1 Application of the concept of bipolar electrochemistry for the design of either asymmetric particles or dynamic systems, that can integrate different functionalities

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Building the Energy Highway

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Future energy needs necessitate the search for alternative catalysts in order to develop less expensive and more efficient means for energy conversion and storage. While the majority of applications today are based upon noble metal catalysts, there is strong need to move to wholly new classes of materials with better functionality. In developing noble metal catalysts, the key to making significant progress was the exploration of model systems in order to understand structure-function relationships, which then allowed the development of a deterministic framework for the design of novel catalysts. In this lecture, we show that this paradigm is also the key to understanding new classes of metal-metal/oxide and oxide catalysts. In exploring the behavior of the oxide materials such as 3d-oxides RuIr-oxides and perovskides, we highlight the strength of this approach to not only understand how to control activity by harnessing the structure and polarity of the surface, but also to reveal the intimate relationship between the activity and stability of oxide catalysts under electrochemical conditions relevant to, for example, hydrogen evolution, hydrogen oxidation and oxygen evolution reactions.

Some Advances and Challenges in Understanding the Influence of Microstructural Heterogeneity on Corrosion

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The corrosion behaviour of many corrosion resistant alloys is governed by a range of nano- and micro-scale chemical and structural non-uniformities in combination with various environmental, geometric and physical conditions. The intrinsic properties, physical attributes and geometric arrangements of such chemical and structural non-uniformities in otherwise homogeneous materials are often key factors controlling alloy corrosion. Moreover, this emerging set of information is becoming mature enough to be incorporated into corrosion resistant materials design. Professor Scully's career has long been devoted to research using a variety of experimental techniques and computational methods to investigate these aspects of corrosion. A common feature has been the use of wide range of less resistant commercial alloys, phases and defects reproduced at a larger length scale, rescaled electrodes using scaling laws, isolated natural phases, mapping methods, as well as natural and synthetic arrays simulating alloy heterogeneity designed to help interrogate independently and elucidate the roles of non-uniformities on corrosion phenomena. This talk highlights one of these studies.

The crystallographic orientation of polycrystalline metallic materials is a well-known structural factor affecting corrosion and other electrochemical properties of metals and alloys. However, previous investigations have often been limited to a few crystallographic planes often leading to contradictory findings. Modern computational, metallurgical "crystal mapping" and corrosion surface "scanning" methods in combination can provide new insights regarding this phenomenon. This talk focuses on understanding crystallographic controlled dissolution and surface faceting in disordered FCC Fe-Pd alloys. Electrochemical dissolution by congruent oxidation in 1 M HCl solution was strongly controlled by crystallographic orientation. Anodic dissolution was characterized over a wide variety of grain surface plane orientations providing a detailed view of the crystallographic nature of electrochemical dissolution and surface facet evolution as a function of grain orientation. Near {100} oriented grains retained low surface roughness after corrosion and low dissolution rates. Grains with orientation within 2° of {111} were also topographically smooth after dissolution and were nearly as corrosion resistant as {100} grains. Overall dissolution depth depended linearly on crystallographic angle within 40° of {100} and within 10° of {111} planes. Post corrosion surface faceting and dissolution were substantially increased at grain orientations near {110} and were highest between 10 and 20° from the {111} plane normal. Grains at these crystallographic angles roughened during corrosion by forming complex semi-periodic topographies. These finely spaced arrays of terraces and ledges likely consisted of combinations of more corrosion resistant low index planes. Therefore, the overall corrosion depth within a grain with an initially irrational crystal orientation was determined by the amount of dissolution required to expose new, slowly dissolving surface facets with low index orientations. Computations of Fe-Pd alloy surface energies as a function of crystal orientation support this explanation.

Electrochemical Sensors in Medicine: Meeting Needs for the 21st Century

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Over the past 30 years, miniaturized potentiometric and amperometric sensors for ions (K^+, Ca^{++}, Na^+, Mg^{++}, Cl^-, H^+), gases (O_2 and CO_2), and nutrients/metabolites (glucose, lactate, creatinine, urea) have revolutionized the practice of critical care medicine by providing tools to measure an array of physiologically important species, simultaneously, in small volumes of undiluted whole blood. Indeed, all modern whole blood analyzers used in hospitals worldwide now employ such electrochemical sensor arrays as either single-use or multi-use devices for near-patient testing, especially in operating rooms, emergency rooms, intensive care units, etc. Further, nearly all glucometers now use electrochemical measurement principles to provide accurate glucose concentrations for millions of diabetic patients each and every day, both in the hospital and at home. A brief overview of these existing electrochemical sensor technologies that have already had such a great impact in medicine will be provided during the introduction portion of this lecture.

At the same time, there remain a number of unmet needs in medicine where electrochemical devices could still play important analytical roles. Therefore, in the major portion of this presentation the following ongoing research projects will be highlighted: 1) devising a simple method to detect levels of potassium within red blood cells (RBC-K) in undiluted whole blood samples as a marker for hypertension; 2) recent efforts to utilize electrochemical sensors for measurement of polyionic drugs and associated contaminants (including the anticoagulant heparin, low-molecular weight heparins, and inflammatory oversulfated chondroitin sulfate (OSCS) contaminants in biomedical heparin preparations, etc.); 3) research related to the development of implantable electrochemical sensors for ions, gases, glucose, etc. that emit low levels of nitric oxide (NO) (a potent anti-platelet and antimicrobial agent) and that can potentially be used to continuously monitor critical care species with intravascular catheters in hospital patients with improved accuracy; and 4) the possibility of measuring glucose levels in tiny volumes of tear fluid with electrochemical enzyme electrode devices as a simple less-invasive means to monitor blood glucose levels for patients with Type 1 diabetes.

ELECTROCHEM
2013
Speaker Abstracts

Keynote

Kinetics of Light-Driven Water Splitting at Semiconductor Electrodes

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This lecture will summarize some of the experimental methods that can be used to study the rates and mechanisms light-driven reactions at semiconductor electrodes and will illustrate their application with some of our recent studies of light-driven oxygen evolution on hematite films. The term ‘solar fuel’ refers to materials such as hydrogen and methanol that can store the energy of sunlight in chemical bonds to be released later in, for example, a fuel cell or conventional internal combustion engine [1]. A key part of this process is the generation of oxygen by a four electron process

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

A system known as the *tandem water splitting cell* has been proposed as a way of overcoming the thermodynamic constraints that limit the efficiency of simple systems. This *photoelectrolysis cell* consists of an electrode coated with a film of an oxide such as WO_3 or Fe_2O_3 that absorbs shorter wavelength visible light to drive the oxidation of water to oxygen. The longer wavelength light that is transmitted through this *photoanode* is absorbed by a solar cell that applies a voltage to the photoelectrolysis cell to allow reduction of water to hydrogen to occur at the *cathode*.

Hematite (α-Fe_2O_3) has been studied extensively as a photoanode material. It is red, absorbing light with energy greater than 2 eV, so it looks like a suitable material for the tandem cell. The oxide is an n-type semiconductor, and holes produced by excitation of electrons from the valence band to the conduction band are able to oxidize water. In alkaline solution this reaction can be written as

$$hv \rightarrow h^+ + e^-$$

$$4OH^- + 4h^+ \rightarrow O_2 + 2H_2O$$

Our studies [2,3] show that this four hole reaction is incredibly slow, so that the efficiency of the process is limited.

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Charge Transport and Reactivity of Metal/Diamond Nanocomposites

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The use of diamond as support for metal nanoparticles has gained interest in various fields, such as heterogeneous catalysis, electrocatalysis and sensors. It was recently shown, for example, that Pd supported on non-boron doped diamond particles can potentially be used as electrocatalysts in fuel cells.[1] Despite the inherent bulk resistivity of these diamonds, good electrical connectivity was observed. In this work, we have investigated the charge transport properties of non-boron doped high-pressure, high-temperature diamond particles in the presence and absence of metal nanostructures, employing electrochemical field effect transistors featuring interdigitated electrodes (see Figure 1). This system allowed the determination of conductivity in the presence of electrolyte and in air.[2] The effects of surface termination and metal loading were considered, as well as the composite preparation method (incorporation of pre-synthesised metal particles vs. direct nucleation on the diamond). In the absence of metal, the conductivity of the diamond assemblies in air is over an order of magnitude higher on hydrogenated diamond, in agreement with studies at diamond single crystals; results suggested that conductivity is also determined by particle-to-particle charge transfer. Interestingly, the latter contribution effectively controls the assembly conductivity in the presence of an electrolyte solution, as the conductivity difference between hydrogenated and oxygenated particles vanishes. On the other hand, although in the presence of metal nanoparticles the conductivity is mainly determined by the metal loading, the reactivity of the nanocomposites for various electrochemical oxidations was found to be heavily dependent on the type of surface groups on the diamond particles.

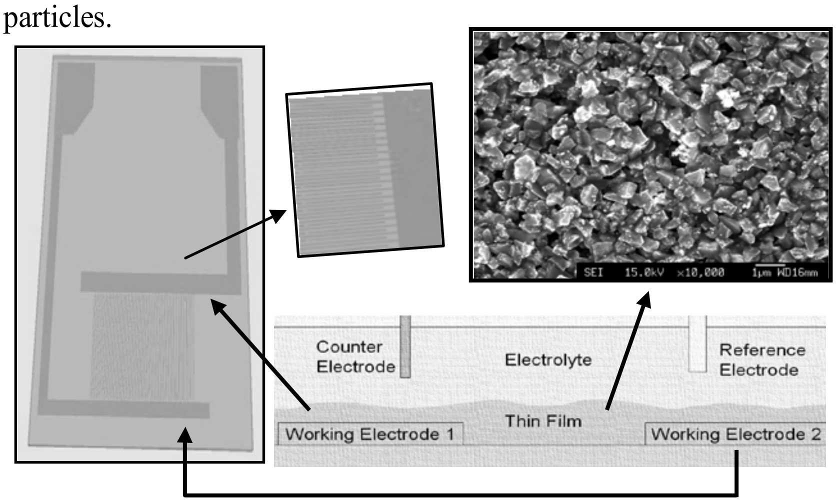

Figure 1. Electrochemical field effect transistor, featuring an interdigitated Au electrode, used to study charge transport phenomena across metal/diamond nanocomposites, such as that shown in the SEM image.

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Study of the Potential Oscillations During Electrodeposition of Ag-Cd Alloys

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During galvanostatic electrodeposition of cadmium and silver-cadmium alloys potential oscillations were observed [1-3]. Experiments at different cathodic current densities were performed showing a dynamic behaviour of the potential oscillations [4]. Those oscillations in silver-cadmium alloys were analyzed by Fast Fourier Transform (FFT). The potential oscillations start at 12.5 mA cm^{-2} (Fig. 1.a) and they are periodical with a frequency of 1.26 Hz, and an amplitude of about 0.305 V. At higher current density of 15 mA cm^{-2} (Fig. 1.b), their signal dynamic is more complicated. Potential oscillations with amplitude of 0.860 V and frequency of 0.05 Hz were interrupted by small oscillations with almost the same amplitude located in a range of potentials similar to those that at a current density of 12.5 mA cm^{-2} and have a frequency of 0.71 Hz. The dynamic of the oscillations becomes regular again at higher current densities where only the potential oscillations with amplitude of about 0.860 where observed. The small oscillations disappear and it supposes that they correspond to the electrodeposition of the Ag-Cd alloy and its different phases, while the oscillations with the biggest amplitude correspond to diffusion phenomena of the metal ions in the solutions near the electrode, and also to hydrogen evolutions, which is presented when the potential oscillations reach more negative values.

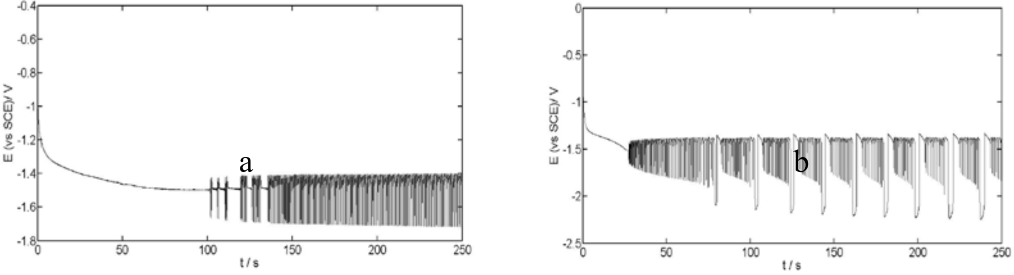

Fig. 1. Chronopotentiometric curve during electrodeposition of Ag-Cd from cyanide electrolyte, onto a vertical cooper electrode at: a) 12.5 mA cm-2; b) 15 mA cm-2.

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A Laboratory Study of the Feasibility of Applying Electrobioremediation for the Treatment of Diesel-Polluted Soils

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This work focuses on electrokinetic enhanced bioremediation, an emerging technology that it is supposed to combine the advantages of the well known electrokinetic and biological soil remediation processes. Sandy, clay and silty soils polluted with diesel have been remediated in bench scale plants and effect of applied electrical field (within the range 0.0 -1.5 V/cm) on the process performance has been assessed. To do this, microorganisms, pollutant (diesel), and nutrients (nitrates, phosphates and ammonium) have been monitored during long term tests in which electric field is applied between an anode and a cathode placed inside electrolyte wells. Experimental setups were equipped with graphite electrodes and flushing fluid consists of a buffer solution of sodium bicarbonate.

Opposite to it was expected, results demonstrate that electrokinetic enhanced bioremediation is not the single addition of the two treatments in any of the three types of soils studied. Thus, important differences are obtained showing that direct combination of treatments is not completely positive and in several cases it is even negative. Electrokinetic processes produce a great change in the nutrient profiles and also a significant change in the pH, being these effects more important with increasing electric fields. The first change is related to the transport of anions to the anodic wells and to the consequent depletion of nutrients in the soil. The second is related to the formation of the acidic and basic fronts, with pH close to 2 near the anode and to 12 close to the cathode wells, in spite of the buffer capacity of the flushing fluid. Both changes greatly affect the bioremediation processes, contributing to decrease the biological degradation rate and even to increase the decay rate of diesel degrading microorganisms.

On the basis of these results, this work tries to determine the way in which these processes can be combined in a synergistic way, looking for an efficient treatment in which electrokinetic processes and microorganisms metabolisms can co-exits.

Financial support from the Spanish Minister of Economy and Competitivity is gratefully acknowledged (project CTM2010-18833).

Photoelectrochemistry at Liquid | Liquid | Electrode Triple Phase Boundary Interfaces

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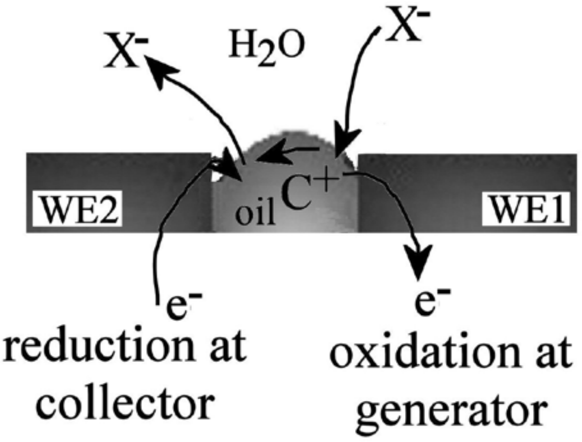
Ion transfer at liquid | liquid junctions can be investigated at the line junction (or triple phase boundary) formed in contact to an electrode surface [1]. Ion transfer voltammetry measurements at this type of electrode are enhanced for (i) electrodes with extended triple phase boundaries, (ii) porous membrane, (iii) with hydrodynamic effects, and (iv) generator – collector triple phase boundary systems [2] (see Figure).



Novel facilitated ion transfer processes and photo-electrochemical processes [3,4] at triple phase boundary electrodes are discussed.

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Keynote

Towards Electrochemical Artificial Muscle: Electroactuation with Single Charge Carrier Ionomers

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We review here novel theory of electroactuation with single charge carrier ionomers that reveals the interplay between the effects of electrostatic pressure resulting from ionic repulsion, and of the steric strain caused by the volume of ions in the double layer (and missing from the depletion layer). The theory shows that the electrostatic pressure can either reinforce or compete with steric strain, depending on the effective volume of the polarized ions in the double layer.

Theoretical predictions are obtained for the electroactuator equilibrium deflection and bending dynamics, showing good agreement with available experimental data. Insights are offered into two directions of rational design of smart ionomer materials for actuators.

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Electroactuation with single charge carrier ionomers: the roles of electrostatic pressure and steric strain
Soft Matter 9 (2013), 3767–3776

Sampled Current Voltammetry as a Means for Probing the Oxygen Reduction Reaction on the Sub-Second Time Scale

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The oxygen reduction reaction (ORR) may proceed via either a two electron pathway, through a peroxide intermediate, or a four electron direct reduction. The peroxide formed may be subsequently reduced to give an overall 4 electron pathway, or may diffuse into the bulk solution. If the rate of mass transport is high, then the rate of diffusion of the peroxide away from the electrode increases, and so the apparent number of electrons involved in the reaction, n_{app}, ends up being less than four. In the steady state, n_{app} has previously been determined by the rotating disc electrode, microdisc electrodes [1] and scanning electrochemical microscopy [2]. However, to our knowledge, it has not been reported how n_{app} depends on the timescale of observations. The aim of the present study is to develop a methodology to probe this dependence, particularly on the sub-second time scale.
The number of electrons transferred during reduction was probed using sampled current voltammetry (SCV). This is a multistep procedure that builds a current transient by recording the current separately for each potential along the reduction wave using a series of potential step experiments. This allows the current to be recorded from the same starting point at each potential, and for the electrode to be pre-treated between each data run using a conditioning waveform.

Sampling the current at the same time after the potential step on each transient allows an SCV to be constructed. In this way multiple SCVs can be recorded from the same collection of transients. The current was normalised by dividing the experimental current by the theoretical diffusion controlled transient current, calculated using the expression reported by Mahon and Oldham [3] for a 1 electron process. This approach causes the data to converge to n_{app}. The method was verified using the single electron reduction of ruthenium hexamine as a model system, before being used to probe the transient oxygen reduction in varying electrolytes and varying pH with a platinum microdisc electrode. The presentation will describe the experimental methodology, the data treatment and typical results obtained for the model system and for the ORR.

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Electrochemical Oxidation of Silver Nanoparticles

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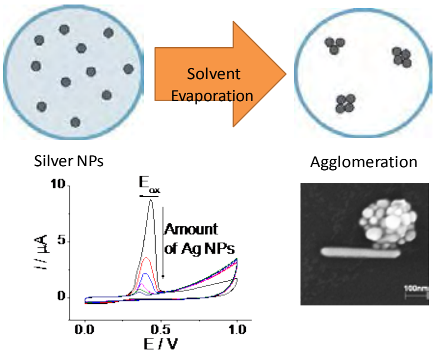
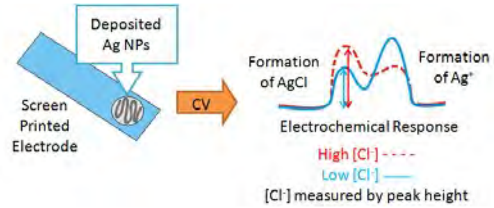
We report the anodic stripping of silver nanoparticles (Ag NPs), demonstrating both its suitability for the determination of concentration and size of Ag NPs on electrode surfaces and for gaining information of the electrolyte.



Schematic diagram of effects of surface coverage on oxidation peak potential, proving surface agglomeration of Ag NPs



Schematic diagram of chloride ion concentration determination with Ag NPs modified electrode

The first section provides analytical expressions for the size and surface coverage dependency of anodic stripping voltammograms of oxidising metallic NPs. For reversible electron transfer, two limits are studied: that of diffusionally independent NPs and the regime where the diffusion layers originating from each particle overlap strongly. The derived analytical expressions are applied to the stripping of Ag NPs from a glassy carbon electrode. The stripping peak potentials at high surface coverages of silver and low surface coverages of silver are found to give information on the diffusion layer thickness and NPs size respectively. Agglomeration of the NPs was shown to occur on the electrode surface.

The second section concerns the use of Ag NPs modified electrodes as a novel chloride sensor. The presence of chloride ions in the electrolyte for electrochemical oxidation of Ag NPs give two voltammetric signals which relates to the oxidation of silver to silver chloride and silver(I) ions. This signal at the lower potential has a peak height which correlates linearly with chloride ions concentration. Furthermore, chloride ion levels of standard solutions and diluted synthetic sweat samples are measured accurately with the Ag NPs modified electrodes. This concept can be applied to develop a point-of-care system for preliminary screening of cystic fibrosis (CF) as CF has a characteristic condition of high sweat chloride content.

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Keynote

Electrochemical Study of a Tyrosine Radical in an Asymmetric Three-Stranded Coiled Coil Peptide

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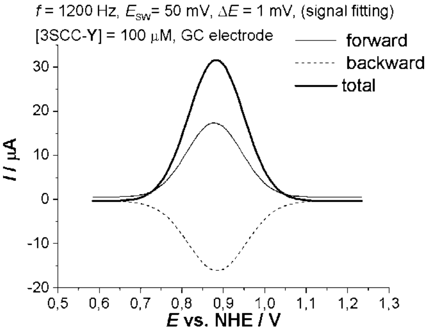
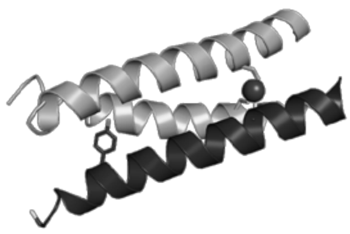
Three-stranded coiled coil peptides (3SCC) are a bottom-up approach to the *de novo* design of model peptides. These well-known self-assembling structures can be engineered to perform catalytic reaction [1] or to contain specific amino acids. Tyrosine (Y) radicals play a key role in photosystem II, eliciting several fundamental studies of Y oxidation in artificial peptides [2]. Y oxidation is a proton- coupled electron transfer (PCET), in which electron and proton transfers can be concerted or stepwise events, as previously discussed for phenol [3]. However, Y radicals are short-lived because of coupling reactions, hampering electrochemical studies of Y oxidation. This calls for a peptide design encaging and protecting the radical, as well as novel experimental approaches. Our strategy is based on an asymmetric 3SCC: only one of the three strands features the Y residue, while the others self-assemble in a trimeric bundle. Thus, the Y residue is buried in the core of the 3SCC, impairing coupling reactions. Additionally, a terminal cysteine residue allows the entire 3SCC to be grafted on Au electrodes. The oxidation of the Y residue was investigated with cyclic and square- wave voltammetry (SWV). A prolonged lifetime of Y radicals in the 3SCC was showed with respect to free, solution-phase Y. Insight into thermodynamics (Pourbaix diagrams) and kinetics (Y radical lifetime) was obtained for both solution-phase and Au-grafted 3SCC. Preliminary studies on intramolecular PCET to a base (histidine, H) have been performed with a modified version of the Y- carrying strand with neighbouring H and Y residues.





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A New Family of Oligomeric, Redox-Active Metal Complexes as 'Molecular Wires'

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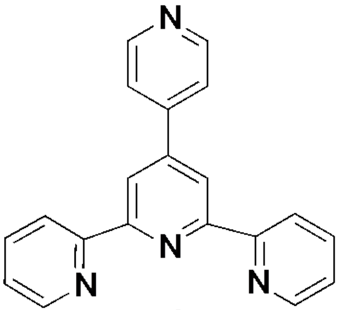
The ligand 4'-(pyridin-4-yl)-2,2':6',2"-terpyridine (1) has been used to synthesise octahedral complexes $[Co(1)_2]^{2+}$, $[Fe(1)_2]^{2+}$ and $[Ru(1)_2]^{2+}$ (as PF_6 salts). By using the relative inertness of Ru(II) and Ru(III) complexes with terpy ligands, well-defined linear oligomeric complexes $[(1)Ru(\text{-}L)Ru(1)]^{4+}$, $[(1)Ru(\text{-}L)Ru(\text{-}L)Ru(1)]^{6+}$ and $[(1)Ru(\text{-}L)Ru(\text{-}L)Ru(\text{-}L)Ru(1)]^{8+}$ (where 'L' is 1,4-di([2,2':6',2"-terpyridin]-4'-yl)benzene) have also been prepared and characterized. Scanning tunneling microscopy-based techniques have been employed to measure the electrical properties of metal | single molecule | metal junctions involving these complexes, using their terminal pyridyl groups as contacts. This paper will discuss the length dependence of the conductance of the Ru(II) oligomers and its implications for the conductance mechanism (tunneling or hopping?), and the electrochemical potential-dependent conductance of $[Co(1)_2]^{2+}$ (measured in ionic liquid).



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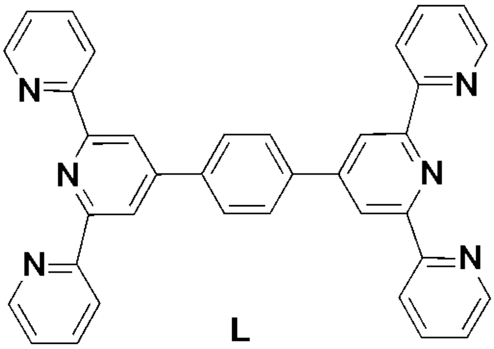

L

Electrochemical Formation/Reduction of PtO on Bulk Pt Electrode at Elevated Temperature in Concentrated H3PO4

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High temperature fuel cells with proton exchange membrane (HT PEM FC) represent viable compromise between high temperature and low temperature fuel cells (LT FCs). They are much less sensitive to catalyst poisoning than LT FCs and their operating temperature of 150-200 °C does not restrict their utilization to rather stationary applications. Most common PEM membranes used in HT PEM FC's are based on polybenzimidazole doped with concentrated orthophosphoric acid (H_3PO_4). However, combination of elevated temperature and H_3PO_4 can under certain conditions lead to a gas diffusion electrode (GDE) degradation. It can be expected that rate of such degradation will increase in the case of HT PEM FCs compared to LT PEM FCs due to higher operating temperature. GDE usually consist of precious metal (Pt) nanoparticles dispersed on various forms of high-surface carbon. Detailed information on the GDE degradation in HT PEM FCs is still missing in literature. In principle the degradation can proceed by various mechanisms. One of them is Pt sintering due to Ostwald ripening (anodic Pt dissolution and redeposition) or Pt nanoparticle migration and coalescence. Extend of Pt sintering will most likely depend on the state of the Pt nanoparticles surface. Thus, it will depend on the presence and properties of surface oxide layer.

Aim of this work was to determine kinetics of PtO anodic formation and cathodic reduction on the bulk Pt electrode in concentrated H_3PO_4. Voltammetry experiments were performed in 3-electrode arrangement in Teflon cell heated to required temperature. Working and counter electrodes were made of Pt. As reference electrode served calomel electrode saturated with KCl. To simulate conditions present in polybenzimidazole membrane based HT PEM FCs at 160 °C a 99% H_3PO_4 was used as electrolyte. Electrochemically active surface area of pre-annealed Pt working electrode was followed by means of hydrogen underpotential deposition method in 0.5 M H_2SO_4.

Results showed that at elevated temperature H_3PO_3 anodic oxidation originating from H_3PO_4 reduction within the preceding potential scan interferes with the studied electrode reactions. Therefore electrode potentials in vicinity of hydrogen evolution, where H_3PO_4 is being reduced to H_3PO_3, has to be avoided to prevent its generation. Thickness of anodicaly formed PtO layer is increasing with increasing electrolyte temperature. This is documented by increasing number of PtO monolayers formed at elevated temperature. Kinetic parameters of PtO formation/reduction at 160 °C are estimated by fitting the experimental voltammetric curves. Emphasis during fitting was placed on value of current density plateau of oxide formation, equality of anodic and cathodic charge and position PtO reduction peaks.

Financial support by the EU commission within the framework of the DEMMEA project FCH-JU-2008-1, No. 245156 is gratefully acknowledged.

The Use of Metallocenes as Redox Probes in Supercritical Fluids

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Supercritical fluids have received increasing attention due to their unique solvent properties, such as low viscosity, high mass transport and an absence of surface tension. Modest changes in temperature and pressure can dramatically affect the properties of the supercritical fluid. Previously we have demonstrated the electrodeposition of metals, namely copper[1], into small diameter nanopores (≈ 2.5 nm Ø) from supercritical fluids. As the pore diameter is decreased, a greater understanding of the phase behaviour inside the nanopores, along with the interaction of ions with the pore walls under supercritical conditions is needed.

There are still some fundamental issues that need to be addressed in supercritical fluids. As specialised equipment is required to achieve supercritical conditions, conventional reference electrodes such as the standard calomel electrode (SCE), cannot be used. To overcome this, a redox species can be used in combination with a *quasi*-reference electrode to provide an internal reference.

We will present fundamental studies of the solubility limits and diffusion coefficients of metallocenes (namely decamethylferrocene and cobaltocenium hexafluorophosphate) in supercritical fluids. We will also present studies of diffusion into nanopores using metallocenes of varying size and charge. These variations in size and charge will give a greater understanding of the phase behaviour in the nanopore under supercritical conditions, and the interaction of ions with the pore walls. These studies should offer further understanding of the optimal complexes and reagents suitable for electrodepositing various metals into small diameter nanopores (e.g. < 1 nm Ø) in supercritical conditions.

This work is part of the Supercritical Fluid Electrodeposition project (www.scfed.net) which is a multidisciplinary collaboration of British universities investigating the fundamental and applied aspects of supercritical fluids.

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From Double Layer Properties to Charge Storage in Nanostructured Supercapacitors with Ionic Liquids

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This lecture will summarize the results of a transatlantic cooperation supported by the EPSRC (UK) and NSF (USA), with a hub at Imperial College London. The program is focused on (i) understanding the structure and dynamics of ionic liquids at electrified interfaces - from flat interfaces to nano-confinement, and (ii) application of the gained knowledge for rationalizing the laws that control energy storage and power delivery of nanoporous super-capacitors. The studies include theory, computer simulations, and experiments. The following topics will be covered:

1. The basics: flat electrode/ionic liquid interface

Equilibrium structure of the electrical double layer and the capacitance-voltage dependence.

2. Charge-storage capacity of a single nanopore and nanoporous electrodes

a) Screening of interionic interactions in metallic nanopores and their effect on the specific capacitance of the nanopore, including dependence on the voltage and pore size (approximate and exactly solvable models for slit and cylindrical pore geometry, verified by computer simulations).
b) Pore-size distribution in nanoporous electrodes and optimization of energy storage.
c) From ideal metal to carbon electrodes. What will change?

3. The laws of charging dynamics in slit and single file pores

a) Phenomenological theory vs molecular dynamic simulation and experiments.
b) The difference between ionophillic and ionophobic pores.
c) The effect of the pore size, pore shape and voltage

4. The trade-off between energy storage and power delivery

Effects of pore size, shape, and operation voltage on Ragone plots.

Electrocatalytic Properties of Nafion and Carbon Nanotube/Hydrous Oxide Composite Electrodes: Oxygen Evolution & Reduction

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Oxygen electrochemistry is of fundamental importance for the major issue of cheap and renewable energy conversion and storage. Oxygen reduction is the normal cathodic reaction in electrochemical energy conversion devices such as fuel cells whereas oxygen evolution is the anodic process in the production of hydrogen through electrochemical water splitting [1]. Moreover, it is the oxygen reaction, whether evolution (OER) or reduction (ORR), that is the most energy intensive step in the operation of various fuel cells and electrolysers [2]. Consequently, there has been considerable interest in the development of efficient OER and ORR electrode materials [3]. Ultimately, optimizing the oxygen reaction is the key to maximising the potential of these devices as viable renewable energy solutions.

In the present work, novel nafion and single-walled carbon nanotube (SWCNT)/hydrous iron oxide composite films are discussed as dual OER/ORR electrode materials. These novel films can be prepared using a simple and scalable potential cycling methodology [4], resulting in distinct structural properties (Fig. 1). The electrocatalytic properties of the composite films with respect to both the OER and ORR are examined using a range of electrochemical techniques including steady-state Tafel analysis, electrochemical impedance spectroscopy and rotating ring disk electrode studies. It is shown that the nafion and SWCNT layers have a significant and positive effect on the electrocatalytic performance of the hydrous oxide film. In particular, the SWCNT composites exhibit higher currents (× 3) for the OER at lower overpotentials (>50 mV) while a reduction in Tafel slope from 60 mV dec^{-1} to 40 mV dec^{-1} is associated with nafion film modification.

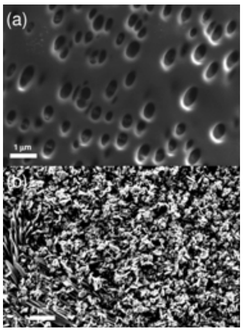

Fig. 1 SEM of (a) nafion and (b) SWCNT hydrous Fe oxide composite film.

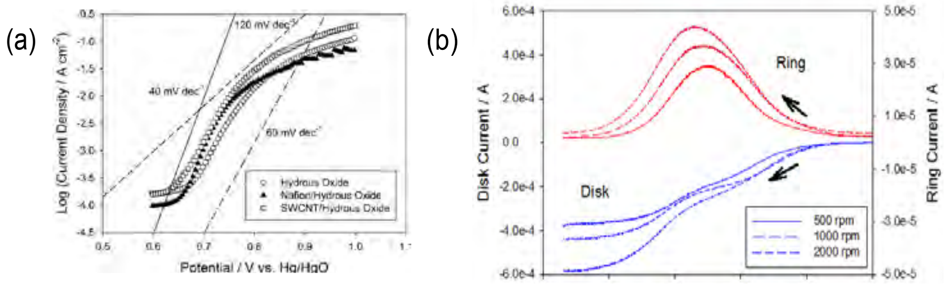

Fig. 2 (a) Steady-State OER Tafel plots for the composite/hydrous oxide films. (b) Voltammograms recorded at various rotation speeds for

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ELECTROCHEM
2013
Speaker Abstracts

Keynote

Advanced Applications of Deep Eutectic Solvent-Type Ionic Liquids in Materials Finishing for High Performance Manufacturing in Electronics and Aerospace

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Ionic liquid electrolytes continue to offer the possibility of delivering novel and exciting new electrochemical processes that are not possible in aqueous or conventional organic solvent media. However, many of the early hopes for these electrolytes have never been developed or scaled up because of concerns regarding economic cost or environmental impact. In contrast, the interest in deep eutectic solvents (DES) as a special case of ionic liquid-like electrolyte has continued to rise rapidly in recent years. This is because the DES electrolytes can be formulated from a mixture of salt and hydrogen bond donor. Typically these can be chosen from a wide range of low cost bulk commodity chemicals such as choline chloride and urea or glycol. The high ionic strength of these media offers ionic liquid-like properties whilst the electrolyte/solute chemistry and electrochemistry are dominated by the H-bond donor.

Here we will describe DES electrolytes that have been developed for specific advanced applications in electrochemical materials processing. These applications focus on high value strategic manufacturing sectors in aerospace and electronics. We will describe the unique role of DES electrolytes in metal dissolution single crystal castings of Ni based super alloys as well as in the formation of immersion coatings for high value, high performance printed circuit boards. In addition we will briefly describe some interesting aspects of DES electrochemistry in respect of charge/ion and solvent transfer dynamics in energy storage membranes.

Quantum Design of Ionic Liquids for Extreme Chemical Inertness, and a New Theory of the Glass Transition

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In many modern technologies (such as batteries and supercapacitors) there is a strong need for redox-stable ionic liquids. Experimentally, the stability of ionic liquids can be quantified by the voltage range over which electron tunneling does not occur, but so far quantum theory has not been applied systematically to this problem. Here we report the electrochemical reduction of a series of quaternary ammonium cations in the presence of bis(trifluoromethyl-sulfonyl)imide (TFSI) anions, and use non-adiabatic electron transfer theory to explicate the results. We find that increasing the chain length of the alkyl groups confers improved chemical inertness at all accessible temperatures. Simultaneously, decreasing the symmetry of the quaternary ammonium cations lowers the melting points of the corresponding ionic liquids, in two cases yielding highly inert solvents at room temperature. These are called hexyltriethylammonium bis(trifluoromethylsulfonyl)imide (HTE-TFSI) and butyltrimethyl-ammonium bis(trifluoromethylsulfonyl)imide (BTM-TFSI). Indeed, the latter are two of the most redox-stable solvents in the history of electrochemistry.

To gain insight into their properties, very high precision electrical conductivity measurements have been carried out in the range +20°C to +190°C. In both cases the data conform to the Vogel-Tammann-Fulcher (VTF) equation with “six nines” precision (R2 > 0.999999). The critical temperature for the onset of conductivity coincides with the glass transition temperature T_g. This is compelling evidence that supercooled ionic liquids behave as glasses. Finally, by focusing on the previously unsuspected connection between the molecular degrees of freedom of ionic liquids and their bulk conductivities, we are able to propose a new theory of the glass transition. This should have utility far beyond ionic liquids, in areas as diverse as glassy metals and polymer science.

On the Electrodeposition of Niobium and Copper in a Ionic Liquid for Multilayer Preparation

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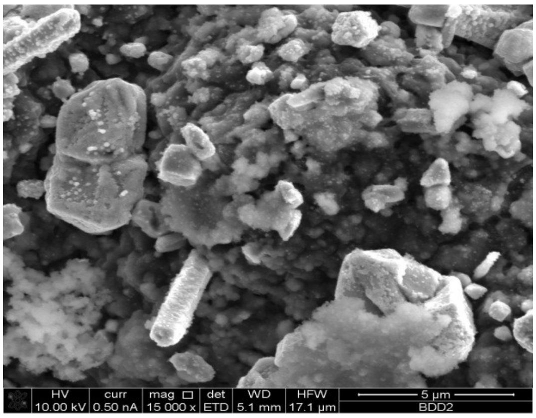
The present work deals with the electrochemical deposition of Nb and Cu for multilayer preparation in the ionic liquid 1-butyl-1-methyl-pyrrolidinium bis(tri-fuoromethylsulphonyl)imide ([BMP]Tf_2N).

The electrochemical behavior of copper and niobium ions has been studied by cyclic voltammetry and chronoamperometry. NbF_5 was used as a source of Nb and a copper sacrificial anode as a source of Cu. The experimental tests were carried out in a conventional three-electrode cell under nitrogen atmosphere, in order to avoid interference of water and oxygen, with Boron doped diamond as working electrode and a wire of platinum as reference and counter electrode. The influence of such parameters as the temperature and supporting electrolyte has been also examined. Cyclic voltammetries were performed at different temperatures and scan rates. According to the electrochemistry of the metals considered and based on the experimental results, the possible reaction path for the oxidation/reduction was proposed. Deposition tests were carried out at different potentials and the related samples were analyzed by SEM, EDX and XRD.



SEM analysis of Niobium-Copper on BDD electrode

Acknowledgments
This activity is supported by the European Community Framework Programme 7, Multiscale Modelling and Materials by Design of interface-controlled Radiation Damage in Crystalline Materials (RADINTERFACES), under grant agreement n. 263273.

Electrochemistry of Nanoparticles at the Liquid-Liquid Interface

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The polarisable liquid-liquid interface permits the separation of reactants and a high tuneability of the reactions through the applied electrochemical interfacial potential. Particles can be electrodeposited at this interface and/or be subjected to potential-dependent adsorption processes. Functionalisation of the interface is possible through adsorption of nanomaterials (as catalysts). A detailed picture of the particle-modified liquid-liquid interface, however, is still lacking.

Nanoparticles adsorbed or deposited at the liquid-liquid interface (Fig. 1a) can be modified through deposition of a different metal and can catalyse electrochemical reactions. The liquid-liquid interface enables the electrochemical properties of nanoparticles to be probed without having to consider the influence from a supporting substrate and is a promising tool to combine metal electrochemistry with the advantage of having two solvents to transport reacting species.

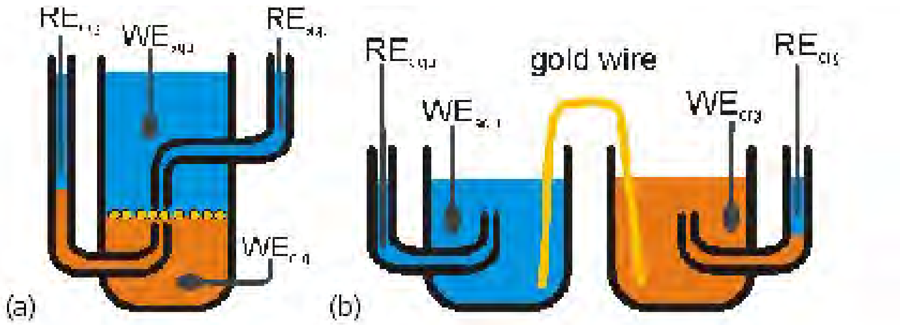

Figure1

This is relevant because liquid-liquid based systems are often used for the synthesis of metallic nanoparticles via electron transfer, but the mechanistic aspects of such processes are far from clear Nanoparticles adsorbed or deposited at the liquid-liquid interface can be modified through deposition of a different metal and can catalyse electrochemical reactions. The liquid|liquid approach therefore sheds light on the origin of the catalytic effect of different kind of nanoparticles, in the absence of a solid substrate, as will be presented for particles adsorbed at the water|1,2-dichlorobenzene interface. In addition first results of copper deposition onto gold particles adsorbed at the liquid-liquid interface will be presented. The results obtained can be directly linked through the bipolar setup, the two half cells of the liquid|liquid setup are connected only through a metal wire (Fig. 1b), to solid liquid electrochemistry.

Progress in the Supercritical Fluid Electrodeposition of Germanium Nanowires

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There is substantial interested in the use of supercritical fluids for the formation of next generation electronic devices in material science. Supercritical fluids have the inherent advantage over conventional solvents in that they exhibit a low surface tension. This enables them to penetrate fine structures which act as a template. Combining the use of electrochemistry within supercritical fluids allows for the electrodeposition of materials into templates to give nanoscale structures. This has been demonstrated for the electrodeposition of Cu nanowires [1].

A more challenging and technically interesting material to electrodeposit it elemental germanium as it is used extensively within the electronics industry. However this is not a trivial route as germanium precursors are very reactive and a large overpotential is required to induce electrodeposition of germanium thin films.

The electrodeposition of germanium from supercritical difluoromethane was reported recently [2]. Here, elemental germanium films where formed on planar electrodes. This work has continued and the electrodeposition of germanium to form higher quality electrodeposits on both planar and template electrodes have been investigated. It is the purpose of this talk to explain the electrochemistry behind this process as well as present materials formed from the electrodeposition of germanium into template electrodes.

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This work is presented as part of the SCFED project (www.scfed.net)

An Electrochemical Cathodic Route to the Production of Few Layer Graphene

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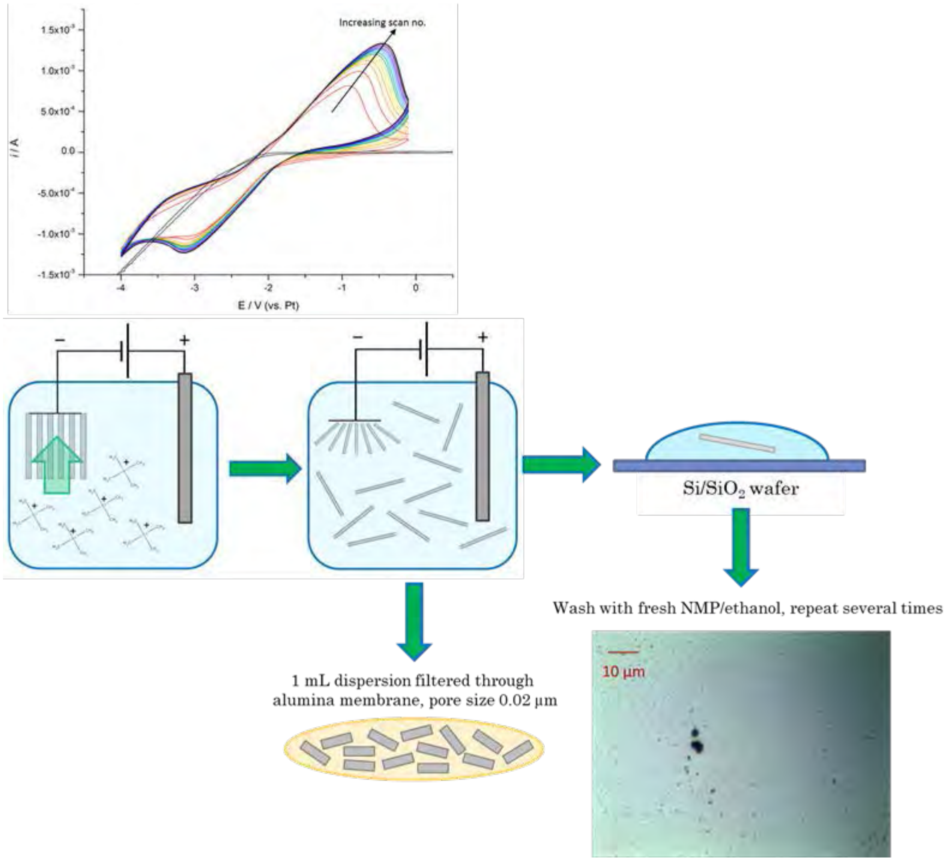
We present a non-oxidative method for the production of graphene *via* the intercalation of tetraalkylammonium cations into a graphite electrode (HOPG and a graphite rod). Significantly, in contrast to more common anodic intercalation routes, this work is cathodically controlled, to avoid any undesired oxidation leading to graphene oxide (GO) products/materials. The procedure utilises intercalated species of comparable size to the interplanar spacing of graphite (0.354 nm) in order to electrochemically expand the graphite source and aims to avoid the use of secondary processes such as sonication in order to maintain large lateral flake sizes.

Essentially, intercalation between every pair of neighbouring graphene sheets is necessary for the exfoliation of monolayer graphene, and therefore the choice of intercalating species is important. A range of species have been investigated for their suitability, as well as source electrode materials and solvents.

Flakes produced by this method have been characterised by Raman spectroscopy, atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS).



Redox Chemistry of Insulators: Voltammetry of Polystyrene Nanospheres

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Electrochemists are usually interested in redox processes that take place on the surface of conducting surfaces; however the focus of this talk is the electrochemistry of a non-conducting material, namely polystyrene. Using nanobeads, with a high surface atom to bulk atom ratio, allows us to investigate redox chemistry associated with the surface of this material. By immobilising the polystyrene nanobeads onto the surface of an electrode we can determine, using voltammetry, the potentials at which they undergo oxidation and reduction. We also use IR spectroscopy and XPS to determine changes to the surface chemistry of the materials under different redox conditions.

The motivation of this work is to understand how insulating materials may accumulate surface charge, for example during electrostatic charging (tribocharging or contact electrification). The mechanism of this well-known phenomena is still not fully understood, despite many decades of study. Recently models of ion transfer [1], electron transfer [2], material transfer [3] and formation of surface mechanoradicals [4] induced by deformation [5] have all been put forward. Here we explore whether an electron transfer model for charge accumulation by insulators is feasible, based on the potentials at which we observe redox chemistry taking place. Additionally we subject the polystyrene nanobeads to different forms of mechanical agitation / deformation to determine the resulting effect on the electrochemical response. We observe that physical agitation of the polystyrene beads results in an enhanced electrochemical response, similar to that observed for beads after chemical oxidation. The implication for the mechanisms for tribocharging will be discussed in the light of these results.

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Nucleation and Growth of Pd Nanodeposits in Lyotropic Liquid Crystal Mixtures

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This project aims to prepare surfaces with controlled size and dispersion of nanoparticles by electrodepositing palladium in presence of a surfactant. Nanoparticles are known to enhance catalytic performance and reduce the amount of noble metal required to prepare active surfaces.[1] The work presented here focuses on the early stages of the electrodeposition of Pd from different aqueous mixtures of octaethyleneglycol monohexadecyl ether ($C_{16}EO_8$). In water this non anionic surfactant behaves as a liquid crystal and the mixtures were chosen to explore its micellar and hexagonal phases. Pd nanoparticles were electrodeposited on various carbon substrates for different deposition potentials and deposition times. Scanning electron microscopy(FEG-SEM), voltammetry and chronoamperometry were used to characterize the palladium centres. The particle size, substrate electroactive area and roughness factor were estimated. Theoretical models were used to investigate the effect of the surfactant on the nucleation and growth of the Pd nanoparticles.

The electroactivity of the Pd nanoparticles prepared in the different liquid crystal mixtures was tested with the oxidation ot ethanol, oxidation of formic acid, oxygen evolution reaction and oxygen reduction reaction. The presentation will describe typical results for the preparation, characterisation and catalytic activity of the particles prepared.

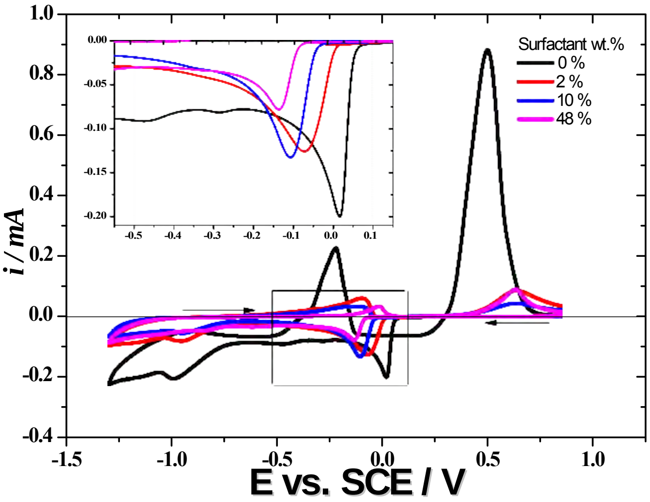

Figure 1: Cyclic voltammograms recorded on 3 mm Ø glassy carbon discs in aerated 10 mM $(NH_4)_2PdCl_4$ + 0.5 M KCl with different concentrations of $C_{16}EO_8$ at υ=10 mVs^{-1}. The inset shows where Pd deposition was studied.

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Electrochemical Behaviour of Mono- and Multi-Layer Graphene on Various Substrates

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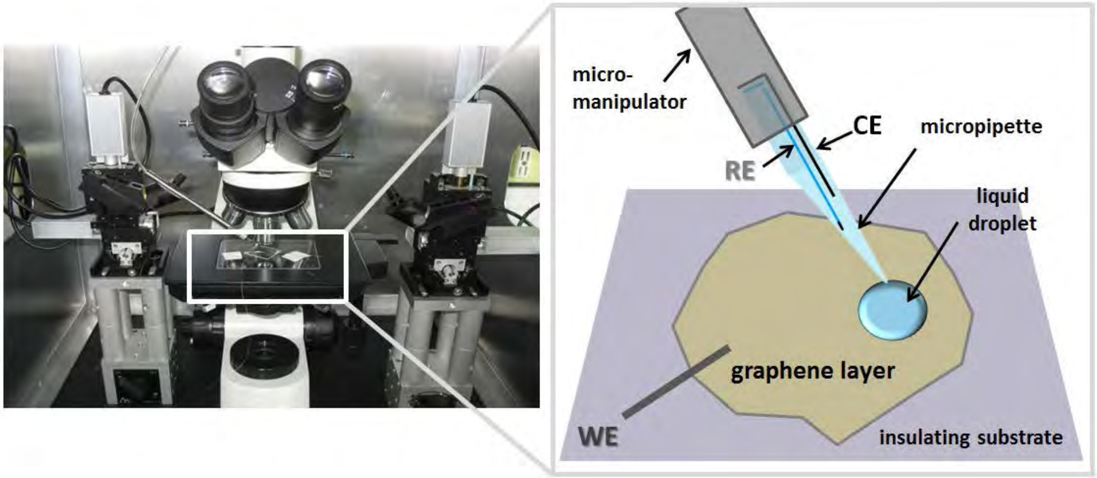
Electrochemical response of mono-layer and multi-layer graphene electrodes, prepared using both mechanical exfoliation and chemical vapour deposition, is presented. Graphene flakes were used as working electrodes in a micro-droplet arrangement.

Experiments were carried out using optical microscopy and a micromanipulator, which enabled precise deposition of controlled-size droplets on the flake surface. The insulating substrates used for flake preparation include inorganic materials and organic polymers. Raman spectroscopy was also used to track changes in the graphene structure induced by the electrochemical measurements.

The stability of the droplets on the surface depends on various factors, such as the solvent choice, electrolyte content, number of graphene layers, underlying substrate and method of flake preparation. The redox couple, number of graphene layers, presence of defects and nature of the substrate are all shown to have a significant effect on the electrochemical activity.



Keynote

Understanding the Link Between Atomic Structure and Reactivity at the Electrochemical Interface

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Discovering the fundamental principles that govern electrochemical reactivity is the key to the design of new materials for a range of scientific applications, particularly in energy-related technologies. Such information can only be obtained from model systems with well-defined elemental reaction sites using state-of-the-art instrumental probes. Improvements in the fundamental understanding of electrochemical interfaces have begun to revolutionize the development of materials that can solve the challenging problems of clean energy production, conversion and storage. These advances have enabled an unprecedented level of detail in the understanding of the atomic-level structural and electronic characteristics of metal-electrolyte interfaces to be attained. In turn this has formed the basis for predictive ability in tailor-making a new generation of electrocatalytic materials that are urgently needed to address the delivery of reliable, affordable, and environmentally-friendly energy.

The deposition of a foreign metal on a metallic substrate, in particular underpotential deposition (UPD) of a single monolayer, has been widely studied in this respect as it represents a methodology for structure formation that is both versatile and reversible, in contrast to structure formation in the ultra-high vacuum (UHV) environment. With emergent interest in materials such as core shell nanoparticles in which the surface atomic layer of the nanoparticle is a different metallic element to that which forms the core, there is a renewed interest in understanding the physical properties of the two-dimensional metal layer and its interaction with adsorbing species. In model electrochemical systems, surface x-ray scattering (SXS) is a unique probe of both the atomic structure of the electrode surface and the ordering in the electrolyte adjacent to the electrode surface and can also give insight into the electron transfer at the interface. Such measurements have been used to probe a wide range of electrochemical phenomena, for example, metal deposition, the adsorption and ordering of spectator species and the adsorption and reaction of reactive species. Recent results will be presented illustrating how phenomena such as surface alloying, thin film growth and surface restructuring can be linked to electrochemical reactivity and stability.

Probing Electrocatalysis at Nanostructured Materials Using Combined Scanning Electrochemical–Scanning Ion Conductance Microscopy (SECM-SICM)

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Scanning electrochemical microscopy (SECM) and related techniques combine the wealth of information that can be gained from analytical electrochemistry with the spatial resolution of scanned probe microscopy (SPM). Advancing such techniques towards the nanoscale requires multiple refinements, the most important of which are the miniaturization from the conventional 10-25 µm electrode diameter and the introduction of accurate positional feedback (to prevent convolution of topography and activity).

Several approaches to introduce positional feedback to SECM have been developed, the more established of which are combined SECM-atomic force microscopy (AFM)[1] and shear force-SECM,[2] though adoption is still not widespread. A more recent method is combined SECM-scanning ion conductance microscopy (SICM),[3] which provides the notable convenience of requiring no further hardware for positional feedback measurement other than electrodes and current amplifiers. This technique can provide impressive resolution on a range of samples using dual channel capillaries incorporating a carbon nanoelectrode.[4]

A major challenge is to increase the functionality of this technique, to move from simple outer sphere electrochemical mediators to small scale sensing of local environments relevant to functional processes, such as pH and concentration of dissolved gases and contaminants, and also to improve the resolution towards the nanometer scale. Herein we present our work towards these goals; incorporating functionalization of carbon nanoprobes for detection of species involved in electrocatalytic processes relevant to key energy applications, using oxygen and proton reduction at nanostructured surfaces as exemplar systems. A range of measurement modes and novel experimental configurations pertinent to these systems are discussed.

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Electrocatalysis at Au-Pt and Au-Rh Nanoalloys

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Nanoparticles have been extensively studied because of the distinct properties that can occur at short length scales.[1] With recent advances in synthetic techniques, it is now possible to control the size and shape of gold nanoparticles, enabling the investigation of the influence of these parameters on nanoparticle properties.[2,3] In addition, there has been much interest in bimetallic particles, for which variation of the composition and chemical ordering can also be used to tune properties.[4] Au- Pt and Au-Pd have attracted particular attention in the field of catalysis, including electrocatalysis, and the composition and distribution of the constituent metals has been shown to affect activity and selectivity.[5]

We present a study of the effect of surface composition on catalytic activity using two systems: Au-Rh and Au-Pt. In each case, the thermodynamically stable system should be a transition metal core with a Au shell. Hence, a sequential deposition approach was used, where Rh and Pt were deposited onto Au seed nanorods to produce bimetallic surface compositions.

Rh forms small, three-dimensional clusters on Au nanorods and electrochemical measurements show an increase in Rh surface area as the Rh:Au ratio is increased. These catalysts show a progressive increase in activity towards oxygen reduction in acidic solution as the Rh loading is increased. The pathway shifts from a 2-electron reduction, forming hydrogen peroxide, to a 4-electron reduction, forming water, as the Rh content is increased. The catalyst with the lowest Rh loading (10% by mole) exhibits slightly enhanced selectivity towards hydrogen peroxide than Au nanorods.

Pt also forms small clusters on Au nanorods, with preferential deposition on the ends of the rods. We have developed a selective blocking method to control the deposition of Pt onto Au, to form smoother, more even deposition. This has the effect of increasing available Pt surface area, which has a strong influence on electrocatalytic activity. The catalysts are more active towards both carbon monoxide oxidation and oxygen reduction and the selectivity of the latter tends towards the formation of water rather than hydrogen peroxide.

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Pt-Pb Bimetallic Thin Film Electrocatalysts

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Bimetallic nanostructures represent a promising route to modifying the electronic and geometrical properties of catalysts, while lowering the noble metal content. A recent, electrodeposition-based, method for achieving atomic scale controlled growth of noble metal is known as the Surface Limited Redox Replacement Method (SLRR) [1]. This method involves the underpotential deposition (UPD) of a non-noble metal, followed by the electroless replacement of the UPD metal by a more noble component. The SLRR method has been successfully applied to the deposition of Pt thin films on Au, using Cu [1], Pb [2] or most recently H [3] UPD as a sacrificial layer.

In the past few years the SLRR method has attracted a lot of attention from the electrocatalysis and electrodeposition community. It has been demonstrated as an effective approach for the design of highly active catalyst materials (so called Pt monolayer electrocatalysts) [4], functional surfaces [5] and growth of ultrathin epitaxial films [2].

Nanoscale platinum-lead (Pt-Pb) structures are of current interest as powerful catalysts relevant in many fuel cell reactions; in particular, formic acid electro-oxidation (FAO) [6, 7], a system in which higher activity has been shown. Here, we will present the optimization and development of the SLRR protocol in single cell configuration using Pb UPD to design ultra-thin overlayers of Pt_xPb_{1-x}. We will demonstrate that by controlling the potential of redox exchange, a surface alloy can be formed and its composition can be varied.

As deposited Pt-Pb thin film alloys have been characterised and examined by cyclic voltammetry and chrono-amperometry. We have examined the correlation between the alloy composition and electrocatalytic activity dependent on Pb content. Our preliminary results suggest a strong third body effect from Pb on the poisoning of the Pt-Pb surface.

The surface morphology and structure is studied with Kelvin Probe Force Microscopy (KPFM) and AFM. We demonstrate quasi 2-dimensional growth and random alloy formation in the deposited films. The composition of the deposited thin films has been examined by XPS and electrochemical measurements.

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Effect of Iron-Doping on Oxygen Electrocatalysis at Barium Strontium Cobaltite

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The efficiency of many energy storage and conversion systems such as hydrogen fuel cells, rechargeable metal-air batteries and water splitting is determined by the kinetics of the oxygen evolution (OER) and oxygen reduction (ORR) reactions.[1] Interestingly, precious-metal-free perovskite oxides display bifunctional activity for both the OER and ORR. Recently, Suntivich et al. have established electron occupancy at the e_g orbital as the key descriptor for their electrocatalytic activity.[2] These authors concluded that $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-}$ (BSCF), a material extensively investigated as oxygen permeable membrane in solid oxide fuel cells, exhibits the highest catalytic activity towards OER. However, little is known about the electrochemical properties of this material, in particular the nature of the surface intermediates as function of the applied potential. In this contribution, we elucidate some of the complex properties of BSCF by studying not only OER but also ORR in alkaline solutions, focusing on the effect of Fe/Co ratios on $Ba_{0.5}Sr_{0.5}Co_xFe_{1-x}O_{3-\delta}$ $(0 \leq x \leq 1)$.

$Ba_{0.5}Sr_{0.5}Co_xFe_{1-x}O_{3-\delta}$ powders were prepared by a new route based on an ionic liquid/cellulose system. The metal precursors are solubilised in 1-ethyl-3-methylimiamidizolium acetate, followed by the addition of cellulose and calcination at 950˚C. When calcined, ionic liquid precursors yield high quality and phase pure products. XRD, EDX and elementary mapping provide strong confirmation of the BSCF composition and phase purity.

Nafion containing inks of carbon supported BSCF were drop-casted onto the disc of a rotating ring-disc electrode. Potentiodynamic experiments carried out in O_2 saturated alkaline solution revealed that oxygen reduction is coupled to a surface confined reduction step at approximately -0.1 V vs. RHE, which is not observed in the absence of O_2. Products during ORR were detected at the Pt ring electrode set at a fix potential. The current at the Pt ring exhibits a complex dependence on the potential applied to the BSCF supported electrode. Detailed analysis of the ring responses suggest that radical species are generated from the reduction of OH adsorbed at the B-sites of the perovskite. We shall establish key links between the intermediate species observed in the ORR and the OER.

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Dispersion and Assembly of Graphitic Particles at the Liquid|Liquid Interface and their Catalysis of Reduction Reactions

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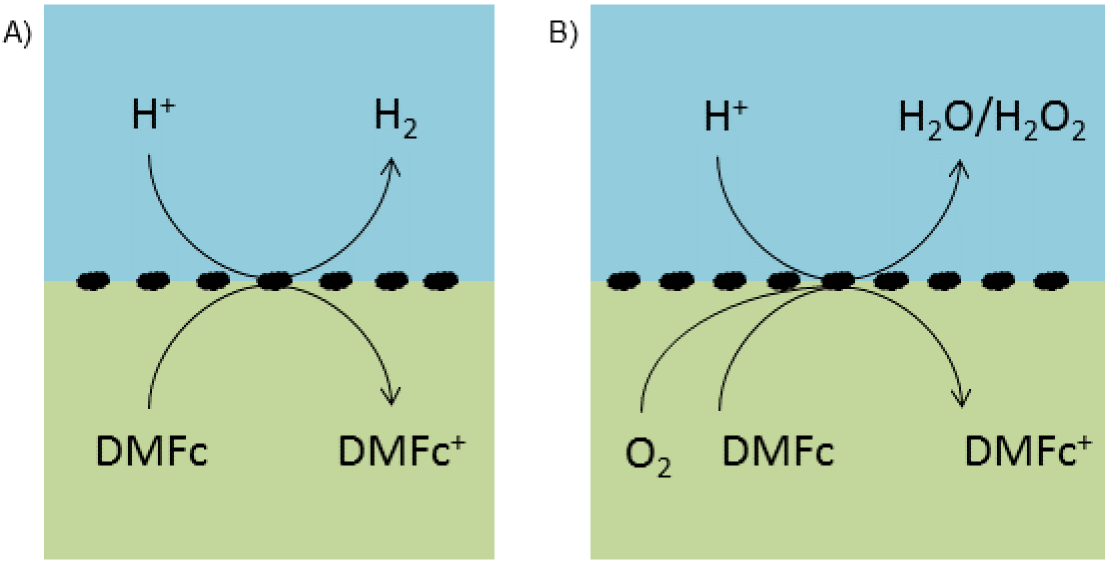
The use of graphite particles, stably attached at the interface between two immiscible electrolyte solutions (ITIES), as catalysts for reduction reactions across the ITIES is presented. The aqueous phase is acidic, while the organic phase contains a reducing agent. Two possible reduction reactions can occur: A) Direct reduction of aqueous protons by the organic reducing agent at the ITIES to produce H_2, B) Proton coupled reduction of oxygen dissolved in the organic phase to produce H_2O or H_2O_2. Both reactions are illustrated schematically below.

These reactions are known to proceed using catalysts such as MoS_2 , both un-supported [1] and supported on graphene [2], cobalt porphyrins [3] and Pt [4]. Un-modified graphite, which has not been reported to have catalytic properties, was used in this work. This was in order to investigate whether reduction reactions at the ITIES require an active catalyst, or simply an electron conductor between the two liquid phases, to facilitate the reduction reaction.

Further to this, the attachment of particles at the liquid|liquid interface is well established and an obvious methodology to use when studying the electrochemistry of particles at the ITIES. However, the effects of electrolyte on such processes are not well understood. Therefore, the effect of the organic phase electrolyte on the dispersion and attachment of graphitic particles at the liquid|liquid interface has also been investigated.



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Electrochromic and Colorimetric Properties of Nickel(II) Oxide Thin Films Prepared by Aerosol- Assisted CVD

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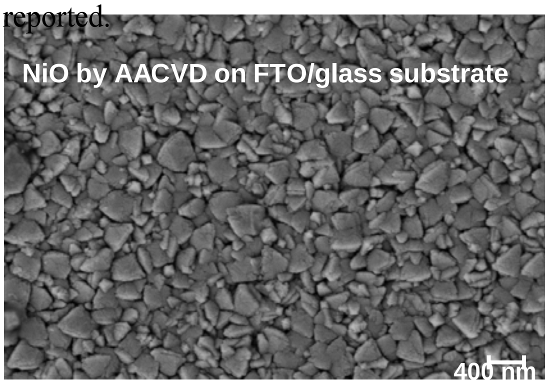
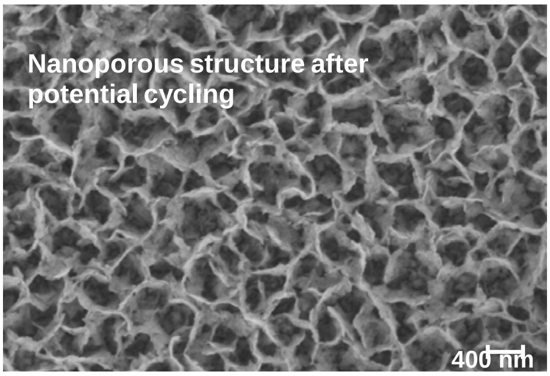
Electrochromic materials have the property of a change, evocation, or bleaching of colour, as effected by an applied electrical potential, sufficient to induce an electrochemical redox process [1]. Applications of electrochromic materials include 'smart' windows for architectural applications, and anti-glare car mirrors, based on the modulation of transmitted and reflected visible radiation, respectively [1].

Aerosol-assisted chemical vapour deposition (AACVD) [2] is here reported for the preparation of thin films of NiO on fluorine-doped tin oxide (FTO)-coated glass substrates. As-deposited NiO film exhibited a nanoscale morphology of octahedral-like grains (Fig. 1). On oxidative voltammetric cycling in aqueous KOH (0.1 mol dm^{-3}) electrolyte the morphology gradually changed to an open porous structure (Fig. 2). The films showed good electrochromic properties with reversible switching between transmissive light green and deep brown states. Using a calculation method [3] based on the integration of experimental spectral power distributions derived from in situ visible region spectra over the CIE 1931 colour-matching functions, the colour stimuli of the NiO-based films, and the changes that take place on reversibly switching between the 'bleached' and coloured states are reported.





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Electrodeposition of Ternary Alloys for Phase Change Random Access Memory Applications

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Phase change random access memory (PCRAM) devices are a strong contestant in the on-going search for faster, more stable and more compact digital data storage and are a potential competitor to the popular FLASH drives in use today.[1,2] Conventionally PCRAM devices consist of a thin film of phase change material addressed by an underlying array of individual heaters or electrodes. In order to drive the miniaturization of PCRAM devices forward, a distinct separation between individual memory cells must be introduced to avoid corruption of neighbouring cells during the write/rewrite processes. This separation can be achieved through preparation of the phase change materials as pillar structures within an insulating template, as illustrated in Figure 1.

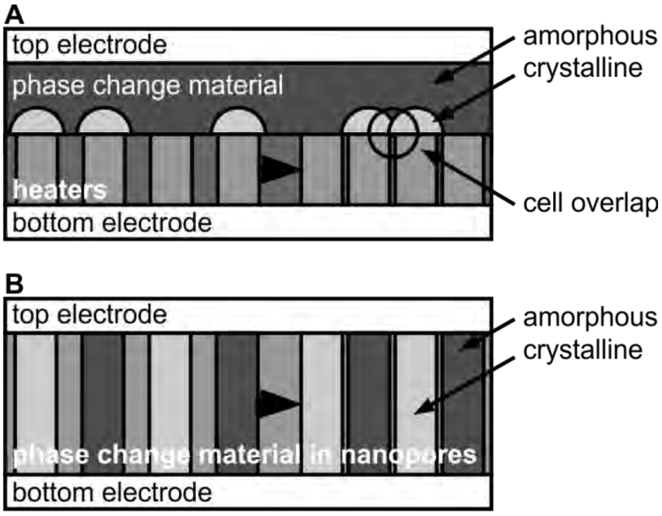

Figure 1. Schematics of phase change random access memory device structures. The downscaling issues with the thin film structure are highlighted (A) and an alternative device structure is shown (B).

We investigate the electrodeposition of phase change materials, such as Sb_xTe_y and $Ge_xSb_yTe_z$, from an inorganic electrolyte system based on dichloromethane and tetrabutylammonium chlorometallate salts. The effect of the electrolyte composition and the deposition potentials on the composition and morphology of the obtained materials will be discussed. Limiting conditions will be explored for the case of the $Ge_xSb_yTe_z$ compounds that allow the combination of deposition conditions that are sufficiently cathodic to incorporate germanium into the material and yet allow accurate filling of the micropatterned electrode substrates. The phase change behaviour of the prepared materials will also be investigated.

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Electrodeposition of n-Type Bismuth Telluride Alloys for Highly Efficiency Thermoelectric Energy Conversion

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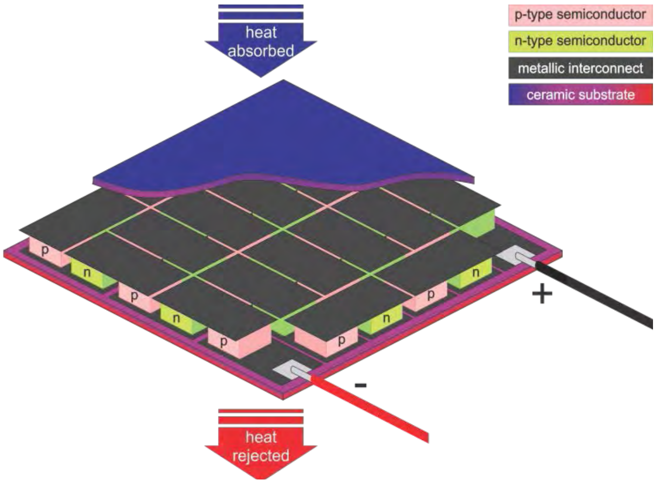
Thermoelectric Devices



Power harvesting from thermoelectric (TE) devices is seen as a highly promising route towards sustainable energy, as electricity can be generated from natural or anthropogenic thermal gradients in the environment. This is, however, contingent on fabricating materials with higher TE efficiencies than currently available, as it cannot always be assumed that large gradients will exist. Bismuth telluride alloys are currently the best commercially available TE materials for applications at room temperatures. Theoretical calculations predict that low-dimensional nanostructures of these materials can spectacularly enhance the figure of merit from currently ~1 to higher values of up to 14 [1].

Electrochemical Fabrication

Whilst a wide range of fabrication techniques exist for the production of TE materials, such as single crystal growth, thin film technologies and bulk powder syntheses, these have proven to be expensive and/or difficult to achieve. Electrochemical deposition provides an attractive low-cost, room temperature and scalable route to the fabrication of high-quality TE materials such as bismuth telluride alloys [1,2].

Microstructural and Physical Properties

The correlation of microstructural properties with TE properties is still a mandatory challenge in order to achieve further progress in this emerging field and has surprisingly received very little attention. The work presented here focuses on a detailed and systematic investigation of the microstructural and thermoelectric/electrical properties of electrochemically deposited bismuth telluride alloys. Doping of the alloys is shown to improve their TE performance.

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Electroless Processing for Nanoscale Interconnect Technology

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Electrochemical deposition for on-chip interconnect has over the past 15 years inspired many aspects of nanoscale electrochemical processing. The controlled deposition of copper in nanoscale features has facilitated the continued scaling of silicon electronics. At ever decreasing dimensions the issues in barrier/seed layer and active interconnect deposition and their nucleation become more critical. Electrochemical deposition in combination with atomic layer deposition (ALD) or chemical vapour deposition (CVD) may deliver the future scaling requirements. Alternative techniques such as electroless deposition should also be considered for future on-chip interconnect applications. This necessitates the development of novel electroless plating solutions to meet the demands of future devices.

Electroless processing has already shown significant potential for IC interconnect applications in self aligned capping layer deposition on Cu. However, the electroless deposition mechanism and the specific roles of the contributing constituents are not fully understood. Detailed electrochemical and microstructural characterisation is needed for a number of aspects of the electroless deposition process.

Dimethylamine borane [1] (DMAB) is a reducing agent that offers the possibility of selective electroless deposition at copper substrates and thus the use in copper interconnect capping. It can also be used to repair seed layers and even, with the use of particular additives, achieve the same type of superconformal deposition as currently used in electrolytic copper manufacturing lines.

Understanding the electroless deposition process requires in the first instance an assessment of the reducing agent reaction mechanism. DMAB is a versatile reducing agent capable of depositing many of the functional interconnect materials such as copper, cobalt and nickel [2-4]. The oxidation mechanism and the role of DMAB in the full electroless deposition solution is still unclear and additional analysis is required to assist with the implementation of electroless processing in widespread nanotechnology applications. This work will describe recent investigations of borane based electroless deposition and borane oxidation electrochemistry.

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ELECTROCHEM
2013
Speaker Abstracts

Keynote

Treatment of Dimethyl Phthalate by Sonoelectrolysis

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Phthalates are chemicals widely used in the manufacturing of plastics, stabilizers, dispersants, film formers and emulsifying agents, and as a consequence, many end-products contain these species. A great number of phthalates are well-known as endocrine disrupters and for some of them, exposure is even suspected to lead to development of breast cancer [1]. Combination of ultrasound irradiation with electrolyses seems to be an interesting topic in the treatment of wastewaters, because of the good properties of the conductive-diamond anode and the ultrasonic cavitation that has shown to be able to improve the mass transfer rate and also to promote the decomposition of water producing hydroxyl radicals and many oxidants from the interaction of these radicals with other species containing in the wastewater [2,3]. This work will study the influence of several operation parameters on the efficiency of the removal of dimethyl phthalate (DMP) and on the intermediates and product formation, trying to clarify if there is any synergistic effect on applying electrolyses and ultrasound irradiation. Both treatments have shown to be very effective, attaining the complete removal of dymethyl phthalate, carbon oxygen demand (COD) and total organic carbon (TOC) from the wastes in the range of concentrations (10^0-10^2 ppm of DMP) studied in this work. Current density influences on the efficiencies of DMP and COD removal and very strongly on the mineralization efficiency. Efficiencies decreases with increasing current density applied. This change is linear in the case of TOC indicating that processes occurring on the nearness of the electrode surface are very important to explain mineralization of DMP. The mineralization in chloride media is much less effective than in sulphate media, maybe because of the lower oxidation capability of the oxidants produced in chloride media with respect to those formed in sulphate media. Experimental results fit well to a first order kinetic. The change in the kinetic constants with current densities can be explained by an increase in the pseudo-steady state concentration of oxidants caused by current density. Ultrasound irradiation only produces small differences in the depletion of DMP but is improves significantly the COD depletion rate and it has an outstanding effect on the mineralization rate and efficiency. Very low concentrations of intermediates are produced during electrolyses and sonoelectrolyses, in most conditions studied, being monomethyl-phthalate, phthalate, hydroxy phthalate are the main aromatic intermediates, and maleic acid, tartaric acid and especially oxalic acid are the most significant non-aromatic intermediates found. Under the presence of chloride ions, electrolyses and sonoelectrolyses also yield chlorophenols as intermediates, caused by the reaction of hypochlorite with aromatic intermediates.

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[3] Sánchez-Carretero, A.; Rodrigo, M. A.; Cañizares, P.; Sáez, C. Electrochemical synthesis of ferrate in presence of ultrasound using boron doped diamond anodes. Electrochem. Commun. 2010, 12, (5), 644.

Degradation of Triclosan by Means of Sono-Photoelectrochemical Oxidation Processes with Conductive-Diamond Electrodes

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Actually, presence of Persistent Organic Pollutants (POPs) or emerging pollutants in waters and wastewaters is an important concern in many countries around the world. In this context, stricter legislations for the control of occurrence of these compounds in the aquatic environment are being developing.

Low concentrations of POPs can lead to toxic effects, affecting the endocrine system. Hence they become a potential risk for the human health [1]. Conventional treatments of wastewaters cannot degrade it completely. Thus, it is essential to get new technologies that can eliminate this type of pollutants from waters and wastewaters efficiently. Advanced Oxidation Processes (AOPs) are considered by many authors as a good option for the removal of POPs [2]. Specifically, Conductive-Diamond Electrochemical Oxidation (CDEO) is a very robust and effective technology to remove emerging pollutants. However, the principal problem of this technology is its high cost and its mass transfer limitations. In this context, an ultrasound generator and ultraviolet radiation can increase the process efficiency. Use of ultrasound entails the improvement of the mass transfer, promotion of the decomposition of water producing hydroxyl radicals and the electrohydraulic cavitations, growth and cyclical collapse of gas bubbles. On the other hand, ultraviolet radiation can generate and activate oxidant agent to degrade organic mass.

A large number of species such as antibiotics, hormones, surfactants, perfluorinated compounds, pesticides, analgesics or anti-microbial are considered as emerging pollutants. Triclosan, 5-chloro-2-[2,4-dichlorophenoxy]-phenol, is a broad-spectrum antibacterial agent. It is widely employed as an antiseptic or preservative in many personal care products (PCP) such as toothpaste and cosmetics. Because of its widespread use and persistence, it can be present in surface water, sediments, aquatic organisms, and even in human milk.

With this background, the goal of this work is to evaluate the combined use of CDEO with ultrasounds and ultraviolet-light irradiation to remove Triclosan from waters and wastewaters. Synthetic wastewaters polluted with this compound were electrolysed with conductive-diamond anodes in order to study the main characteristics of this process. In addition, the influence of the use of an ultrasonic generator and ultraviolet-light irradiation were studied. Results showed that ultraviolet and ultrasonic radiations can improve the process efficiency. The use of sonophoto-electrooxidation technology originates a synergic effect in the degradation of Triclosan (the process efficiency increases around 30 %). Reaction intermediates formed depends on the technology used indicating the use of ultrasounds and ultraviolet-light irradiation produces changes in the oxidation mechanism of Triclosan.

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Acknowledgements

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Wastewater Regeneration by Means of a Sono-Electrodisinfection Process with BDD Anodes

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Within the last years, the treated wastewater reuse has aroused a great interest in many countries due to the increasing water demand and the low rainfall. However, treatment techniques used by wastewater treatment facilities (WWTF) are not efficient enough to provide the quality that water needs to be reused. For this reason, different processes have been developed to obtain high quality regenerated water sources from treated wastewaters.

In Spain, the Law RD 1620/2007 establishes the juridical framework for the quality standard that regenerated water should fulfill depending on its use. This Law differentiates between urban, industrial, recreative, environmental and agriculture uses and it fixes the maximum threshold of microorganisms (nematodes and E. coli), total solids and turbidity that are allowable for regenerated water.

In this context, many different technologies have been studied to obtain reclaimed water with the quality established by the legislation. Thus, among the possible treatment techniques, conductive diamond electrochemical-oxidation (CDEO) has shown promising characteristics (robustness and great efficiency) to be considered as a good choice for disinfection [1]. Nevertheless, one of the drawbacks of electrochemical processes (processes which occur on the surface of an electrode) is related to the limitations in mass transfer. In order to improve the mass transfer of the system, it is possible to use an ultrasound generator, which not only enhances the mass transfer but also promotes the decomposition of water due to water sonolysis, with the subsequent production of hydroxyl radicals [2].

With this background, this work presents a combined CDEO with ultrasound for the disinfection of effluents from the municipal WWTF of Ciudad Real (Spain). Results show that E. Coli is completely removed at low current densities by the generation of oxidizing species during the electrolysis. Moreover, the use of an ultrasonic generator allows to increase the oxidants concentration and makes it possible to work at much lower current densities than those required without ultrasounds.

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Capacitive Deionization

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Capacitive deionization (CDI) is an energy-efficient water desalination technology based on using oppositely placed porous activated carbon electrodes to remove ions from water, see Fig. 1. CDI has similarities with the field of supercapacitors, but now the objective is water desalination, and thus the system must allow for flow of water through the cell. CDI can be operated using different electrical signals, either a constant cell voltage, or a constant current, or a mixed condition. CDI is an electrochemical non-Faradaic technology based on the capacitive storage of charge and ions. In CDI, upon transferring charge from one electrode to the other, ions are temporarily stored in the electrical double layers (EDLs) which form inside the micropores inside the carbon particles that constitute the electrode, see Fig. 2.

In our presentation we discuss the basics of CDI, and report on our recent results, including energy consumption in CDI, and desalination using electrode wires.

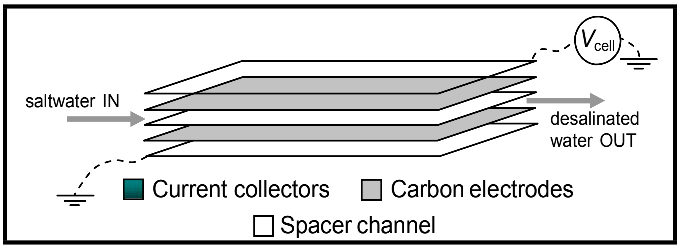

Fig. 1. Schematic representation of a capacitive deionization cell, where salt ions are stored in porous carbon electrodes after application of a cell voltage between the electrodes.

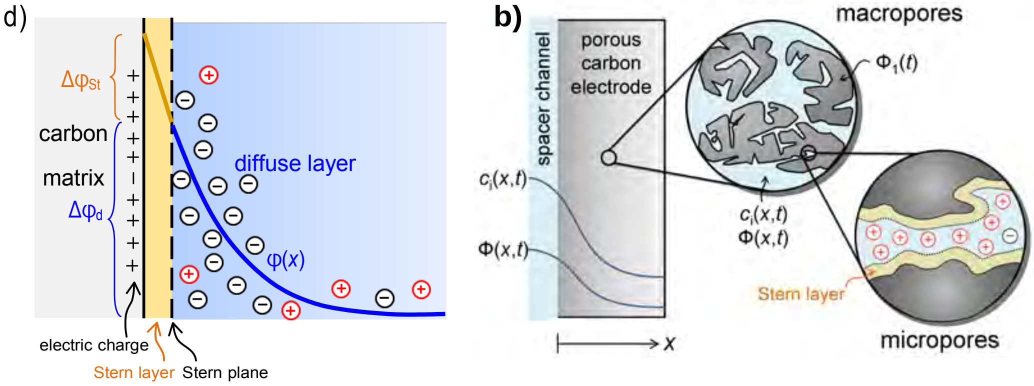

Fig. 2. Electrical double layer structure according to the Gouy-Chapman-Stern theory, and structure of porous carbon electrode.

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Immersion Coatings from Deep Eutectic Solvents, Precious Metal Coatings of Copper

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Immersion coatings of precious metals have wide ranging applications in the metal finishing and catalyst industries. Immersion coatings of silver[1] and gold[2] are used widely in the printed circuit board industry for surface protection. Additionally, immersion coatings of palladium,[3] platinum,[4] and gold[4] have all attracted interest in the area of heterogeneous catalysis. Deep eutectic solvents (DESs), a branch of ionic liquids, have been attracting growing attention in the areas of "green" solvents and metal processing.[5] Deep eutectics have found a niche by being easily synthesised, without the need for silver metathesis or strong acid base neutralisation.[5]

Here we present the electrochemistry of group 10 and 11 elements, in the deep eutectic solvent Ethaline 200. Exploiting the unique solvation properties of metal salts in Ethaline 200, it is possible to produce immersion coatings of precious metals on a copper substrate, without the need for acidic or basic solutions or additives. Immersion coatings of all the group 10 and 11 elements have been produced, including nickel and platinum. These coatings have been analysed using SEM, EDX, and XPS. Further to this, the mechanism of the immersion reactions, have been studied by CV (Figure 1) and QCM (Figure 2).

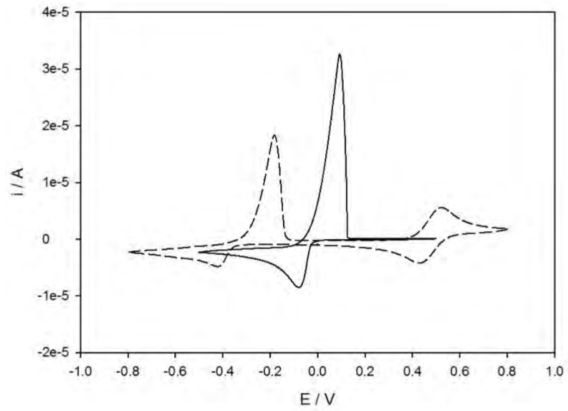

Figure 1: Cyclic voltammagrams of metal salts in Ethaline 200; WE: Pt disk 2mm, CE: Pt Flag, RE: Ag wire, Scan Rate: 10 mVS^{-1}. Dotted: 20 mM $CuCl_2$, solid: 20 mM AgCl.

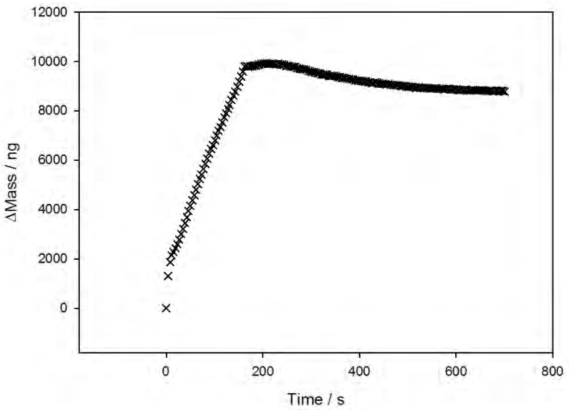

Figure 2: Change in mass Vs. time plot for Ag immersion coating on copper.

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Keynote

Electrochemically Fabricated of TiO2 Layer on Ti-6Al-4V Cylinders

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The need for artificial implants for bone and joint problems is gaining urgency due to the growing problem of osteoarthritis which affects 8 million people in the UK alone. Ti and its alloys are commonly employed as dental and orthopaedic implants due to their corrosion stability, mechanical characteristics and favourable biological interaction with bone. It has been shown that surface topography of implants can improve osseointegration [1].

The effect of electropolishing Ti-6Al-4V alloys in methanol-acid solutions on the genesis and growth of osteo-blasts has been reported by our group recently [2]. In that work, we showed that a nearly pure TiO_2 layer could be formed on the surface of the alloy during potentiostatic electropolishing by attainment of a equipotential surface at 9.0 V (vs. SCE). Experiments carried out using a Ti-alloy sheet, placed in a flat electrochemical cell, under these electrochemical conditions, showed improved cell genesis.

However, in order to carry our *in-vivo* experimentation, it is important to achieve the same surface modification on Ti-alloy implants, such as a pin, which can be implanted into animal models. In order to attain an equipotential surface on a pin or a cylinder, ElSyCA, an electrochemical software, was used to design a reactor where an equipotential cylindrical surface could be created. The Ti-alloy cylinder was to be located at the position where an equipotential surface of 9.0 V is obtained.

In order to verify that the reactor was capable of re-producing surfaces obtained in the flat cell, Ti-alloys were electropolished at a potential of 9.0 V. Impedance analysis was carried out to determine the resistance of the oxide films, and the roughness of the films was determined from optical profilometry. XPS studies were carried out to determine the surface chemistry of Ti cylinders. These experimental data were compared to the surface characteristics of the Ti-alloy sheets used in the earlier work. Our results showed that electrochemical reactors capable of replicating equipotential surfaces on complex (cylindrical) shapes could be designed using ElSy software which could be corroborated by experiments.

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Fabrication, Characterization and Photocatalytic Activity of Oriented Oxide Nanotube Arrays on TiW Alloy

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This work investigated the fabrication, characterization and influence of heat treatment on the photocatalytic activity of oriented oxide nanotube arrays on TiW alloy. Initially, the growth of self- organized oxide semiconductor nanotubes on a Ti-x%W alloy (x= 0.5, 2.5 and 5.0% wt) was studied as a function of the electrolytic solution (aqueous or organic) and anodization time. Ti alloys were fabricated by arc melting with non-consumable tungsten electrode and water-cooled copper hearth under argon atmosphere. The anodization experiments were carried out with a DC power supply and an acrylic electrochemical cell, with a platinum cathode and the Ti alloy anode separated by 2.5 cm. An aqueous solution of 0.2 M HF and two types of ethylene glycol solutions (0.2 M NH_4F and 0.2 M HF) were used as electrolyte solution. All the anodization experiments were carried out at 120 V with applied time that varied between 5 to 120 minutes. SEM-FEG was used to characterization the nanotubes and the X-ray fluorescence results confirmed that the composition of the alloys was as required. After anodization, the nanotubular oxides were annealed at 450, 500, 550, 600, 650 and 750°C in air atmosphere for 2 hours and then, cooled back to room temperature in a box furnace with a view to understand their crystallization behavior as well as the effect of this heat treatment on photocatalytic activity. The characterization of samples after heat treatment involved X-ray diffraction analysis. The photocatalytic activity of nanotubular oxide layer growth on pure Ti and TiW alloy was evaluated by measuring the photodegradation of the remazol blue reactive dye in a glass batch cell under UV irradiation. The dye degradation and discoloration of solution was monitored by total organic carbon and UV-vis spectroscopy analysis, respectively. The best results of anodization experiments were obtained when 0.2 M HF with ethylene glycol solution was used with the Ti-0.5w%W electrode, with an anodization time greater than 20 minutes at 120 V. Under these conditions the oxide nanotubular layer was homogeneous and continuous through the surface. Ti alloy annealed at 500°C presented highest photocurrent values. The nanotubes that nucleated on TiW alloy exhibited an increasing the photocatalytic activity with respect to nanotubes grown on pure Ti.

Acknowledgments

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High Deposition Rate, High Electronic Quality, Low Cost Electrochemical ZnO Deposition

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We have developed a high growth rate, high electronic and optical quality, low cost electrochemical ZnO deposition process for solar cell and other optoelectronic applications. The process has been demonstrated in large scale roll-to-roll (RTR) pilot production for ~200 meter long substrate. The surface morphology and crystallographic structure of the ZnO films were investigated using AFM, optical microscope and XRD. Optical characterization on the ZnO films has included optical transmission, reflection, scattering and elipsometry. Electronic properties have been studied using Hull effect, electrical conductance, etc. Additional qualifications have been conducted on solar cells. We have fabricated Ag/ZnO based back reflector on stainless steel web using the solution grown electrochemical ZnO deposition process. The process has been optimized to attain good solar cell device characteristics on thin film, amorphous silicon and amorphous silicon-germanium alloy (a-Si:H/a-SiGe:H/a-SiGe:H) based multijunction solar cells. It is found that for our optimized film with thickness ~2 micrometer, grain size is about 1 μm. The as-deposited film shows random crystal orientation. We have developed a post-deposition treatment process that effectively transforms the randomly orientated film into <00L> preferred orientation, that is found to be beneficial for solar cell performance. We have compared the performance of Ag/ZnO back reflectors prepared using the solution-grown electrochemical ZnO films and vacuum sputtered ZnO films, and found that they both show similar solar cell performance. Comparing to vacuum sputtering process, starting materials cost for the electrochemical process is greatly reduced. Details will be presented.

Direct Cu Electrodeposition on Sputtered Mo Films for Thin Film Cu(InGa)Se_2 Solar Cells

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Cu(InGa)Se_2 (CIGS) has the highest conversion efficiency of all thin film photoabsorbers. High temperature recrystallization of consecutively electrodeposited Cu, In and Ga films in Se vapour is a promising low cost all atmospheric method for large scale industrial CIGS solar cell manufacturing. As a first stage this requires the electrodeposition of adherent and highly uniform Cu films on the sputtered Mo cell back contact. Unfortunately, Cu electrodeposition directly on Mo is difficult because of the complex electrochemical behaviour of Mo, involving multivalent passive oxides, [1,2].

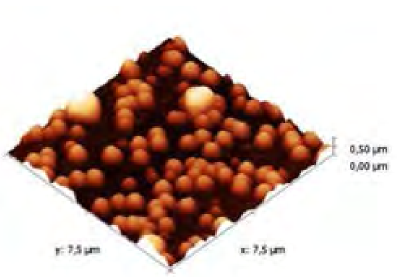

Figure 1: AFM image of Cu nuclei on Mo.

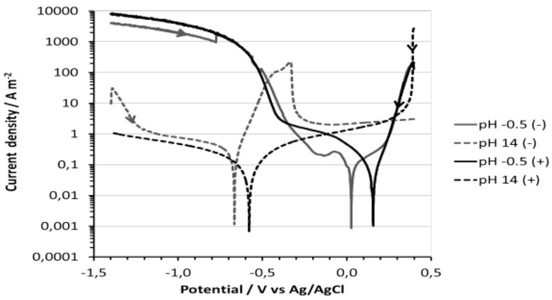

Figure 2: Potentiodynamic polarisation of Mo in sulphuric acid and sodium hydroxide solutions

We investigated electrodeposition of 200 nm Cu films directly onto sputtered Mo from highly acidic sulphate and alkaline sorbitol based Cu baths. In both baths 3D instantaneous Cu nucleation is inferred from potentiostatic transients and AFM imaging (Figure 1). In the acid bath the Cu film delaminates after deposition, whereas the alkaline bath gives adherent Cu films. Potentiodynamic polarisation curves (Figure 2) indicate that in acid conditions passive molybdenum oxides prevent Cu adhesion. In contrast in the alkaline conditions Mo is highly active, also exemplified by Cu cementation at the open circuit voltage. However, both the nucleation density and the Cu film adhesion are also affected by the initial condition of the Mo surface. XPS and various electrochemical measurements suggest that is due to the molybdenum oxide thickness and type, i.e. the molybdenum valency, at the start of the Cu electrodeposition.

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Supported Oxygen Evolution Electrocatalysts for Proton Exchange Membrane Water Electrolysis

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Water electrolysis is of considerable interest because of the need for clean hydrogen as an energy carrier medium. Proton exchange membrane (PEM) water electrolysers typically use iridium, ruthenium and/or their oxides as oxygen evolution reaction electrocatalysts. While these materials represent a good choice of catalyst in terms of overpotential and stability[1], their high cost and low natural abundance are significant limitations for practical application[2]. Reduction of the precious metal content, without compromising catalyst activity or stability, is therefore vital for the commercialisation of this technology.

One method to enhance the usage of precious metal-based catalysts is to deposit them onto a support. Support materials provide a surface for the dispersal of electrocatalyst particles, facilitating high active surface areas and reduced catalyst loadings. Any candidate support material for an O_2 evolution electrocatalyst must be electronically conductive, electrochemically stable at high anodic potentials and chemically stable in highly oxidising and acidic conditions. A range of metal oxides and metal carbides fulfil these criteria and a small number have been investigated[3].

In this work, Ir and Ru nanoparticles have been deposited on various metal oxide and metal carbide supports, at a range of precious metal loadings. The activity and stability of these materials has been examined by cyclic voltammetry, polarisation measurements and chronoamperometry with additional physical analysis by TEM, XRD and EDX. The long-term performance of these supported catalysts in a single cell PEM electrolyser has also been assessed and compared to a state-of-the-art, unsupported catalyst.

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Electrochemical reduction of CO2 on electrodeposited Cu and Zn electrodes

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Global warming is an alarming scientific problem in the current century. CO_2, an important contributor of global warming has reached 400 ppm as of 2013 which is higher than the preindustrial levels of 280 ppm [1]. Utilizing CO_2 as a carbon source to get useful products can be made feasible by electrochemically reducing CO_2 on medium hydrogen overvoltage metals such as Cu, Zn and Ag. In this work, electrodeposited Cu on Cu (Cu/Cu) and Zn on Cu (Zn/Cu) were employed for the reduction of CO_2 in chloride containing supporting electrolyte.

Constant voltage technique was used for the deposition of Cu from $CuSO_4.5H_2O$ solution [2] and Zn from $Na_2Zn(OH)_4$ solution on a Cu substrate [3]. Deposited electrodes were characterized by SEM and XRD for their thickness and crystallite size. The electrochemical measurements were performed in an H-Cell using CO_2 saturated solution, and products obtained during the reduction were analysed by gas chromatography.

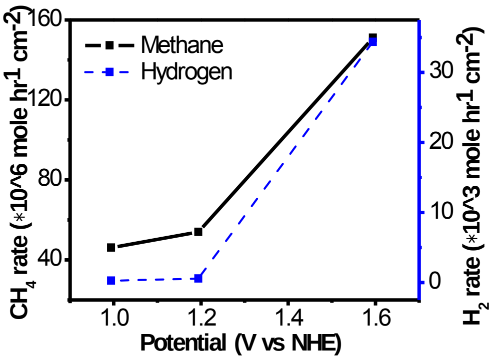

Figure 1: Methane and hydrogen formation rate with respect to electrode potential for Zn/Cu electrode in 0.5 M KCl.

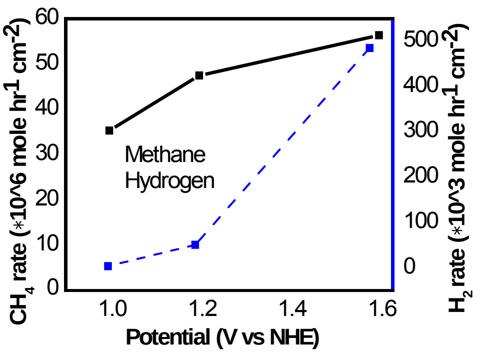

Figure 2: Methane and hydrogen formation rate with respect to electrode potential for Cu/Cu electrode in
• M KCl.

Higher cathodic current obtained in the cyclic voltammogram recorded for CO_2 saturated solution signified the reduction. Methane, ethane and hydrogen were the products observed during electrolysis. Figure 1 and figure 2, shows the product formation over a range of potential studied at Zn/Cu and Cu/Cu electrodes, respectively. Zn/Cu electrode showed more methane production and lesser hydrogen formation than Cu/Cu electrode. i.e., at a reduction potential of -1.2 V, Zn/Cu showed 54 µmol hr^{-1} cm^{-2} of methane while Cu/Cu showed 49 µmol hr^{-1} cm^{-2}, whereas hydrogen formation on Zn/Cu was 0.54 mmole hr^{-1} cm^{-2} compared to 27 mmole hr^{-1} cm^{-2} on Cu/Cu electrode.

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Electrochemical Reduction of Nitrate at Cu/Cu Cathode

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Government regulations concerning nitrate level in wastewater are becoming increasingly stringent worldwide due to the harmful effects of nitrate on the environment and human health. The necessity to remove nitrate from the waste streams of fertilizer/pesticide industries and nuclear plants has led to extensive research in this field. Remediation methods like reverse osmosis, ion exchange and bioremediation are found to be effective, however these methods are expensive and also produce secondary effluents [1]. An alternative to these approaches is the electrochemical reduction, which can offer an elegant contribution towards environmental friendliness by means of removing pollutants through current or voltage [2]. In this work, electrodeposited copper on copper (Cu/Cu) was used as cathode and its effectiveness towards nitrate removal was investigated. Cyclic voltammetry and chronoamperometry were employed to study the catalytic activity of the synthesized catalysts towards nitrate reduction. Effect of deposition parameters such as Cu loading, electrodeposition time, concentration of $CuSO_4$ electrolyte were studied in relation to the effectiveness of nitrate reduction. The Cu/Cu cathode prepared with an optimized condition was characterized for their structure and morphology by X-ray diffraction and scanning electron microscopy (SEM) as shown in Fig.1 (inset). Electrolysis of 1 M $NaNO_3$ in acidic electrolyte was compared between Cu and Cu/Cu electrodes, and the effect of electrolysis potential and initial nitrate concentration were studied. Higher reduction rate was achieved with the electrodeposited Cu/Cu as shown in Fig.1 with removal efficiency up to 60%.

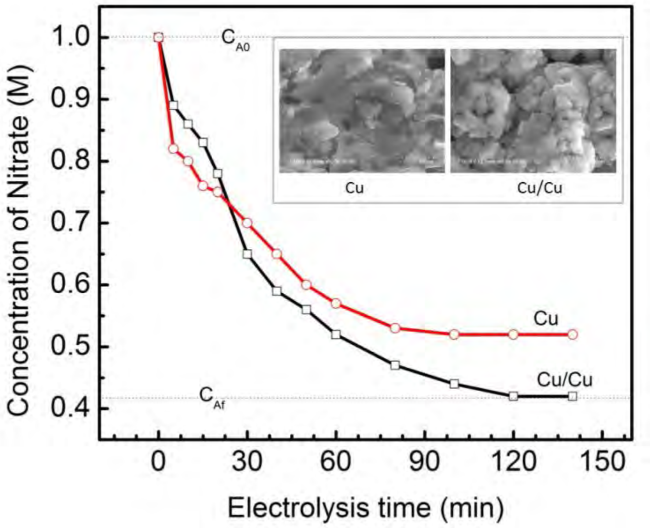

Fig. 1 Concentration profile of nitrate vs. time at -0.45 V (vs. Ag/AgCl). Inset showing SEM of Cu, and electrodeposited Cu on Cu.

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ELECTROCHEM
2013
Speaker Abstracts

A Novel Environmental SVET for the Study of Tin Based Coatings

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The amphoteric nature of tin undergoes an electrochemical phenomenon of polarity reversal in low pH electrolytes and thus, tin acts as a functional coating to sacrificially protect packaging steel. However, the detinning mechanism and kinetics depend on the nature of the environment [1]. In this investigation, SVET was utilised to investigate rapid detinning processes initiated in the presence of aerated malic acid (0.1M, pH 2). Two corrosion mechanisms were detected; de-tinning on unflowed tin coatings, followed by localised pitting on iron rich surfaces. Corrosion pits were subsequently characterised using White Light Interferometry, a practical method for obtaining detailed information on the geometry of the corrosion pits [2].

- VET describes a novel, Environmentally controlled, Scanning Vibrating Electrode Technique which allows the measurement of localised corrosion current flux under conditions of low oxygen partial pressure, which replicates the conditions which occur inside a food can. Particular emphasis is given to the effect of cathodic depolarisers, such as nitrate anions NO^{3-}, which are known to occur in food products. The E-SVET apparatus, shown schematically in Figure 1, employs a Perspex environmental chamber encasing the SVET scanning head and immersion tank. Maximum signal detection and resolution, a function of height and probe vibration [3], are systematically achieved using a three-dimensional surface profiling function.

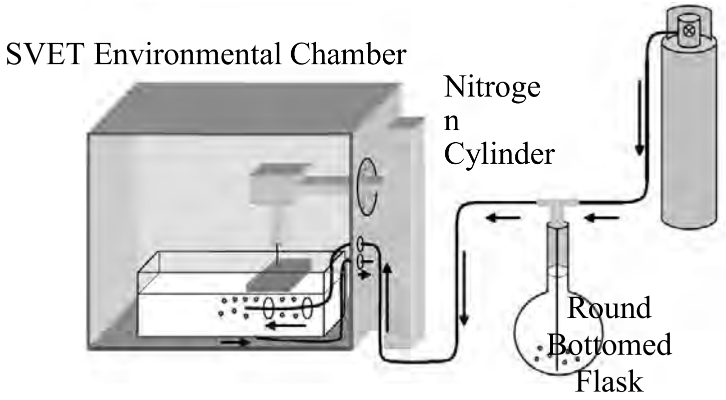

Figure 1 – E-SVET set-up used for scanning in controlled low oxygen partial pressure conditions.

In conjunction with White Light Interferometry, E-SVET achieves high resolution characterisation of many corrosion systems. The technique used in this study is not necessarily limited to packaging applications and presents great potential for future use in multiple areas of electrochemical research.

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Multiscale Insights into the Passive and Localised Corrosion Behaviour of Magnesium

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The corrosion behaviour of high magnesium alloys is of substantial industrial interest, not least in the UK civil nuclear sector where the material is used as a cladding material for fuel elements. Despite a large body of work on magnesium corrosion, certain aspects of the corrosion mechanism are not well characterised, notably, the growth kinetics of surfaces with thick passive films, the manner in which chloride initiates film breakdown and the underlying mechanism of localised corrosion in alkaline environments.

A variety of corrosion investigation techniques have been applied to address these knowledge gaps and provide mechanistic insights. This work has a strong focus on approaches which bridge length scales, from the atomistic dimensions which typify dominant processes (such as passive film interfaces), to the macroscale dimensions pertinent to the highly heterogeneous “real” objects which require corrosion management.

Extensive electrochemical work, including novel use of microelectrodes, has been supported by characterisation of the corrosion morphology with *in situ* observations including correlated videomicroscopy, quantitative image analysis and micro-tomography. These results have allowed targeting of quantum mechanical atomistic calculations on ionic adsorption and substitution at a simulated passive film lattice interface. Finite element modelling has been used for interpretation and reconciliation of these results, allowing comparison between techniques, previous observations and with plant experience.

The findings of these studies have provided clarity on a number of aspects of magnesium corrosion behaviour. Consideration of these findings in the context of previous mechanistic work has led to the proposal of a reaction scheme which reconciles the very different behaviours of high magnesium alloys with a small number of underlying reactions. These describe corrosion according to reactions across a very thin surface film (whether oxide or salt film) with the rate, evolution and morphology being determined largely by the specific mass transport processes at work.

Chromium Electroplating of Selected Aluminium Alloys

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The growing demand for chromium coated aluminium components especially for the automotive industry is due to their favourable physical properties (density, strength to weight ratio etc). However, their frequent use under harsh environmental conditions renders them corrosion sensitive and consequently they need to be protected. An approach that has been applied in industry is to directly electroplate nickel onto aluminium substrate prior to a top metallic finish; however, in components with complex geometry, certain areas could become exposed to corrosion attack due to poor surface coverage during plating.

In this study, selected pre-treated aluminium alloys were plated with duplex nickel and chromium plating with a view to enhance corrosion resistance, improve coating adherence and durability, while achieving substrate protection. Hexavalent and trivalent chromium were applied to pre-treated Al 1050 and Al 6061, and plating performance was assessed by surface and corrosion techniques. Overall, plating performance was found to be alloy specific and varied with alloy composition.

Environmental Degradation of a Mg-Rich Primer: Comparison of Selected Field Environments with Laboratory Exposures

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Recently an organic coating system containing a Mg-pigmented organic primer (MgRP) for corrosion protection of precipitation age hardened Al 2024-T351 has been developed as a candidate to replace chromate-containing surface pretreatments and primers. Corrosion inhibition mechanisms of the MgRP [1] include sacrificial anode based cathodic protection of the aluminum as well as barrier protection by the primer and topcoat polymers. King and Scully [2] have shown this capability is mediated by the percent volume concentration of Mg and the conductivities of the organic polymers in the primer and topcoat. A test protocol was also developed [2] that could be extended to assess the degradation of the MgRP coating system throughout environmental exposure.

This talk reports on a comparison of field and lab exposures of MgRP in a non-topcoated and topcoated condition. Commercial MgRP was utilized for the corrosion protection of an AA2024-T351 substrate pretreated with PreKote™ surface pretreatment. Exposures were conducted in the field at a coastal marine site at Kennedy Space Center, FL (KSC), at an inland rural site at Birdwood Golf Course in Charlottesville, VA, in ASTM B-117 with 5% NaCl and the same standard test modified with ASTM Sea Water as well as in full immersion in ambiently aerated 5% NaCl solution. Mg pigment depletion rate, galvanic protection potential and coating barrier properties were tracked throughout exposure periods in both field and laboratory environments. Preliminary acceleration factors with respect to pigment depletion and residual barrier properties were developed. Analysis near and far from a scribe exposing bare 2024-T351 was performed. Post-mortem characterization with SEM/EDS was conducted to elucidate coating and scribe morphology, corrosion products present, corrosion of the AA2024-T351 substrate, as well as in an attempt to determine the “throwing power” of the MgRP coating system based on cathodic protection of a scratch exposing bare AA2024-T351. No blistering or similar macroscopic coating failure phenomena were observed in the MgRP or along the scribe lines after exposure in any of the studied environments. Additionally, in contrast to similar environmental exposures of earlier generation commercial products in the past, no indications of cathodic corrosion, as evidenced by narrow pinholes, or underpaint corrosion or anodic undermining, as evidenced by large areas of coating delamination above regions of Al corrosion, were visible at the coating/metal interface when viewed in SEM cross-section.

The differences in rate-of-change of Mg depletion from the coating upon environmental exposure was found to be related to differences in time-of-wetness and in rates of polymer degradation, specifically resistivity, due to environmental severity factors such as UV exposure. Differences in throwing power in lab and field environments, as elucidated by finite element modeling of current and potential distributions, were traced to differences in electrolyte geometries; continuous thin-layer in salt fog cabinet exposures compared to isolated droplets which do not form a connected path in field exposures.

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A Study into the Formation of Patina on Copper-Containing Antifouling Marine Coatings

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Antifouling paints are used to prevent the build-up of biofouling organisms on manmade hard underwater surfaces. Biofouling is most detrimental on ships reducing their sailing efficiency causing them to burn more fuel, increasing the work of the engines, adding more weight to the ship, as well as reducing the aesthetics (The Marine Corrosion Sub-committee 1944). There are a range of different types of paints that can be used to prevent fouling, many of which contain a selection of pigments used as marine biocides. One of the main biocidal pigments used is cuprous oxide, which when dissolved in oxygen rich sea water oxidises to Cu^{2+}, the main biocidal agent (Yebra, Kiil and Dam-Johansen 2004). Although copper is an essential metal used for growth, when the concentration of copper in the marine organism gets above a critical level, it acts to prevent the growth, settlement and colonisation of copper rich substrata (Cid et al. 1995). However Cu^{2+} is thermodynamically unstable and therefore readily reacts with ions in the sea water forming an insoluble copper compound (Woods Hole Oceanographic Institute 1952), which can redeposit on the antifouling paint in the form of patina, with obvious detrimental aesthetic impact for the vessel. The aim of this study is to characterise patination on cuprous oxide based antifouling coatings, determine the mechanism that causes the paints to patinate under different environmental conditions and hence develop a method of predicting when patina may form. This knowledge will also be beneficial in finding ways to prevent patina from developing and informing the formulation of new antifouling coating systems that are resistant to patination. Patinated coatings have been characterised using X-ray Diffraction (XRD), Scanning Electron Microscopy and Energy Dispersive X- ray analysis.

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Influence of Localised Pit Distribution and Bench-Shape Pits on the Ultimate Compressive Strength of Steel Plating for Shipping

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The worldwide fleet of ships is ageing, with many vessels being over 15 years old. For such vessels, corrosion is an on-going concern and indeed recently a severe corrosion situation termed 'super-rust' [1], with corrosion rates of up to 5 mm/y, has been observed within the ullage space of oil cargo holds. Thus, to guarantee structural integrity, facilitate maintenance decisions economically, and even extend the structural life, it is becoming essential to investigate the ultimate strength of such aged and corroded ship structures based on a comprehensive understanding of the corrosion mechanisms. This work has developed numerical models simulating steel plate corrosion degradation and presents a series of novel finite element (FE) modelling approaches to assess the influence of localised pit distribution [2] and bench-shape pits (degree of pitting in the range of 2% - 25%), which are often observed in long-term exposures [3]. Four location patterns of one-side corroded shipping steel plates have been considered which include both geometric and material nonlinearities. Validation of the FE method is achieved by a thermoelastic stress analysis, which is a full-field measurement technique providing the principle stress distribution over the plate surface, thus allowing direct comparison with the FE data. The modelling results demonstrate that localised pit distribution can be more detrimental than randomly distributed pits (up to 10.3%). In addition, the typical bench-shape pits may further decrease the ultimate strength by up to 14% compared to the unbenched condition with the same degree of pitting.

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Galvanic Interactions in the Corrosion of AZ91 Mg Alloy and its Implications for the use of Mg-Al Intermetallic Coatings

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The low density and high relative strength of magnesium (Mg) alloys means they can offer engineering benefits over steels or aluminium (Al) alloys. However, the corrosion susceptibility of Mg alloys has restricted their use to more benign environments and limited the exploitation of this plentiful material

The corrosion behaviour of the AZ91 Mg alloy is dominated by micro-galvanic couples between primary (solid solution) and secondary ($Mg_{17}Al_{12}$ intermetallic) phases; with the noble intermetallic phase causing preferential attack of the solid solution. This mechanism has implications for the use of an Mg-Al intermetallic layer, formed by diffusion of Al at the surface, as a corrosion protection method for Mg alloys

A number of techniques for producing intermetallic surface layers on Mg alloys have been described in the literature and the improvements they can confer have been comprehensively examined. However, given the noble nature of this layer and the possible ‘worst case’ scenario of a large cathode/small anode, it is conceivable that damage which penetrates to the substrate could lead to a serious loss of corrosion protection. With this in mind a series of galvanic corrosion experiments between pure Mg and Mg alloys (with increasing quantities of Al) have been conducted to simulate the couples involved in Mg alloy corrosion.

A brief background describing the self corrosion mechanisms of Mg alloys and the possible methods of forming protective Mg-Al intermetallic layers will be presented. The results of the galvanic corrosion experiments are then discussed with reference to their implications for the use of this type of noble coating.

In-Situ Synchrotron and Electrochemistry Studies of Fe Artificial Pits

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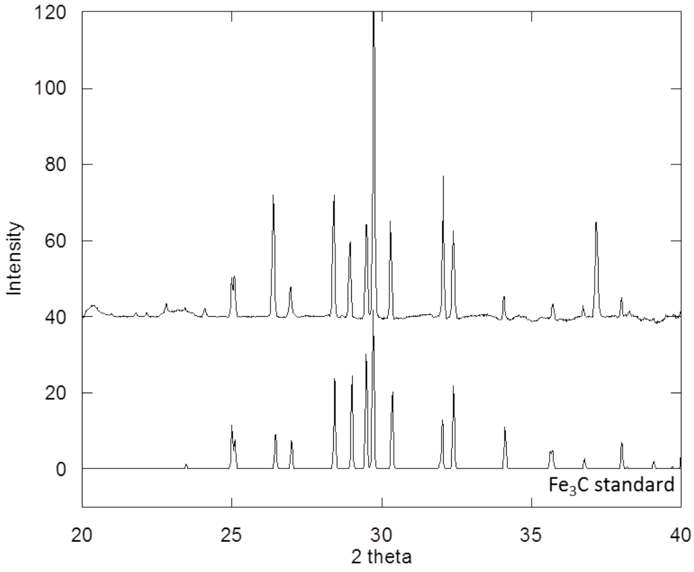
Localised corrosion of iron was studied using artificial pits in solutions containing chlorides, nitrates and mixtures of the two. Black deposits were observed inside pits grown in nitrate and mixed solutions in commercial purity Fe (99.5%), which can act as a barrier for ions diffusion and also induce extra resistance in the pit, but these deposits were difficult to observe in high purity Fe. Evidence for the presence of Fe_3C was found in pits in commercial purity iron using synchrotron X-ray diffraction (Figure 1).

In the presence of nitrate, the salt film deposited at the pit bottom became anisotropic (Figure 2), and the metal surface at the pit bottom became crystallographically etched.



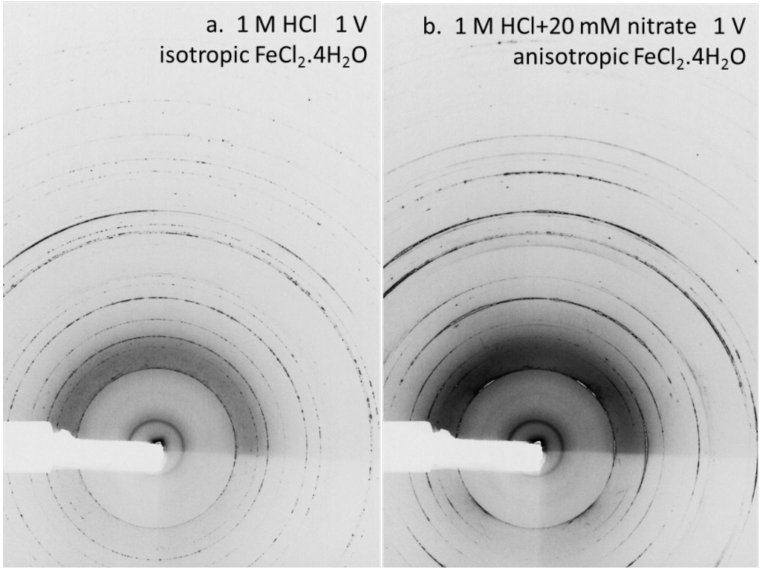


Figure 1. summed pattern of the diffration frames collected in pit solution, compared with Fe_3C standard pattern below, Fe was dissolved in 1 M HCl and 20 mM nitrate mixed solution, some small salt crystals are detected, too.

Figure 2. isotropic $FeCl_2.4H_2O$ diffraction frame in HCl solution (a) and anisotropic $FeCl_2.4H_2O$ diffraction frame (diffraction rings broken) in mixed solution (b), potential with respect to Ag/AgCl.

Acknowledgements
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Synchrotron X-ray Diffraction Study of the Effect of Nitrate on Salt Films in Pitting Corrosion of 304 Stainless Steel

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In mixed nitrate/chloride solutions, nitrate can either enhance or inhibit localized corrosion of stainless steel, depending on the NO_3^{2-}/Cl^- ratio[1]. When just below the passivation potential, current densities can be increased by the presence of nitrate. It has been claimed that the stable current oscillations observed in one-dimensional pit systems, may be caused by nitrate salt film formation [2]. In this work, the nature of the salt film is investigated using in situ synchrotron X-ray diffraction of one-dimensional pits [3].

A one-dimensional pit was grown in 1 M NaCl using 304 stainless steel foils embedded in amorphous epoxy resin. The cell was held at a range of potentials from 0.3 V – 0.7 V (Ag/AgCl). At each potential, XRD patterns were taken at 2 μm intervals through the salt film. Current and resistance were measured concurrently. This was repeated with progressive addition of $NaNO_3$ to a solution of 1 M NaCl.

When the nitrate concentration in the solution was increased to 75 mM, a stable diffusion-limited current of ~0.1 mA was seen at 0.3 V (Figure 1). The current observed gradually became more unstable as potential increased. At 0.5 V, strong periodic oscillations in current were seen, reaching 0.18 mA but never dropping below 0.05 mA (Figure 2). The resistance was also seen to oscillate.
Diffraction patterns taken of the salt film in nitrate-free solution and nitrate-rich solutions show the same salt species, even during current oscillations. These patterns approximately match $FeCl_2.4H_2O$[4], with some minor peaks missing.

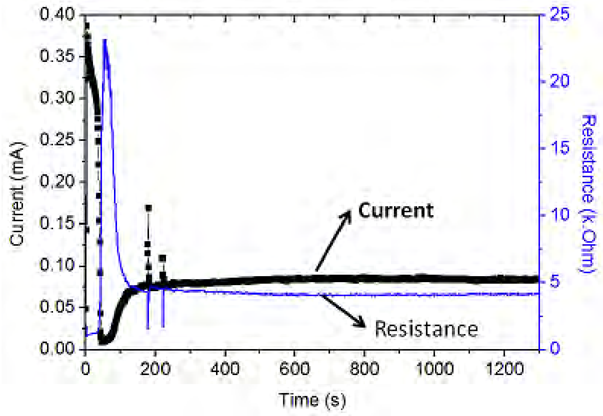

Figure 1 –Current and resistance in 1D pit corrosion of 304ss in 1 M NaCl/ 75 mM $NaNO_3$ at 0.3V

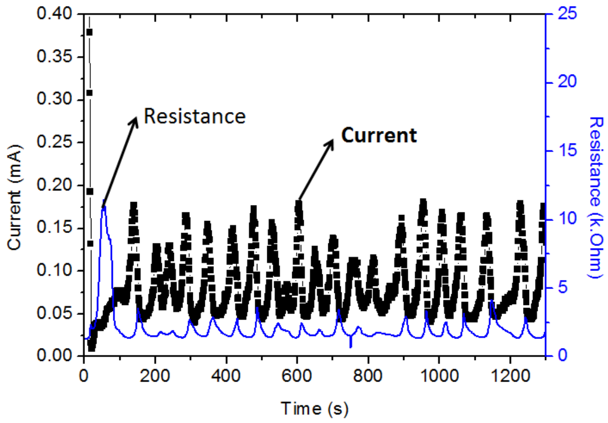

Figure 2 – Current and resistance 1D pit corrosion of 304ss in 1 M NaCl/ 75 mM $NaNO_3$ at 0.5V (Ag/AgCl)

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This work was supported in part by Diamond Light Source and the University of Birmingham.

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Synchrotron Microtomography Studies of Atmospheric Pitting Corrosion of Stainless Steel

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Atmospheric corrosion of stainless steel can take place when airborne salt particles deposit on the metal surface and form droplets when the relative humidity reaches a critical value [1]. Studies curried out so far about atmospheric corrosion of stainless steels have examined the influence of pure $MgCl_2$ [2, 3] or NaCl [4]. Near coastal areas, the atmospheric environments contain relatively high levels of chloride. In such environments, NaCl is the major chloride component while $MgCl_2$ is a minor constituent. However, the deliquescence relative humidity (DRH) of NaCl and $MgCl_2$ are75% and 35%, respectively, so at relatively low relative humidity, $MgCl_2$ will deliquesce forming a salt droplet where corrosion will take place whereas NaCl will remain solid [5].Therefore $MgCl_2$ was selected as a contaminant salt.

In the current project, synchrotron X-ray microtomography is being used to measure the rate of pit growth in situ and in real time in a controlled humidity environment.
Type 304L stainless steel, which is being used to manufacture waste containers for ILW, has been investigated. Rod samples of 2 mm diameter were machined in the direction of rolling from stainless steel plate. Droplets of 0.4 M $MgCl_2$ salt solutions giving a chloride deposition density of 1 mg/cm^2 were placed on the top surface which was polished to 800 grit. The samples were contained in silicone tubes containing filter paper saturated with salt solutions to control the relative humidity.

The results show that pit growth rate was influenced by the RH. Pits initiated rapidly on the metal surface and penetrated down tens of microns into the metal, forming dish like pit shaped pits. At 35%RH, the pits were very shallow and grew slowly over a period of several days. Deeper pits were observed at 60%RH in both tomography and lab based samples. The pit depth was found to be in the order of 60%RH > 45%RH> 35%RH. However, the number of pits per droplet was found to be in the reverse order. It was also possible to observe the shape of the salt droplet on the surface of the rod, so that the geometry of the corroding system can be clearly defined.

Acknowledgements
This work was supported by the Kurdistan Regional Government. Measurements were carried out at I12 beamline at Diamond Light Source with support from Christina Reinhard.

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In-Situ Tomography Studies of Atmospheric Corrosion of AA2024

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Atmospheric corrosion of aluminium aerospace alloys is an area of increasing concern, as aircraft used for prolonged service periods begin to age. It is an area which has been given relatively little attention, but recently the need to develop prognostic ahead of life models has emerged. Improvements in micro-tomography techniques have enabled key data to be collected based on in-situ time dependent measurements carried out in a non-destructive manner.

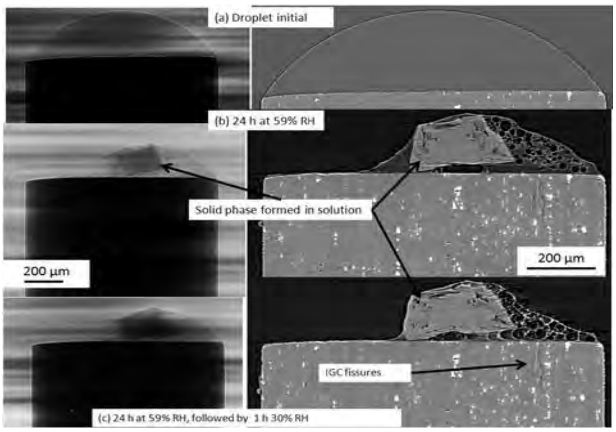

Figure 1 - AA2024-T351 sample, exposed to mixed salt NaCl/$MgCl_2$ solution droplet, chloride density ~4 mg/cm^2, exposed at 59% RH. Top: Initial droplet following deposition and sealing in simulated atmosphere.
Middle: after 24 hours exposure, salt crystals have formed in solution, intergranular corrosion is visible under hydrogen bubbles.
Bottom: Following drying in 30% RH, solution dried to gelatinous layer surrounding solid phase.

Using µCT observation of the formation and growth of corrosion fissures in a non-destructive manner was possible. Data from both µCT and lab based droplet studies has evidenced that there is a very real influence of the environment to which metal surfaces are exposed on the amount of observed corrosion and how it develops. Figure 1 demonstrates the formation of IGC fissures during steady state exposure, measurements made using µCT. Figure 2 shows how during study of the simulated wet/dry cycles commonly occurring in atmospheric exposure, there are time periods during which bursts of acceleration in corrosion rate have been observed for a range of different salt types and environments, as well as different cyclic regimes.

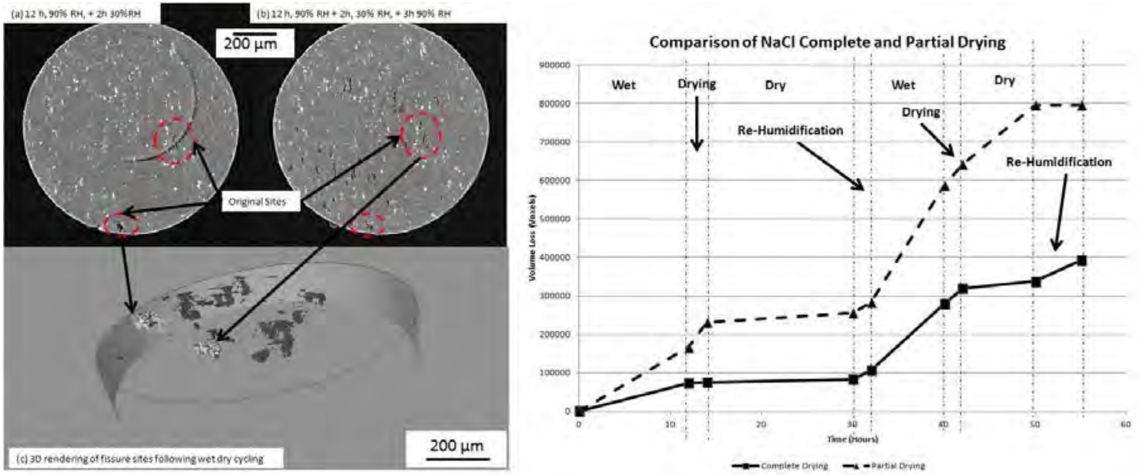

Figure 2 – [left] AA2024-T351 pin exposed to 90% RH, $MgCl_2$ solution droplet, chloride density ~4 mg/cm2, (a) following 12 hours in simulated atmosphere, and dried 2 hours at ~30% RH. (b) following 2 hours dry at 30% RH and 3 hours re-exposure to 90% RH, multiple new sites are visible, original sites are circled. (c) 3D rendering of sites formed during initial wet cycle (white), and during second wet cycle (dark), [right] progression of corrosion volume during wet/dry cycling under NaCl solution.

Why Ruthenium Oxide-Based Cathodes in Alkaline Media are Sensitive to Reverse Currents

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Ruthenium dioxide, RuO_2, or mixtures of RuO_2 and other metal oxides (TiO_2, IrO_2, etc.) deposited on a titanium support, have successfully been used as catalytic and durable coatings for decades in different industrial processes like chlorine or oxygen gas production. These types of electrodes are often referred to as dimensionally stable anodes (DSA®). RuO_2-based coatings have also found practical applications as a catalyst for hydrogen evolution in chlor-alkali production and alkaline water electrolysis [1]. The most challenging task for RuO_2-based cathodes is not activity or duration for hydrogen evolution but reverse currents at power shutdowns. When the chlor-alkali process shuts down, e.g. for maintenance, a reverse current will flow in the electrochemical cell due to the battery effect, obtained when hypochlorite and other active chlorine species close to the anode surface are reduced. As a consequence the RuO_2-based coating starts to degrade [1].

In this work we produced RuO_2 coatings by thermal decomposition of $RuCl_3$ dissolved in 1-propanol, which was deposited in thin layers on nickel substrates through the spin coating technique. The electrodes were then subjected to different electrochemical treatments like hydrogen evolution, oxygen evolution or reverse current in 8 M NaOH (90°C). The reverse current was simulated by introducing polarity inversion after hydrogen evolution. Structural changes in crystallinity was found by X-ray diffraction and revealed that a new phase appeared during hydrogen evolution (figure 1), which corroborates an earlier report [2] although it was not discussed. Our study indicates that this new phase is far more sensitive to corrosion during anodic polarization after hydrogen evolution compared to the RuO_2 coating itself while subjected to plain oxygen evolution. To our best knowledge, this has never been reported before.

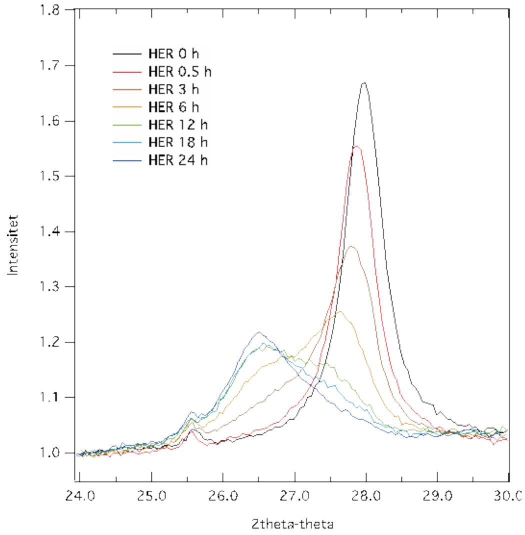

Figure 1. High resolution XRD in the rutile RuO region indicates phase transformation

The present study shows why RuO_2-based cathodes are sensitive to reverse currents in strong alkaline media, obtained during power shutdowns in industrial processes like chlor-alkali production or alkaline water electrolysis.

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The Involvement of Stress in Uranium Corrosion Phenomena

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The hydriding of uranium is an important corrosion consideration. The University of Manchester in collaboration with AWE are modelling the hydride growth within uranium and how the stress levels within it contribute to the growth of the hydride and the formation of further hydride spots, with a focus on the stress contained within the oxide layer. The model that we are creating focus on the initial stages of the reaction in a finite element modelling program Comsol. So far, hydride position, shape and the temperature effects of the reaction have been examined, whilst also modelling the stress levels within the oxide layer. The models accuracy will be verified with experimental data collected. The overall aim is to improve the understanding of the hydriding process in the early reaction stages, which is difficult to study experimentally. The presentation will discuss the background of the subject, current results and further work.

Electrochemical Investigation of the Corrosion of Different Microstructural Phases of X65 Pipeline Steel Under Saturated Carbon Dioxide Conditions

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The aim of this research was to investigate the influence of corrosion scales on the corrosion behaviour of different microstructural states of X-65 pipeline steel in a CO_2 saturated environment. Corrosion scaling was studied on the weld zone and parent plate region at 80^{o}C at a solution condition pH=4. Static immersion tests were carried out for 3 days within a nitrogen glove box, maintaining the dissolved O_2 concentration in the cell below 5 ppb. Electrochemical impedance spectroscopy (EIS) and linear polarisation resistance (LPR) were used to evaluate the corrosion behaviour. While the parent plate corroded at a steady rate for the duration of the experiment, the weld region demonstrated a noticeable corrosion rate decrease.

Results obtained from Grazing incidence x-ray diffraction studies suggest that the deposits formed on the parent plates consist mainly of ferrite (α-Fe) and cementite (Fe_3C), with minimal siderite ($FeCO_3$). In contrast, weld zone surface deposits were found to consist of siderite and chukanovite ($Fe_2(OH)_2(CO_3)$), along with α-Fe. Scanning Electron Microscopy (SEM) examination demonstrated isolated deposits of siderite with characteristic cube-shaped morphology, and clusters of plate-like chukanovite.

Here, we advance the effort to understand the particular impact of metallurgy on the nature of sweet corrosion scaling on X-65 pipeline steel.

Furthermore, Electron Backscattered Diffraction (EBSD) mapping – for grain size, orientation and elemental texture - and Scanning Electrochemical Microscope-Scanning Kelvin Probe Force Microscopy (SECM-SKPFM) – for local potential differences - were used to understand the impact of microstructure, prior to CO_2 corrosion and scaling.

The Corrosion of Carbon Steel in the Presence of Monoethylene Glycol and Iron Carbonate Scale

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Gas condensate system uses Monoethylene glycol (MEG) as a hydrate inhibitor. The study investigates the influence of MEG on corrosion of carbon steel pipeline in the presence and non-presence of iron carbonate scale. Iron carbonate scales were first build up under CO_2 saturated environment in the presence of iron ion. The pH was raised between 6.8 and 7 to enable the saturation of iron ions and deposition of iron carbonate scale. The corrosion rate at this temperature (80°C) was measured. The pre-corroded carbon steel samples were then tested using electrochemical method under different temperature and different mass% of MEG. The effect of MEG on the corrosion rate was then determined. Surface analysis was used to analysis the samples after the electrochemical test. The result shows that the presence of MEG does not actually encourage the formation of iron carbonate at low temperature (i.e.20°C) as the SEM shows a distorted iron carbon scale formation. At high temperature (i.e. 80°C), the iron carbon scale were stable and well formed without distortion as seen at low temperature. This suggests a problem of iron scaling may be prominent at high temperature region in MEG system. The synergistic and antagonistic effect of MEG on the corrosion of the pre-corroded carbon steel is considered.

Corrosion Behaviour of Ultrafine-Grained Titanium Alloys Processed by High-Pressure Torsion

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In recent decades, severe plastic deformation (SPD) has successfully produced ultrafine-grained (UFG) bulk materials for the improvement of mechanical properties of metals. Although a significant amount of work has been dedicated to the mechanical properties and the microstructure evolution of metals processed by SPD, little attention has been paid to the relationship between corrosion behaviour and grain size and microstructure of UFG bulk metallic materials. In this study, the corrosion behaviour of commercially pure titanium (commercially pure Ti) and Ti-6Al-4V processed by high pressure torsion (HPT) was investigated in 3.5% sodium chloride and 1M hydrochloric acid solutions by different electrochemical techniques. A range of grain and microstructure refinements of titanium alloys were obtained with HPT processing under different applied pressures (4, 6 and 8 GPa) and torsional strains (0, 1, 5 and 10 turns). As-processed titanium samples were exposed to sodium chloride or hydrochloric acid solutions for open-circuit potential measurements followed by electrochemical impedance spectroscopy and potentiodynamic polarization tests. The electrochemical testing exhibited a complex relationship between corrosion behaviour and grain size. For example, the corrosion resistance of the Ti samples processed by HPT at 6 GPa is generally 10 times lower in NaCl solution than that of the as-received sample, but improved with increasing torsion strain. The effect of grain size and microstructure on the corrosion properties of ultrafine-grained Ti bulk alloys processed by HPT will be discussed in detail.

Corrosion of Titanium for Biomedical Applications

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Because of their biocompatibility, suitable mechanical properties and good corrosion resistance, Ti and its alloys have been routinely used in the manufacture of biomedical implanted devices since the 1950s. However, some corrosion-related failures of Ti implants have been observed [1] and Ti corrosion products have been found in human tissues from around retrieved implants [2]. The corrosion products can induce pain, cause adverse cellular responses, and peri-implant inflammation, which in turn may lead to failure of Ti implants.

It has been demonstrated that lipopolysaccharide (LPS) [3], a driver of inflammation, and hydrogen peroxide, a product of inflammation in the body, can influence the corrosion resistance of Ti implants. In this present work, in-vitro research about the influence of factors including pH value, LPS and hydrogen peroxide in simulated media (physiological saline) on corrosion properties of Ti and its alloys has been investigated by measuring the released ions concentration, electrochemical test and surface analysis.

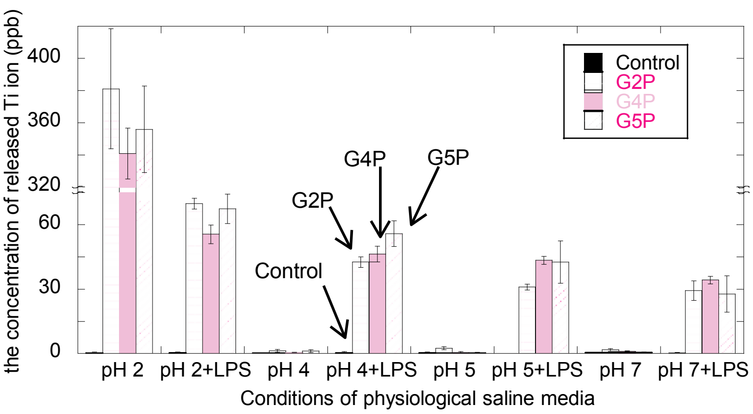

Figure 1. Ti ion release of three types of mirror-like polished Ti, Grade 2 (G2P), Grade 4 (G4P) and Grade 5 (Ti6Al4V, G5P) in different physiological saline media of pH 2, pH 4, pH 5, pH 7 with and without lipopolysaccharide

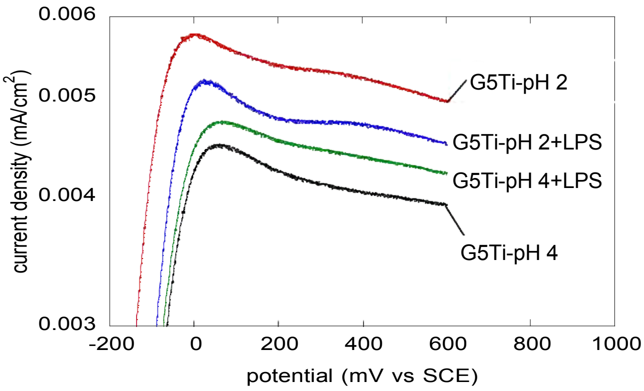

Figure 2. Anodic polarisation curve of Ti Grade 5 (Ti6Al4V) in physiological saline solutions of pH 2 and pH 4 with and without additions of lipopolysaccharide

Acknowledgements
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Uses of Scanning Electrochemical Microscopy in Corrosion Research – An Update

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Chemical imaging of reactive surfaces with high spatial resolution has become available with the introduction of scanning electrochemical microscopy (SECM). In fact, this technique has become a powerful tool in the study of a wide range of corrosion processes. This presentation provides a brief review on the applications of scanning electrochemical microscopy (SECM) in measuring, characterising and evaluating corroding systems. Localized corrosion processes and electrochemical activity distributions in surfaces can thus be investigated in real time with high spatial resolution. The SECM is a unique near-field scanning technique that is electrochemically integrated as to detect chemical and electrochemical activities in electrochemical heterogeneous systems such as those operating in corrosion research. The SECM can be used in a variety of ways, which can be broadly classified into amperometric and potentiometric modes, depending on the type of the sensing probe, namely an ultramicroelectrode (UME) and an ion-selective microelectrode, respectively. The operation modes of the instrument are described together with typical experiments selected to illustrate their application in sensing localized corrosion. Selected examples regarding the characterization of corrosion processes using scanning electrochemical microscopy that have been performed in our laboratory are presented, including passivity breakdown and pit initiation, galvanic coupling, and blistering and delamination processes in coated metals.

Evaluation of Inhibitor Performance against Localised Corrosion in Welded Pipelines Using the Microcell Technique

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Rigid oil risers are critical structures in deep-water oil and gas exploration. During operation, they are often subjected to combined damage from internal corrosion and cyclic mechanical loading which can lead to reduction in service lives. An accurate corrosion fatigue lifetime model for such structures must consider the combined effect of environment and cyclic stress on all the stages of corrosion fatigue. The pit growth stage is considered in this work because pits are often considered as precursors to cracks and the lifespan of such structures depends on the rate of propagation of such defects.

An important step towards achieving fundamental understanding of this combined effect on the rate of propagation of localised defects is to compare the individual and synergistic effects of both factors under similar conditions. This paper considers the individual effect of inhibition against localised anodic dissolution in different corrosive environments under flow conditions. The objectives are to gain more detailed understanding of the effectiveness of inhibition on the pitting regime. Preliminary studies revealed microstructural differences across the weld cross-section hence the inhibition efficiency is evaluated as a function of the microstructure.

Using a microcell with capillary diameter of 500 microns (area=1.97 x 10^{-3}cm^2), we carried out localised potentiodynamic polarisation tests and in-situ evaluation of the effect of introduction of an organic corrosion inhibitor on the open circuit potential and on the current density of single pits that were already propagating. Tests were carried out under flowing conditions to represent the flow in a pipeline. Solution conditions included; naturally aerated and CO2-saturated brine containing different inhibitor concentration.

This work demonstrates the use of the microcell technique for evaluating inhibitor efficiency at spatially resolved sites. Localised open circuit measurements showed that potentials increase to more positive values in the presence of the inhibitor. For all microstructural regions, localised polarization tests showed that the inhibitor acts as a mixed-type inhibitor while inhibitor efficiency is directly proportional to inhibitor concentration within the selected inhibitor concentration levels.

ELECTROCHEM
2013
Speaker Abstracts

5: Energy storage: batteries, redox flow cells, supercapacitors

Keynote

Atomic and Nano-scale Design of Electrode Materials for Lithium Rechargeable Batteries

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Rapidly-growing demand for better-performing lithium-ion batteries has driven researchers and engineers to intensively search for new materials having enhanced electrochemical properties. As the key technology for further development of hybrid or all-electric vehicles, lithium-ion batteries having higher power and energy density, safety, and cycle stability need to be developed. With this goal in mind, several groups of new compounds have been discovered, including fluorosulfates, pyrophosphates, silicates, borates and fluorophosphates. The diverse electrochemical properties of these compounds are critically affected by the species of anions and how they, as the building blocks, are arranged in the crystal lattice.

In the first part of this presentation, we report a novel layered lithium vanadium fluorophosphate, $Li_{1.1}Na_{0.4}VPO_{4.8}F_{0.7}$, as a promising positive electrode contender. This new material has two-dimensional lithium pathways and is capable of reversibly releasing and reinserting ~1.1 Li^+ ions at an ideal 4 V (versus Li^+/Li) to give a capacity of ~156 mAh g^{-1} (energy density of 624 Wh kg^{-1}). Moreover, outstanding capacity retentions of 98% and 96% after 100 cycles were achieved at 60°C and room temperature, respectively. Unexpectedly high rate capability was delivered for both charge and discharge despite the large particle size (a few microns), which promises further enhancement of power density with proper nano-engineering.

In the second part, we will report a new Li storage mechanism involving nano-composites of redox couple host and lithium host. Only a small number of Li-containing cathode material groups have been so far considered for practical use in Li-ion battery systems. Open anion framework and Li-containing conditions restrict the choices of materials for positive electrode. To expand the sight for seeking new positive electrode material, we suggest a novel strategy to use Li-free transition metal ionic compounds (MX, M = transition metal, X = anion or polyanion group) as a positive electrode material for Li-ion batteries. MX is blended with a simple Li ionic compound (LiY, Y = anion or polyanion group) in nanoscale. In this nanocomposite electrode, MX provides a redox couple for an electrochemical reaction, while Li ions are supplied from LiY.

Is There Life in the Li-air Battery?

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Li-ion and related battery technologies will be important for years to come. However, society needs energy storage that exceeds the capacity of Li-ion batteries. We must explore alternatives to Li-ion if we are to have any hope of meeting the long-term needs for energy storage. One such alternative is the Li-air ($Li-O_2$) battery; its theoretical specific energy exceeds that of Li-ion, but many challenges must be overcome before this technology can be realised.[1-5] First, we must understand the processes that occur in the cell on discharge and charge, then use such knowledge to address the problems.

A typical aprotic $Li-O_2$ battery, shown in Figure 1, consists of a Li anode and a porous cathode, separated by an organic electrolyte. On discharge, O_2 from the atmosphere enters the porous cathode, where it is reduced and is supposed to form Li_2O_2, which can be then be oxidized on charging.[1-5] Charge is stored in the cathode by reversible Li_2O_2 formation/decomposition. However, it is now understood that the reactive nature of the reduced O_2 species results in decomposition of the cathode and many electrolytes.[6-8] Recent results on electrolyte and cathode stability will be discussed, with a particular focus on the instability of the ubiquitous carbon cathode.[9-10] By understanding these instabilities, it has been possible to demonstrate a cell that sustains reversible Li_2O_2 formation/decomposition at the cathode on cycling, which is essential if the $Li-O_2$ battery is ever to succeed.[11] Recharging the $Li-O_2$ cell presents a particular problem at the cathode; an approach to this problem shall also be considered.

Figure 1. Schematic representation

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The Study of Oxygen Reduction in Room Temperature Ionic Liquids for use in a Lithium-Air Battery

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The Lithium-air battery is predicted to be the next generation of lithium batteries for use in automotive vehicles. This battery will harvest oxygen from the atmosphere and generate energy through its reaction with lithium. The specific energy is expected to be 11425 Wh kg^{-1}.[1]

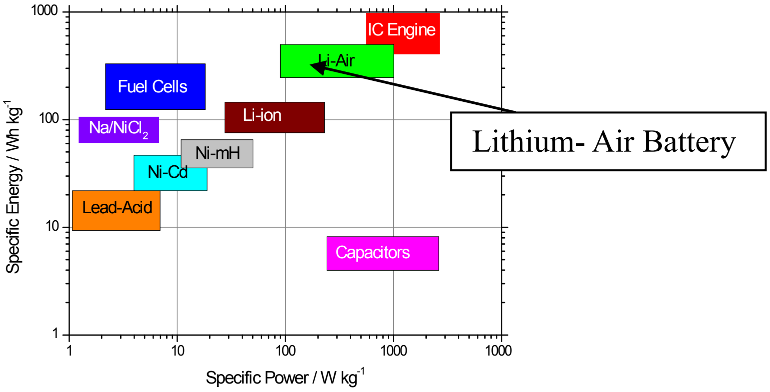

Fig 1. A chart showing the theoretical energy density and power density of various battery systems[2,3].

Room Temperature Ionic Liquids (RTILs) are molten salts which show potential for use as the electrolyte and O_2 carrier in a Lithium-Air battery due to their high oxygen solubility, and stability towards superoxide and peroxide [4]. The main figures of merit for the use in a lithium-air battery are the diffusion coefficient (*D*) and the solubility (*c*) of oxygen in the ionic liquid. The diffusion coefficient-solubility product (*Dc*) is also an important figure of merit relating to the current produced when the battery is at a steady state.

In this work, *D* and *c* of O_2 in several pyrrolidinium-based RTILs have been measured through the use of potential step chronoamperometry at a gold microdisc electrode, at several temperatures. The resulting current curves were analysed using a method used by Denuault et al.[5]. The diffusion coefficient-solubility product (*Dc*) was also found. The values of *D* increased with temperature while the values of *c* decreased with temperature. The *Dc* was found to increase with temperature, giving a higher current. The *Dc* product was the most reproducible result while the values of *D* and *c* showed less reproducibility.

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Redox Shuttles to Relocate Oxygen Reduction in the Lithium-Air Battery

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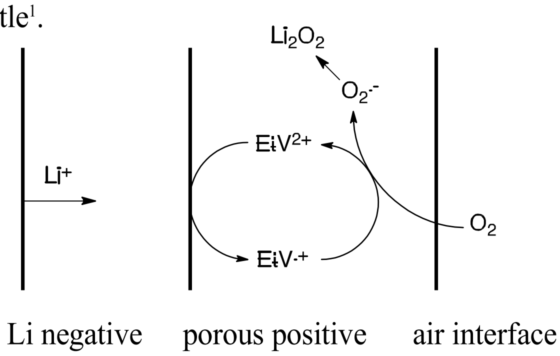
The nonaqueous lithium-air battery has been studied intensively as an energy storage devices with theoretical specific energies close to the maximum possible values that can be achieved using electrochemistry. The power available during discharge is limited by electrode surface passivation due to the deposition of products of reduction such as lithium oxide and peroxide, which have a very low solubility in most organic solvents. This work seeks to alleviate that problem by the use of Ethyl Viologen (EtV^{2+}) as a redox shuttle[1].



An alternative oxygen reduction reaction is demonstrated; EtV^+ is produced at the electrode, reduces oxygen in solution, and is regenerated at the electrode as shown in Fig. 1. This is analogous to the oxygen evolution mediator reaction recently proposed for the recharge reaction[2].

Acknowledgement
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The Electrochemistry of Dioxygen in Li-O2 Cell Electrolytes

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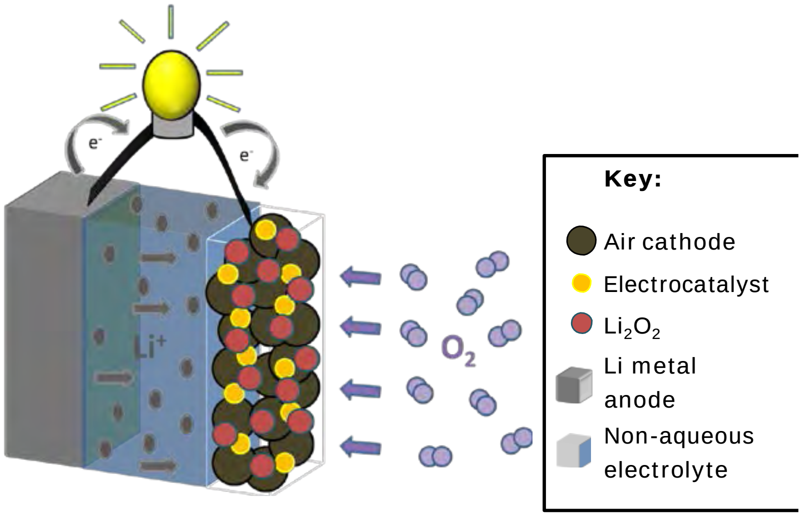
To satisfy the energy storage needs of society in the long-term, an advance in battery energy density is required. The non-aqueous lithium-oxygen (Li-O_2) battery is one of the emerging opportunities available for enhanced energy storage [1]. Unlike a conventional battery where the reagents are contained within the cell, the Li-O_2 cell uses oxygen from the atmosphere. 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. Surprisingly, the reaction is reversible, Li_2O_2 can be oxidised, releasing oxygen gas, thus making this an energy storage device: $2Li + O_2 \leftrightarrow Li_2O_2$.



The challenge for the Li-O_2 cell is the progress of development of the air-cathode that allows reversible formation of Li_2O_2 in a stable electrolyte within its pores [2-5]. This presentation will provide an overview of current developments in non-aqueous Li-O_2 cells, followed by discussion of the particular electrochemistry of dioxygen in Li-O_2 cell electrolytes.

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Keynote

Following Function in Real Time: New NMR and MRI Methods for Studying Structure and Dynamics in Batteries and Supercapacitors

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A full understanding of the operation of a battery and supercapacitor requires that we utilize methods that allow devices or materials to be probed while they are operating (i.e., *in-situ*). This allows, for example, the transformations of the various cell components to be followed under realistic conditions without having to take apart the cell. To this end, the application of new *in* and *ex-situ* Nuclear Magnetic Resonance (NMR) and magnetic resonance imaging (MRI) approaches to correlate structure and dynamics with function in lithium-ion and lithium air batteries and supercapacitors will be described. The *in-situ* approach allows processes to be captured, which are very difficult to detect directly by ex-situ methods. For example, we can detect side reactions involving the electrolyte and the electrode materials, sorption processes at the electrolyte-electrode interface, and processes that occur during extremely fast charging and discharging. Ex-situ NMR investigations allow more detailed structural studies to be performed to correlate local and long- range structure with performance in both batteries and fuel cell materials.

In this talk, I will describe the use of NMR spectroscopy to probe local structural changes in lithium ion batteries discussing our work on the anode material Si, manganese spinel cathodes, olivines cathodes and lithium air cathodes, and to investigate Li dendrite formation in lithium metal batteries. Studies of paramagnetic systems are complemented by DFT calculations of energetics and relevant NMR hyperfine parameters. Finally, the application of NMR and MRI to examine double layer formation in electrolytic double layer capacitors (supercapacitors) will be described.

Flexible Li-ion Batteries Based on Nanocellulose

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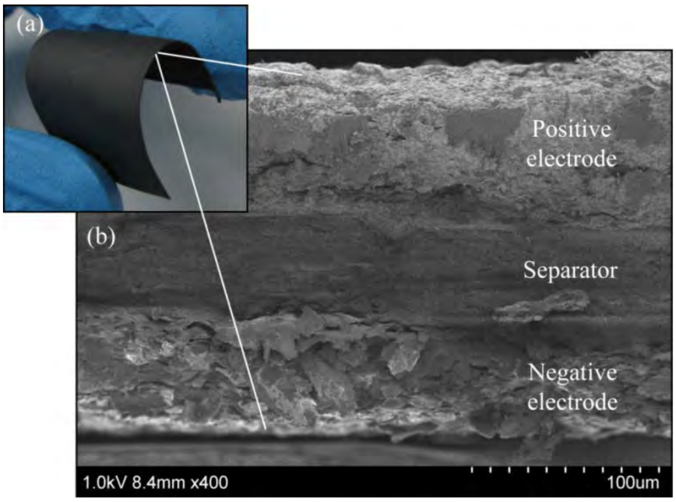
Paper batteries – light-weight, strong, bendable, rechargable, with high energy density and based on renewable raw materials. Li-ion batteries, where the structures of the electrodes and the separator are based on nanocellulose (NFC), will be presented. By producing thin, strong nanopapers of NFC with different electroactive materials incorporated, we can make electrodes and separators that can easily be assembled to batteries.

Three-layered papers with electrode – separator – electrode ”all-in-one” have also been successfully produced. The papers are about 250 µm thin and can be discharged and recharged several hundred times. These paper-battery cells are mechanically strong and flexible with good cycling properties (up to 101 mAh/g $LiFePO_4$ at 1C and 188 mAh/g at C/10) and made using renewable cellulosic materials. They may on a larger scale be produced at low cost by using existing paper-making procedures.



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Aluminium Can Battery

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Electrochemistry is an important and fundamental part of the physical chemistry curriculum, where the principles can best be demonstrated through experiments. The construction and understanding of a simple battery system can aid teachers in explaining many of the challenging concepts. The development of a teaching guide is presented which demonstrates a series of simple steps to utilise common household items such as aluminium cans, and iron wool to generate electricity that can power simple electrical devices. The key teaching outcomes which are demonstrated include understanding cell potentials, oxidation and reduction and redox reactions. A review of the current curriculum at GCSE and A-level is also presented.

The Design, Construction and Characterisation of an Iron-Air Battery for use in Automotive Vehicles

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The Iron-air battery is a suitable candidate for use in automotive electric vehicles because iron is a globally abundant, inexpensive battery material that is non-toxic to the environment and capable of being recycled. The iron-air battery is a redox cell involving the following electrode reactions:

$$O_2 + 2H_2O + 4e^- \underset{charge}{\overset{discharge}{\rightleftarrows}} 4OH^- \qquad \text{positive electrode (1)}$$

$$Fe + 2OH^- \underset{charge}{\overset{discharge}{\rightleftarrows}} Fe(OH)_2 + 2e^- \qquad \text{negative electrode (2)}$$

Both electrodes benefit from having a porous, high surface area and as the cathode can use oxygen sourced from the surrounding atmosphere, only the anode reactant is stored in the cell. The cell can therefore be fabricated from smaller and lighter battery designs that are capable of much higher energy densities.

The iron electrode can realise over 3000 charge - discharge cycles due to its high stability in alkaline media, and has a high tolerance to overcharging and over discharging [1]. In the 1980s, considerable research and development resources were invested in the progression of iron-air batteries [2, 3]. However, the research was limited after it was found that the performance of the iron-air battery was dependent upon the poor structural stability of the air electrode, and poor oxygen kinetics. Recent improvements in cathode technology have now re-invigorated iron-air battery development. This talk considers the design of an iron-air battery recently fabricated in our laboratories, along with its current performance, and concepts to improve the battery.

Acknowledgements
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Novel Nanostructured Materials for an Air-Breathing Electrode: A Comparison with State-of- the-Art Commercial Electrodes

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Metal-air fuel cells (M= Fe, Zn, Al or Li) are promising sources of power for electric vehicles and other mobile devices due to their large theoretical energy densities and use of abundant and inexpensive materials.[i] However, there are currently several factors which strongly limit their performance, including poor durability of the air electrode [i] and lower efficiency caused by the slow kinetics of the oxygen reduction reaction. [i] The air electrode kinetics are determined by the rate of electron-transfer in the following reactions:

(1) $O_2 + 2H_2O + 2e^- = H_2O_2 + 2OH^-$ (2) $H_2O_2 + 2e^- = 2OH^-$ ($2e^-$ pathway)

or (3) $O_2 + 2H_2O + 4e^- = 4OH^-$ ($4e^-$ pathway)

To improve the performance of the air electrode for use in a secondary battery, a suitable catalyst with significant activity towards both oxygen reduction and oxygen evolution must be used. Additionally, the available surface area for the three-phase boundary reaction between electrolyte, air and catalyst must be increased by using a catalyst support with a high surface area. [1,i] Both the catalyst and support should be inert towards the strongly oxidising conditions encountered during cell recharging.

In this contribution, a comparison of the performance of several state-of-the-art commercial air electrodes (composed of Pt/C, Raney nickel, manganese oxide, silver oxide and nickel nanopowders) is presented, alongside the performance of novel electrodes containing Mn(IV)-based oxide nanoparticles supported on carbon nanoparticles and multilayered inorganic nanoparticles. This system is designed to provide a maximal surface area whilst simultaneously providing channels through which OH^- can be conducted from the electrode surface toward the catalyst particles. The electrode surface shows a high resistance towards oxidative damage. The multilayered inorganic nanosheets adsorb dissolved CO_3^{2-}, which consequently minimises carbonisation of the catalyst nanoparticles.

The surface structure of all the electrodes before and after use was examined in detail using SEM, EDX, BET and XRD methods. The durability and energy density of the air electrodes was measured over multiple charge-discharge cycles. These parameters were tested for both the half-cell reaction and for an iron-air fuel cell system using a commercial iron anode (Sichuan-Changhong Battery Co.).

Acknowledgements
This research has received funding from the European Community's Seventh Framework Programme (FP7/2012-2015) under the call GC.NMP.2012-1; NECOBAUT Project n° 314159.

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Aggregated Use of Vehicle Battery Technology for Electricity Grid Support Applications (V2G) and the Effect on Lifespan

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Vehicle to Grid (V2G) is a set of technologies designed to enable the use of aggregated Electric Vehicle (EV) batteries as a storage medium by electricity grid operators. Implementing V2G across the power network will facilitate provisioning of ancillary services such as:

- Load Balancing

In 2011 the UK had installed 12,000 MW of renewable power, with over 4,000 MW coming from onshore wind generation [1]. In order to prevent potential power going to waste during times of low demand it must be stored for later use. The UK's current dominant source of energy storage lies in the 2,788 MW capacity of pumped storage hydroelectric stations [2]. The concept of V2G aims to provide the network with a larger aggregate distributed capacity of highly efficient battery storage that can be used to bolster the reserve capacity of the grid, allowing for reduced dependency on non-renewable sources to provide balancing services.

- Frequency Response

Throughout a standard day electricity demand constantly fluctuates. Load Serving Entities (LSE) predict in advance how much power they will need each day and purchase this capacity from Generators. On the day, however, if demand rises higher than predicted the energy providers must start buying extra capacity at a premium through the electricity balancing markets. In order to be able to provide this extra generation the grid keeps a 'reserve' generation capacity on standby. This reserve generation can come from large coal and combined-cycle gas turbines which the grid pays to run below full capacity, generally at sub-optimal efficiencies. For larger, more infrequent imbalances the grid contracts a capacity of open cycle gas turbines and diesel generators as 'standing reserve', named as they are only run when necessary due to their much higher running costs [3]. V2G aims to reduce LSE dependency on such sources by providing a fast acting reserve of clean energy.

Figure 1: Illustration of the basic concept of V2G

A full V2G enabled network has 4 key technology areas. These include: i) charger technologies, ii) vehicle communications, iii) network control software and iv) the battery technology itself. The latter battery technology, due to the potential to significantly increase the charge/discharge cycling of the EV battery as a consequence of providing V2G support, will impact the ultimate lifetime of the battery. The authors have simulated a range of electricity network scenarios both with and without provision of V2G services, to study the expected increase in battery cycling and hence to begin to define the impact on battery service life caused by V2G operation. This will inform both battery choice and rating for V2G enabled EVs, as well as the ongoing economic analysis of V2G, and initial results will be presented in the full paper.

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Advances Vanadium Redox Flow Battery Using Flexible Nano-Structured Carbon-Based Electrodes Materials

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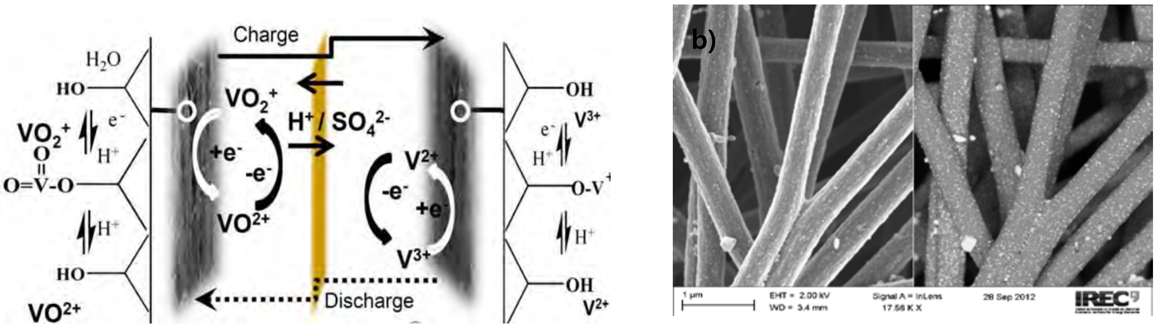
We present an advances vanadium redox flow battery (VFRB) using a newly developed flexible nano-structure materials such as electrode being a pioneering work to the best of our knowledge in this application The introduction of nano-electrochemistry features leads to a highly performances, being mandatory the innovative designs and components in VRFB system. These nano-structured electrode materials have been synthesized by electrospinning techniques and offers several advantages in comparison with commercial micro-structured felts, i.e. higher surface area, higher electrical conductivity, binder free materials, excellent mechanical, chemical stability, cost-effective, etc. showing a excellent electron transfer properties.

The nanostructure and electrochemical property of the all electrode synthesized as well as the performance of the VRFB single cell with it have been characterized by scanning electron microscopy, X-ray photoelectron spectroscopy, cyclic voltammetry and charge/discharge test. The electrochemical activities of the nano-structured electrode have been improved dramatically and the reversibility of the VO2+ /VO2+ and V3+/V2+ redox couples increased greatly using several electrolytes. The VRFB single cell with these novel electrodes exhibits higher coulombic efficiency (98%) and energy efficiency (90%) than that with the commercial felts.



a) Working principle of VFRB and b) FE-SEM images of nano-structured electrode materials.

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The Next Step Towards Safer Lithium-Ion Batteries: Replacing LiPF6 by LiTFSI Using Fluorinated Carbonates

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Lithium-ion batteries are currently the leading electrochemical energy storage devices, offering efficient energy storage as well as high power and energy density and thus, dominating the market for batteries used in portable consumer electronics.

Nonetheless, future large-scale applications require further improvement in terms of energy and power density and particular in terms of safety. Severe safety issues are, for instance, related to the utilization of $LiPF_6$ as lithium salt in common organic electrolyte containing batteries. In fact, $LiPF_6$ offers a combination of well-balanced properties [1]. Most importantly, however, it is able to passivate metallic aluminum, used as current collector for lithium-ion cathodes, by forming a protective layer of AlF_3 and AlO_xF_y, thus preventing oxidative aluminum dissolution at high anodic potentials [2]. Nevertheless, $LiPF_6$ suffers two major safety hazards: thermal instability at elevated temperatures, leading to a decomposition into gaseous PF_5 and LiF, and high sensitivity towards hydrolysis, resulting in the formation of highly toxic HF, which is moreover detrimental to the cell system [3]. Accordingly, research activities focused on the investigation of alternative lithium salts and among others lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). LiTFSI offers a comparable electrochemical performance as $LiPF_6$, but provides a significantly enhanced thermal stability and a dramatically reduced sensitivity towards hydrolysis, hence resulting in a substantially improved safety of the battery [4]. However, its practical and commercial application has not been realized yet, since LiTFSI - in contrary to $LiPF_6$ - does not prevent the aluminum current collector from anodic dissolution at potentials higher than 3.5 V *vs.* Li/Li^+ [5].

Herein, we will present a new approach for suppressing anodic aluminum dissolution using fluorinated linear carbonates as electrolyte (co-)solvents [6]. It will be shown that such solvents are able to form a protective fluorine-containing film on the aluminum current collector thus, preventing it from anodic dissolution at potentials greater than 3.5 V. Electrodes based on standard anode and cathode materials, such as for instance graphite or $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$, show a highly stable cycling performance and good high rate capability, confirming that $LiPF_6$ can be fully replaced by LiTFSI, enabling safer lithium-ion batteries for future large-scale applications.

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Large Signal Impedance Analysis for the Characterisation of Supercapacitors

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Capacitance and resistance are the fundamental electrical parameters used to evaluate the performance and health condition of a supercapacitor. Capacitance, the charge storage capacity of a capacitor, can be determined in two ways: first, by measuring the amount of charge stored/released for a voltage change of one Volt; second, by measuring the reactance of the device. The former involves constant current charging/discharging whilst the latter involves impedance analysis such as electrochemical impedance spectroscopy (EIS). In conventional EIS, a small sinusoidal excitation signal within the millivolt (mV) or milliampere (mA) range is used to measure the impedance of a test sample, i.e. a supercapacitor in this case, across a range of frequencies. In this paper the author's discuss and present details of large signal impedance analysis of a 650F supercapcitor, at current levels up to 35A, performed using a high current test system developed by the authors. The experimental results, viz. resistance and capacitance as a function of frequency as shown in Figure 1, show good agreement between the large and conventional 'small' signal impedance analysis (derived using a Gamry Instruments analyser) except for low frequencies <50mHz. Investigation of the differences at frequencies <50mHz is on-going, and will be further reported in the full paper, supported by further sample analysis between these EIS techniques. In practice, this large signal impedance method could be integrated into high current test systems to support online characterisation of supercapacitors, without requiring use of a 'conventional' impedance analyser.

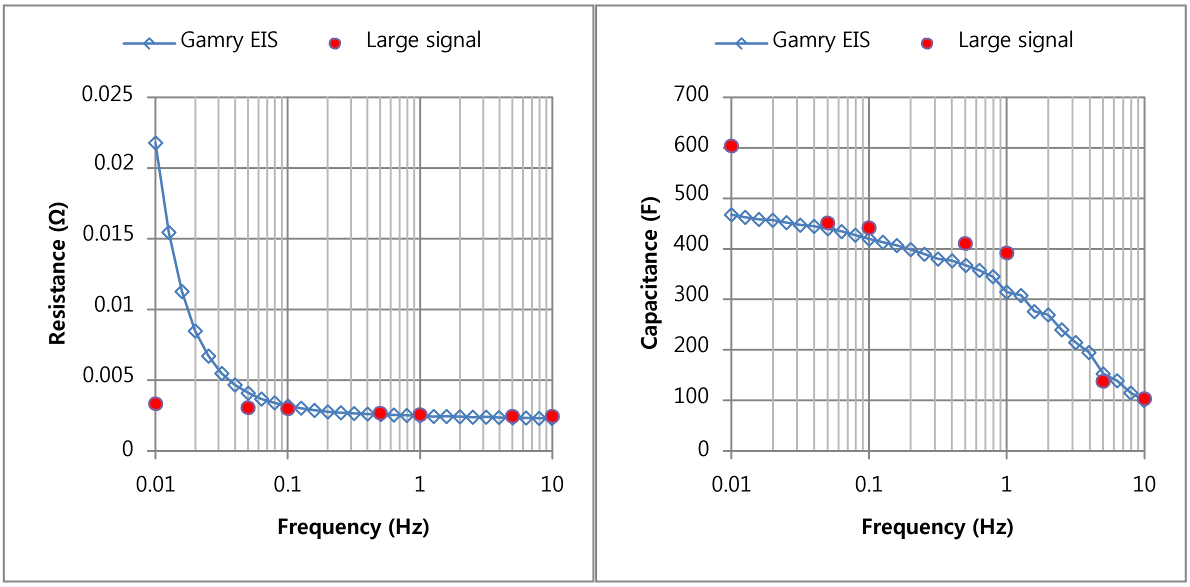

Figure: The resistance and capacitance of a 650F commercial supercapacitor determined via 'conventional' EIS (blue line) and 'large signal' impedance analysis (red circles).

Self-Discharge in Ionic Liquid Supercapacitors

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Ionic Liquids (ILs) are the liquid phase of organic salts that derived from a variety of cations and anions. Owing to the asymmetry of the components, the melting point of ILs is typically below ambient temperature. ILs have attracted much attention for use in Electrochemical Supercapacitors (ECs) due to their low volatility and wide ranges of electrochemical stability in comparison with organic based electrolytes [1].

However, ILs often exhibit high viscosity, which results in an increased internal resistance and hinders the power output capability. Also, the presence of impurities either in the carbon electrode or the electrolyte, result in occurrence of faradaic reactions, which contributes to current leakage. Loss of energy through self-discharge is a problem for supercapacitors. This paper investigates methods to minimise this for IL based devices.

To investigate the influence of the electrolyte properties on cell discharge, two ionic liquids with two different cations, 1-ethyl-3methylimidazolium [EMIm] and 1,2-dimethyl-3-propylimidazolium [DMPIm], were studied. The same anion, bis(trifluoromethanesulfonyl)imide [TFSI], was chosen for both ILs. As the properties of the ILs were influenced by oxygen and moisture, the cell assembly was carried out in an oxygen and moisture deficient environment.

The ability of the cell to retain energy over period of 24 hours was studied under open circuit conditions, where no current is applied across a fully charged EC cell. If the electrodes are not fully polarized then the self-discharge mechanism can occur as a result of the ‘charge redistribution’ process when a voltage gradient is produced in the carbon pores while charging the cell. By maintaining a longer potentiostatic period after charging, the surface polarization is maximized and an equilibrium position will be reached. The charge will then be redistributed in the pores while discharging. This process will be repeated until a point where the charge is evenly distributed through the pores of the electrode. Thus more energy will be retained in the cell through the subsequent self-discharge, *Figure 1*.

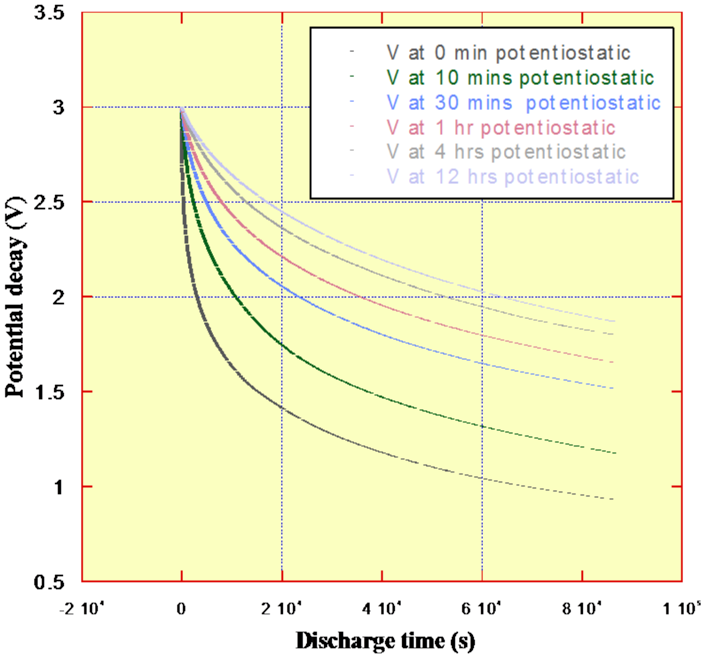

Figure 1: Self-discharge through cell containing DMPIm electrolyte

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Investigation of the Electrochemical Behaviour of a Vanadium Species using a Nanoelectrode Structure

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Nanoelectrode structures have been of intense interest in recent years, due to their numerous advantages over conventional macroelectrodes including higher sensitivity, inconsequential mass transport limitations and significantly lower raw material consumption.[1] Such nanoelectrode structures may be of benefit in the energy sector, from electroanalysis of fuel cell components, to incorporation into redox flow battery systems. Vanadium-based electrolytes in redox flow batteries show great promise mainly due to the use of a single species at both electrodes, which prevents cross-contamination of electrolytes.[2] Carbon electrodes have proven to be popular in redox flow batteries mainly due to their low cost and the abundance of carbon, despite the fact that the vanadium redox couples V^{2+}/V^{3+} and V^{4+}/V^{5+} tend to be more reversible at metallic electrodes.[2] However, nanoelectrodes contain incredibly low levels of raw materials, such as noble metals like platinum or gold. It is hoped that in the future, nanoelectrode technology can be successfully incorporated into a redox flow battery. With this in mind, we have investigated the electrochemistry of a vanadium species at a platinum nanoelectrode structure and report on preliminary results.

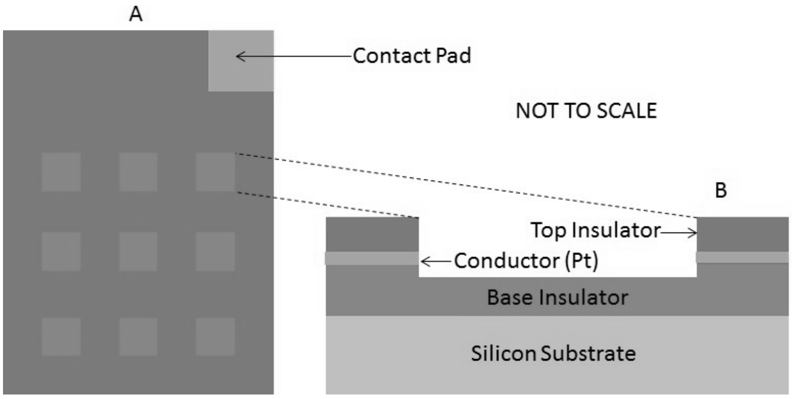

Figure 3. Schematic of a CAVIARE™ Nanoelectrode Substrate, Platinum 303D. The nanoelectrode (A) consists of an array of 42x42 apertures, each aperture (B) containing a 50 nm wide platinum band on the inner vertical wall.

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Molybdenum Nitrides as Electrochemical Capacitors

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The application of nanostructure materials with ordered morphologies and properties to electrochemical supercapacitors is being studied in order to provide enhanced energy density without comprising their inherent high power density and excellent cyclability.[1] The major classes of materials used for electrochemical capacitors (ECs) include various forms of carbon, conductive polymers, and transition metal oxides. Electronic conductivity, chemical stability to alkaline, acidic or organic electrolytes, low cost, and high specific area are the key properties for a material to be used in ECs.[2] Ruthenium oxide (RuO_2) and hydrous ruthenium oxides ($RuO_2 \bullet 0.5H_2O$) have been intensively studied to be used in redox ECs.[3] However, commercial applicability of RuO_2 is hindered by its high cost.[1] TMN electrode materials attracted attention as possible candidates for supercapacitors applications due to their high electrical conductivity and chemical stability. Nano- structured VN shows capacitance of 1340 and 554 Fg^{-1} at 2 and 100 mV/s respectively.[5] In this study we report the solution phase ammonolysis reactions of $MoCl_5$ and $Mo(NMe_2)_4$ to form polymeric precursors, and their decomposition in ammonia at high temperature to produce molybdenum nitrides in nanocrystalline, nanorod and nanotube form. The main focus of our study is in the adaptation of the reactions to control the polymerization process and use it to make controlled material morphologies suitable for electrochemical capacitors.

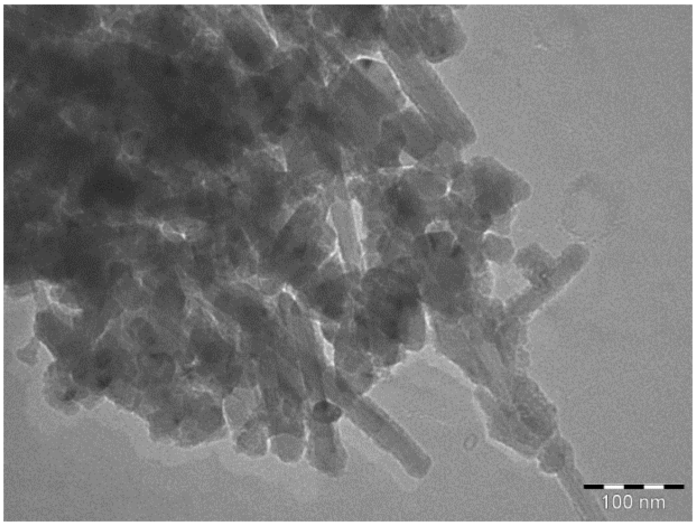

Fig. TEM image for MoN nanotubes obtained by ammonolysis of $Mo(NMe_2)_4$ and annealing the polymer at 500 °C for 48 hrs.

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ELECTROCHEM
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Speaker Abstracts

6: Energy conversion, fuel cells, biofuel cells, solar cellsensors, medicine, biology

Keynote

The Development of Novel Super Powerful PEM Electrolyser Membranes

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In a world in which fossil fuel energy is becoming ever more scarce and expensive and countries are struggling to meet their carbon reduction obligations, hydrogen solutions have finally reached the top of energy agendas. The only industrially applicable zero carbon method to produce hydrogen is via electrolysis utilizing renewable sources of electricity.

ITM Power is at the very heart of the initiatives and programmes to adopt hydrogen technology that will reduce both carbon footprints and energy costs. Using its technology and knowhow, ITM Power is aiming to be the world leading supplier of both infrastructure products for the production of green hydrogen transport fuel, and products for the production and storage of hydrogen fuel from unpredictable renewable energy sources.

Despite having a number of electrolyser products on the market, ITM Power has an active PEM electrolyser research and development programme aimed at the next generation of electrolysers. ITM have recently developed ground breaking new low cost membranes that dramatically lower the cost of producing hydrogen whilst significantly lowering the infrastructure costs.

ITM's approach to membrane development is the UV polymerisation of low cost hydrocarbon monomers. A new highly conductive membrane has been developed and tested to 3 $A \cdot cm^{-2}$. This membrane is 125 ∝m thick to minimise hydrogen crossover, has a conductivity of 260 $mS \cdot cm^{-1}$ and is extremely low cost. When made into a MEA, this membrane allows a voltage of below 1.6 V at 1 $A \cdot cm^{-2}$ at only 55°C. This has been benchmarked against Nafion 115.

This is an early stage membrane and has been tested in a single cell only but demonstrates a significant step towards the production of low cost energy storage using hydrogen.

Acknowledgment
The research leading to these results has received funding from the European Community's Seventh Framework Programme (7FP7/SP1-JTI-FCH.2011.2.7) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement ELECTROHYPEM n° 300081.

Zinc Oxide: An Illuminating Photocurrent Response

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Zinc oxide is a promising transparent n-type semiconductor for cheap extremely thin absorber solar cells, to fully gauge its potential applications requires looking at the combination of optical and electronic properties. Vertically aligned arrays of zinc oxide can be easily grown on almost any substrate; the rods shown in fig. 1 have been grown on top of fluorine doped tin oxide, conductive glass. To understand the electronic properties of the nanorods under illumination, chopped light photocurrent has been recorded. A drop in photocurrent at increasingly positive potentials often seen in nanorods prior to thermal annealing is currently unexplained; photocurrent transients have been measured in an attempt to explain the shape of photocurrent-voltage graphs. Further measurements and optoelectronic modelling are being run in order to explain the mechanism, which is expected to provide an insight into how defect states affect charge transport within the zinc oxide nanorods.

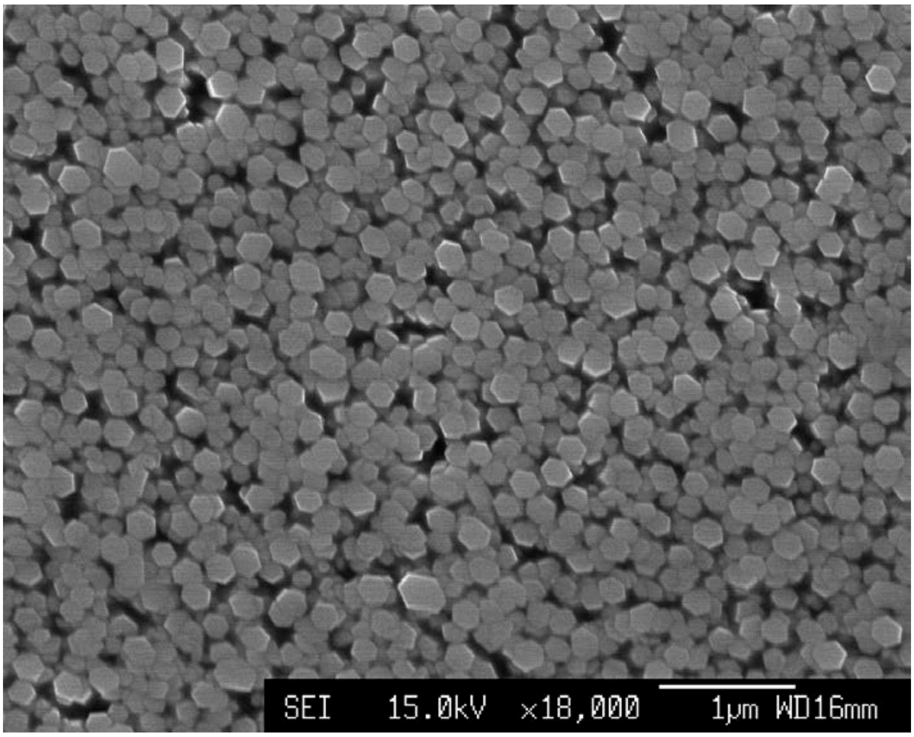

Fig.1 Vertically aligned zinc oxide nanorods grown hydrothermally onto fluorine doped tin oxide conductive glass (FTO).

Pt Nano-Particle Performance for PEFC Reactions at Low Catalyst Loading and High Reactant Mass Transport

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An alternative approach to the rotating disk electrode (RDE) for characterising fuel cell electrocatalysts is presented [1]. The approach combines high mass transport with a flat, uniform, and homogeneous catalyst deposition process, well suited for studying intrinsic catalyst properties at realistic operating conditions of a PEFC.

Uniform catalyst layers utilising standard fuel cell catalysts were deposited onto a porous substrate to loadings as low as 0.16 μg_{Pt} cm^{-2} and catalyst layer thicknesses as low as 200 nm. Such ultra thin catalyst layers are considered advantageous to minimize internal resistances and mass transport limitations. The electrodes were floated on aqueous electrolyte, whereby reactant gas diffused through hydrophobized pores to the catalyst layer. Modelling of the associated diffusion field suggests that such high performance is enabled by fast lateral diffusion within the catalyst layer. The electrodes operate over a wide potential range with insignificant mass transport losses, allowing the study of the ORR kinetics at high overpotentials, Figure 1.

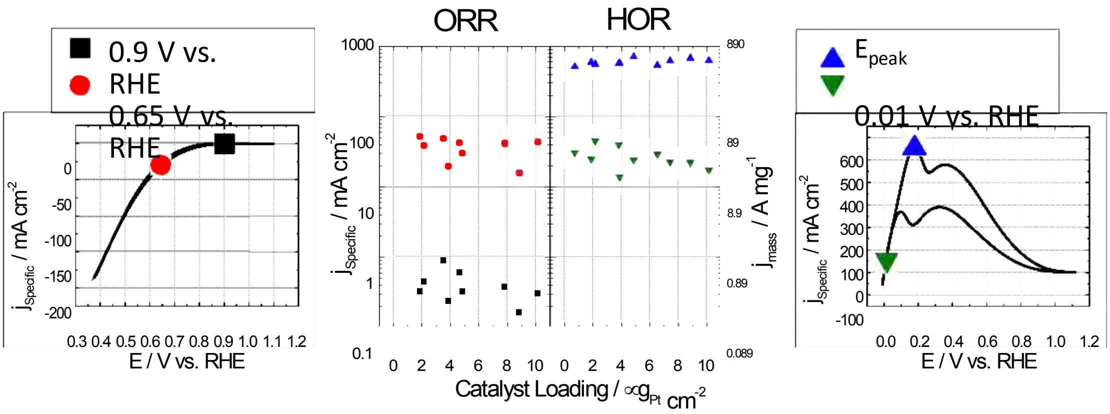

Figure 1. Performance as a function of applied potential (centre) of a range of ultra-low loading electrodes utilizing Johnson Matthey Hispec 9100 (60 wt% Pt/C) catalyst towards the ORR (left) and HOR (right), utilizing the floating electrode technique. 4 M $HClO_4$ at 25°C.

Geometric current densities as high as 5.7 A $cm^{-2}{}_{Geo}$ were experimentally achieved at a loading of 10.15 μg_{Pt} cm^{-2} for the HOR at room temperature, which is three orders of magnitude higher than current densities achievable with the RDE. Electrodes produced a specific current density of 31 ± 9 mA $cm^{-2}{}_{Spec}$ at a potential of 0.65 V vs. RHE for the ORR and 600 ± 60 mA $cm^{-2}{}_{Spec}$ for the peak potential of the HOR.

The mass activity of a commercial 60 wt% Pt/C catalyst towards the ORR was found to exceed a range of literature PEFC mass activities across the entire potential range. The HOR revealed fine structure in the limiting current range and an asymptotic current decay for potentials above 0.36 V. These characteristics are not visible with techniques limited by mass transport in aqueous media such as the RDE.

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Implementation of Hematite (α-Fe2O3) Photo-anodes in Photo-Electrochemical Reactors for Water Splitting

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Hematite, ⟨-Fe_2O_3, is a cheap, earth-abundant semiconductor material with a 2.2 eV band gap, in principle enabling it to harvest up to ca. 30 % of incident solar radiation. While its electron affinity of -4.7 eV [1] is too large for spontaneous H_2O reduction to H_2 to be feasible, the energetic position of its valence band (-6.9 eV) enables photo-generated holes to oxidise H_2O to O_2. Hematite appears stable to decomposition by electrons and holes in alkaline aqueous solutions over a wide potential range; hence, it is a practical photon absorber and a viable water oxidation catalyst.

Light-driven water oxidation micro-kinetics were investigated on ca. 30 nm-thick Sn^{IV}-doped Fe_2O_3 films, deposited onto fluorine-doped tin oxide coated (FTO) glass by spray pyrolysis at ca. 480 °C. Upon illumination with 49 W m^{-2} white light from a Xe lamp, an anodic photocurrent was detected with an onset at the flat band potential of +0.18 V in 1 M NaOH solution, then limited to 2.5 A m^{-2} at +0.4 V (vs. HgO | Hg), at which it exceeded the dark current by three orders of magnitude. The Sn^{IV}-doped Fe_2O_3 films were found to be *n*-type, with a separation of only 0.013 eV between the conduction band and the Fermi level at the flat band potential.

The contribution of the photocurrent generated in a hematite photo-anode to the rate of cathodic hydrogen production in an electrochemical reactor has been assessed both experimentally and by computational modelling. A reactor [2], utilising a 0.1x0.1 m^2 Sn^{IV}-Fe_2O_3 | Ti plate photo-anode and a 0.1x0.1 m^2 Pt | Ti mesh cathode, separated by a cation permeable membrane, was operated potentiostatically as hematite's conduction band edge energy limits its operation to photo-assisted water splitting only. Current densities and hydrogen fluxes were measured and compared as a function of applied cell bias in the dark and when the anode was illuminated with white light. COMSOL™ finite element software was used to model the distribution of electric potential and current in the photo-anode and cathode, as well as the ionic flux profile between the electrodes under selected operating conditions. The results of experiments and modelling will be presented.

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Indirect Water Electrolysis at a Ce-V Redox Flow Battery

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Energy storage is a matter of increasing urgency as the move towards intermittent renewable energy becomes more established. A number of technologies exist that are designed for large-scale electricity storage, such as the well-established redox flow battery (RFB). Other systems aim to convert electricity into transportable chemical species such as hydrogen, in so called power-to-gas arrangements. Water electrolysis is a clean means of directly converting renewable energy directly into hydrogen. Current electrolysers, mostly based on alkaline and proton-exchange membrane electrolysis, present a number of issues regarding the stability of the electrodes over long-term and discontinuous use however [1]. RFBs in turn have a number of advantages, but are disadvantaged by poor energy density, and a volume limited charging capacity.

Here, we present an alternative means of generating hydrogen as an energy carrier, using the charged redox species of a conventional RFB [2]. The system comprises a cerium-vanadium redox flow battery [3] (Ce-V RFB) combined with a secondary circuit of two catalytic chambers. During charging the acidic electrolytes are charged, producing V(II) in the catholyte and Ce(IV) in the anolyte. On complete reduction the catholyte is redirected to a catalytic chamber, where the protons reduce over a low-cost Mo based catalyst to generate hydrogen gas and regenerate the discharged redox species, V(III). On the anodic side Ce(IV) is redirected to its catalytic chamber producing oxygen and protons from water and regenerating Ce(III). The resulting Ce(III) and V(III) electrolytes are then directed back into the Ce-V RFB, in order to start a new cycle.

The reactions at the electrodes, the kinetics of the catalytic reactions, as well as the performance of the Ce-V RFB itself are presented. The catalytic efficiency for the generation of hydrogen is *ca.* 100%, whereas oxygen efficiency is 86%. Such a system is highly suitable to store renewable energy, either in the electrochemical form (conventional RFB), or as hydrogen gas. It increases the flexibility of a RFB when used for storing discontinuous energy sources, whilst retaining its conventional features.

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Keynote

Electrochemistry at Soft Interfaces

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Soft interfaces, such as the interface between two immiscible electrolyte solutions (ITIES), can be polarised and represent a class of electrochemical interfaces where many charge transfer reactions such as (assisted-) ion transfer and (photo-induced-) electron transfer reactions can take place in parallel.

In the recent years, these interfaces have been investigated in relation to energy research, for example to mimic photosynthesis.

In this lecture, we shall present the concept of electrocatalysis at soft interfaces. In particular, we shall discuss oxygen reduction at ITIES, and reactions related to the production of solar fuels namely photo-hydrogen production in the presence of sacrificial donors, photo-water oxidation in the presence of sacrificial acceptors and also the reduction of carbon dioxide at the water-supercritical CO_2 interface.

For oxygen reduction, we shall focus on the interfacial self-assembly of molecular catalysts.
For hydrogen evolution, we shall emphasize metallocene electrochemistry at the ITIES.
For water photo-oxidation, we shall discuss the inherent experimental difficulties.
For CO_2 reduction, we shall present both electrochemical and photochemical approaches.

References can be found at the following address: www.lepa.epfl.ch

Energy Conversion at Soft Interfaces Using Floating Nano-Catalytic Rafts

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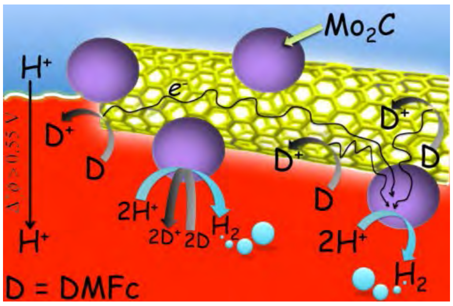
In this presentation recent advances towards achieving the two half-reactions for water splitting, the H_2 evolution reaction (HER) and the O_2 evolution reaction (OER), using aqueous-oil biphasic systems are addressed.



Schematic of the biphasic H_2 evolution reaction in the presence of the conductive catalytic CNT/Mo_2C nanocomposite floating at a polarised interface. The electron donor, decamethylferrocene (DMFc), may inject electrons anywhere on the carbon support and these electrons are then efficiently shuttled along the conductive CNT electron "transport superhighway" to the Mo_2C active sites where proton coupled electron transfer (PCET) H_2 evolution occurs. Alternatively, DMFc may take part directly in a PCET process at the Mo_2C active site to evolve H_2. The aqueous phase is on top and the denser organic phase is on the bottom.

Biphasic systems offer a new perspective for the production of H_2. The interfacial Galvani potential difference may be controlled potentiostatically or chemically (by distribution of electrolyte ions) and used to pump protons from the aqueous to the oil phase. Under anaerobic conditions this enables their reduction to H_2 in the presence of strong organic reducing agents (i.e., decamethylferrocene)[1] in the dark or the excited states of weaker electron donors (i.e., decamethylosmocene)[2] under UV/vis irradiation.

Catalysis of the HER is achieved by various precious and non-precious nanoparticulate "floating rafts" at the aqueous-oil interface. Advanced carbon supported nanocomposites incorporating non-precious H_2 evolution catalysts, such as MoS_2 grown on reduced graphene oxide or Mo_2C grown on CNTs, display exceptional catalytic responses towards the otherwise kinetically sluggish biphasic HER.[3,4] The stability of the interfacial catalysts during these biphasic reactions was confirmed using a novel electrolysis cell.

Recent advances towards achieving the more challenging biphasic OER are outlined, as are achieving the biphasic HER in the presence of weak reversible electron donors using carbon nanocomposites with both catalyst (MoS_2) and sensitizer (TiO_2) elements present. Achieving the biphasic HER in the presence of such weak electron donors is advantageous in so far as relatively weak electron acceptors (generated from the light driven biphasic OER) would be required to regenerate both donor and acceptor species, thereby "re-setting" this photo-system.

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Spinel Ferrites as an Emerging Class of Semiconductor for Solar Energy Conversion

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Hydrogen could be the fuel of the future, providing that it can be produced in a clean, environmentally and economically friendly way. Photoelectrochemical (PEC) water splitting is an environmentally-sustainable and low-cost route to produce hydrogen by splitting water molecules into its constituents, using sunlight. If succeeded this technology has the potential to produce hydrogen to meet the fast growing world energy demand while producing almost no pollution. Direct PEC water splitting requires a material that satisfies several key criteria. The semiconductor must have a suitable bandgap (1.6 – 2.3 eV) to generate the water splitting potential while still absorbing visible light, the conduction and valence band edges must straddle the hydrogen and oxygen redox potentials, it must have a high conversion efficiency of photons to electrons, must be stable under operational conditions, and must be abundant and inexpensive.

Recent work conducted by our group and others indicate that spinel ferrites (general formula MFe_2O_4) have become an emerging class of semiconductor material for solar energy conversion applications (i.e. in PEC water splitting cells as well as in thin film photovoltaics) [1]. It has already been shown that spinel ferrites can exhibit *n*-type or *p*-type conductivity, depending on the choice for M [1,2]. Here we present the PEC properties for $ZnFe_2O_4$ prepared by aerosol-assisted chemical vapour deposition (AACVD) [2]. Figure 1 shows the surface and cross-sectional images, and the current-voltage curves for $ZnFe_2O_4$ thin films [1]. The films are highly nanostructured and exhibit high photocurrents of around 1 mA cm^{-2} at 0.7 V vs. Ag|AgCl. Results show that these films are highly stable in aqueous electrolytes and are resistant to photocorrosion.

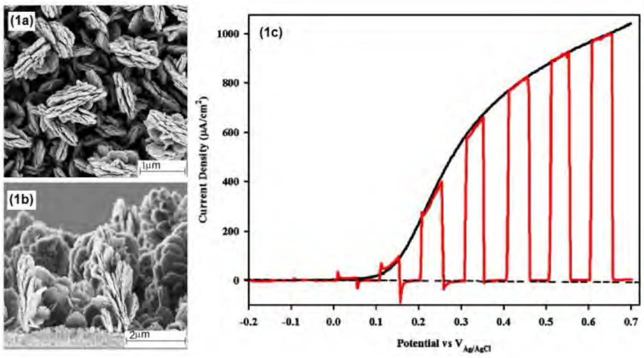

Figure 2. Showing the surface (a), cross-section (b) and current-voltage curves (c) for $ZnFe_2O_4$ thin films [1].

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Electrochemical Analysis of the Effect of Electrodeposited Mg(OH)2 Layer on the Performance of Mechanically Compressed Flexible Dye Sensitized 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. 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 ED $Mg(OH)_2$ conformal layer.[3] Furthermore, the effect of the electrodeposited $Mg(OH)_2$ coating on the displacement on the conduction band of the semiconductor is also analysed to describe differences found in device characteristics.

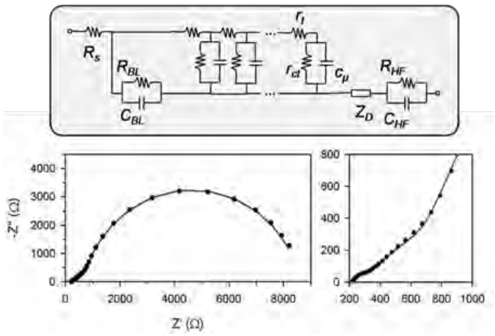

Fig. 1 The Impedance spectrum of the cell with $Mg(OH)_2$ layer in the dark at -0.70 V (dots) and fitting to the spectrum by using the equivalent circuit above the plots (lines). The right plot shows a zoom at high frequency.

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Infrared Spectroscopic Study of Anatase TiO2 Photocatalysis. Formate Adsorption, Hole Scavenging, Electron Trapping with Proton Intercalation

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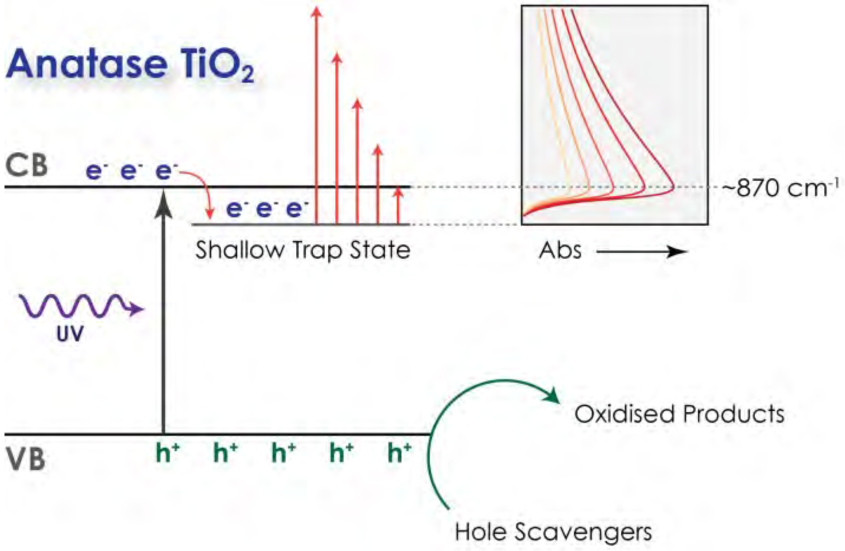
The UV irradiation of anatase TiO_2 particle films immersed in acidic anoxic aqueous solution results a broad infrared (IR) absorption peaking at ~870 cm^{-1} which has been attributed to electron transitions from a shallow electron trap state to a continuum of conduction band states [1]. In adsorption/desorption experiments to anatase TiO_2 of oxalate ion the broad IR absorption correlates with the outer-sphere adsorbed oxalate IR signal rather than that of the inner-sphere species suggesting that hole trapping is predominantly via outer-sphere adsorbed species [2]. Related IR studies of anatase TiO_2 in near vacuum conditions have also observed the shallow trap absorption and suggested it arises from protonated oxygen bridges [3].



Formate ion has been frequently used as a simple hole scavenging species in TiO_2 photocatalysis studies. The present work shows that formate ion is adsorbed predominantly as the outer-sphere species which greatly enhances the shallow trap IR absorption. This results in efficient capture of photogenerated holes while the trapped electrons drive the charge balancing intercalation of protons. Comparisons of results from different size particles indicate the shallow traps are formed in the bulk following proton intercalation.

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Tailoring Carbon Electrodes, Redox Complexes and Polymer Supports for Glucose Oxidase Bioelectrocatalysis of Glucose

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The immobilisation of an enzyme and redox mediators on an electrode surface to provide an electrocatalytic biofilm is of critical importance for biosensor and biofuel cell development. Immobilisation can have a significant impact on the magnitude and stability of the electrochemical response. Here we examine immobilisation strategies for grafting/adsorption of osmium-based redox mediators onto carbon electrodes, for enzyme electrode fabrication.

A redox active monolayer is immobilised on the electrode surface by simple electrochemical oxidation of alkyl amine ligands of the redox complex. The redox active surface was characterized by XPS and voltammetry.

Thicker films can be produced by crosslinking alkyl amine ligands of the redox complex with functional polymers as a support, with concomitant adsorption/grafting to the carbon surface. Polymers investigated as suitable supports include carboxymethylated dextran, polyacrylic acid, chitosan and polyethylenimine. Amine functional groups are introduced at the electrode surface by electrochemical reduction of a diazonium cation, generated in-situ by diazotisation of p-phenylenediamine. Following this, co-immobilisation of enzyme, redox complex and polymer support using a chemical crosslinker provides a 3-dimensional biofilm for electrocatalysis.

Here we examine the electrochemical response of crosslinked biofilms composed of glucose oxidase, $[Os(2,2\text{-bipyridyl})_2(4\text{-aminomethylpyridine})Cl]PF_6$ redox complex and a range of polymer supports. Addition of multiwall carbon nanotubes into the 3D- matrix provides significant improvement to current signal magnitude and stability. Overall, a maximum glucose oxidation current density of 1.5 mA cm^{-2} at 0.45 V vs. Ag/AgCl, in pH 7.4 phosphate buffer containing 100 mM glucose at 37 °C was achieved, showing promise as a glucose oxidising anode in a biofuel cell for electrical power generation.

The Development and Characterisation of Silver Electrodes for Alkaline Membrane Fuel Cells

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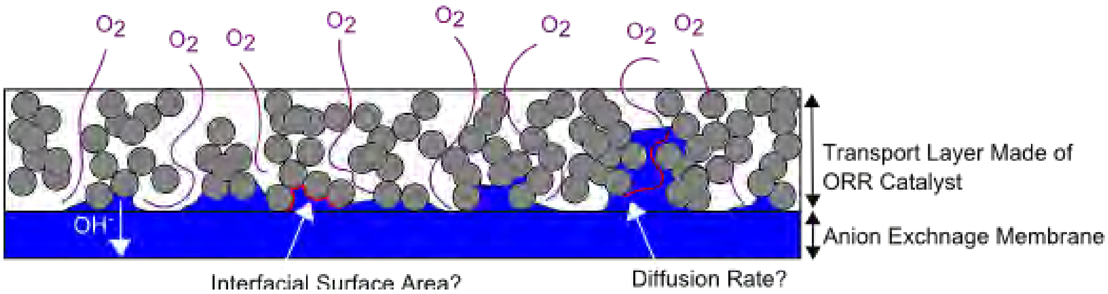
Alkaline membrane fuel cells (AMFC) offer an interesting route to reduce the material cost of low temperature fuel cells. In contrast to traditional proton exchange membrane fuel cells (PEMFC) hydroxide ions rather than protons carry charge [1]. The resulting rise in pH increases the stability and possibly reactivity of some oxygen reduction reaction (ORR) catalysts such as Ag and Ni [2]. Critically, unlike alkaline fuel cells (AFC) AMFC are resistant to metal carbonate precipitation and can purge themselves of carbonate anions during operation [3].

We will present the development of an MEA based on a transport layer made of silver [4]; with techniques to characterise the electrochemical surface area, reactant transport though ionomer and carbonate anion concentration of the system. We believe these manufacturing and characterisation techniques to be widely applicable to other AMFC MEA’s and essential in understanding optimisation.



As well as having exceptional conductivity silver has been shown to have an ORR price activity (£/mA) similar to the archetypal PEM catalyst platinum when in contact with alkaline membranes [5]. It is an outstanding material for both transport layers and cathode catalysts in AMFC. Unlike platinum, it is not possible to measure the specific surface area of a silver catalyst using hydrogen adsorption or oxide formation. We will show specific surface area measurements on both the silver transport layers and silver nanoparticles down to 10nm in size, using the well-known technique [6] of lead under potential deposition (UPD) and correlate this with ORR activity.

In an MEA, active catalyst is at least partially covered with ionomer. To achieve the same cell performance, catalysts less active than platinum may require thicker catalyst layers and subsequently more ionomer than in traditional PEMFC. The reactant transport properties of anion ionomers is largely unreported. We will present measurements of both the diffusion coefficients and equilibrium concentrations of reactants in anion exchange membranes.

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Enhanced Oxygen Evolution at ‘Aged’ Hydrous Nickel Oxide Electrodes in Alkaline Solution: Kinetics and Mechanism

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Electrochemical water splitting via alkaline water electrolysis is currently an extremely active research area of intense 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] 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). Dimensionally stable anode (DSA®) electrodes, based on RuO_2 and IrO_2 currently exhibit the lowest overpotential for the OER at practical current densities.[2] Despite their excellent OER performance, the relative high cost of these materials renders their long term use as anode materials for water electrolysers impractical. Because of this problem we and other groups 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. [3,4]

In this work we have adapted an ‘ageing’ method, discovered initially for electrodeposited nickel hydroxide on gold support electrodes to further enhance the OER performance of hydrous nickel oxide films as presented recently in papers emanating from our research group. [5–8] Electrochemical ageing was found to significantly enhance the OER performance of the hydrous nickel oxide electrode (fig.1) with the OER overpotential decreasing by 60 ± 2 mV and experiencing a 10 fold increase in OER rate for a fixed overpotential over that of an un-aged electrode.

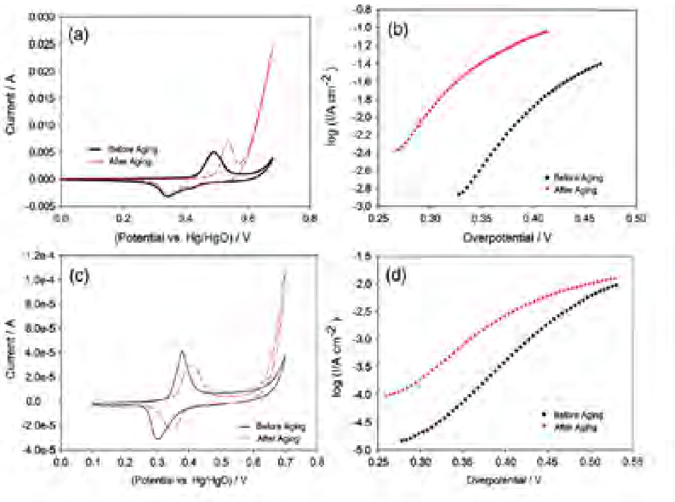

Fig. 1. (a) Typical cyclic voltammogram (b) Tafel plot of a hydrous nickel hydroxide electrode before and after electrochemical ageing by slow potential multicycling in 1 M NaOH across the Ni(II/III)/Ni(III/II) redox peaks shown. (c) Cyclic voltammogram (d) Tafel plot of an electroprecipitated ‘battery type’ nickel hydroxide electrode on an Au substrate before and after aging using the same slow potential multicycling regime. Potentials quoted against Hg/HgO. Scan rate 40 mV/s for cyclic voltammograms and 1 mV/s for Tafel plots.

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The Design and Characterization of a Standalone Hydrogen Generator Operating Via Catalytic Borohydride Decomposition

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A laboratory glass hydrogen generator from sodium borohydride was designed and constructed. The reactor consisted of two main compartments: a lower chamber, where the borohydride solution was introduced and an upper reaction chamber, containing the catalyst, as shown in Figure 1. By pressurizing the lower chamber, the borohydride solution was forced up to the reaction chamber to make contact with the catalyst and generate hydrogen[1]. Several catalysts such as platinized titanium, Pd-Ir alloy, Pt nanoparticles on carbon paper and Pd deposited on granular carbon (Pd/C) were evaluated. The effects of borohydride concentration, sodium hydroxide, water quality and catalyst loading have been studied. The fastest hydrogen generation rate obtained was 600 cm^3 min^{-1} during 120 minutes using 15 g of palladium on granulated carbon and a solution of 4 mol dm^{-3} $NaBH_4$ prepared with distilled water. The use of river water showed a lower activity for hydrolysis leading to low gas flow rates while commercial ‘still’ drinking water was more active. Mixing borohydride (53 g) and catalyst (15 g Pd/C) in the reaction chamber and adding 350 cm^3 still drinking water produced no hydrogen during the first 30 min of reaction but the hydrogen generation rate increased gradually, reaching more than 500 cm^3 min^{-1} after 170 min reaction[2]. SEM images and EDX analysis of the Pd/C catalyst suggest some decrease in the palladium content after it had been used three times. The results are encouraging but further investigations should be carried out using a more robust catalyst able to maintain its mechanical integrity over a larger number of operations[2].

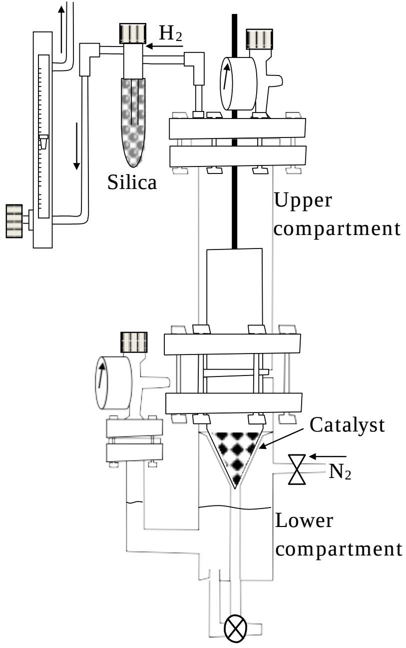

Figure 1. Hydrogen generator reactor

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The Stability of LaMnO3 Surfaces: A Hybrid Exchange Density Functional: Theory Study of an Alkaline Fuel Cell Catalyst

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$LaMnO_3$ is an inexpensive alternative to precious metals (e.g. platinum) as a catalyst for the oxygen reduction reaction in alkaline fuel cells. In fact, recent studies have shown that among a range of non-noble metal catalysts, $LaMnO_3$ is one of the most catalytically active. Despite this, very little is known about $LaMnO_3$ in the alkaline fuel cells environment, where the orthorhombic structure is most stable. In order to understand the reactivity of orthorhombic $LaMnO_3$ we must first understand the surface structure. Hence, we have carried out calculations on its electrostatically stable low index surfaces using hybrid-exchange density functional theory, as implemented in CRYSTAL09. For each surface studied the calculated structure and formation energy is discussed. Among the surfaces studied the (100) surface was found to be the most stable with a formation energy of 0.98 J m^{-2}. The surface energies are rationalised in terms of the cleavage of Jahn-Teller distorted Mn-O bonds, the compensation of under-coordination for ions in the terminating layer and relaxation effects. Finally, the equilibrium morphology of orthorhombic $LaMnO_3$ crystals is predicted, allowing us to speculate about likely surface reaction sites.

Kinetics of Solid Oxide Fuel Cells with Molten Tin Anodes

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Carbonaceous fuels including coal, lignite, biomass, waste materials such as paper and plastics, toxic wastes (cyanides, polychlorinated biphenyl, etc.), and refining by-products such as coke, are widely-dispersed regionally and easily accessible. In a carbon-air fuel cell (CFC), atmospheric oxygen is reduced at the cathode to oxide ions, O^{2-}, which migrate through the electrolyte and react with the carbonaceous fuel housed in the anode to produce electrical energy. Alternatively, a metal oxide (e.g. SnO_2, Bi_2O_3 and Sb_2O_3) can be produced at the anode as an intermediate by-product to be reduced externally in a combustion reactor. This latter method avoids the accumulation of undesirable compounds such as ash, which could affect the stability and performance of the fuel cell materials (1, 2).

The kinetics and performance of a solid oxide fuel cell with a molten tin anode (Sn(*l*)-SOFC) at 900 °C were studied using electrochemical kinetic techniques. Reproducibility and stability were obtained with a cell consisting of a 2 mm thick yttrium-stabilized zirconia (YSZ) pellet as electrolyte, a double layered lanthanum strontium manganese (LSM) - YSZ/LSM cathode printed on the electrolyte using a doctor blade, and a pure molten tin anode directly in contact with the YSZ electrolyte. Platinum wires and mesh attached to the cathode with platinum paste, and a graphite rod immersed in the molten anode were used as current collectors.

Atmospheric oxygen is reduced at the cathode and the resulting oxide ions injected into the YSZ electrolyte:

$$O_2 + 4e^- \longrightarrow 2O^{2-} \qquad [1]$$

while at the anode | electrolyte interface, oxygen dissolves in the molten tin (Sn(*l*)) to its temperature-dependent solubility limit, above which tin dioxide forms locally:

$$2O^{2-} \longrightarrow 2[O]_{sn} + 4e^- \qquad [2]$$

$$Sn + 2[O]_{sn} \longrightarrow SnO_2 \qquad [3]$$

The kinetic parameters α, $j_{0,a}$ and $j_{l,a}$ related to the anode activation polarization component of the cell voltage were obtained using the experimental polarization curves acquired using the Sn(*l*)-SOFC described above. Kinetic data for the cathode reaction [1] and diffusion of dissolved oxygen in molten tin was found in the literature (3, 4), while ohmic losses of 9.7 Ω cm^2 were determined from impedance spectroscopy measurements at an open circuit potential of 0.85 V. Using these data together, a MATLAB code was developed to estimate oxygen transport rates in molten tin and hence anode reaction kinetic parameters: transfer coefficient 0.6, exchange current density ca. 205 A m^{-2} and limiting current density ca. 1980 A m^{-2}. The limiting rate process corresponds to the formation and deposition of SnO_2 at the electrolyte | anode interface by reaction [3], which inhibits reaction [2]. Based on these kinetic parameters, an optimized experimental reactor was modeled, excluding the undesirable ohmic losses components related to current collection and contact potential losses.

Results are presented in Figure 1 and Figure 2 for cell potential difference (U), power density, and concentration and activation overpotentials as a function of operating current density. A maximum power density of ca. 470 W m^{-2} was derived at a current density of ca. 1,130 A m^{-2} and a cell potential difference of ca. 0.42 V for the quiescent molten Sn anode at 900 °C. These data are in accordance with a previous model developed for a micro-tubular Sn(*l*)-SOFC (5), and correspond to the minimum operating potential to avoid precipitation of SnO_2 by reaction [3]. Additional modeling predictions will be reported for a Sn(*l*)-SOFC in which a carbonaceous fuel is used to reduce *in-situ* the SnO_2 by-product at: $SnO_2 + C \rightarrow Sn + CO_2$. The objective of this model was predicting its effect on the reactor kinetics.

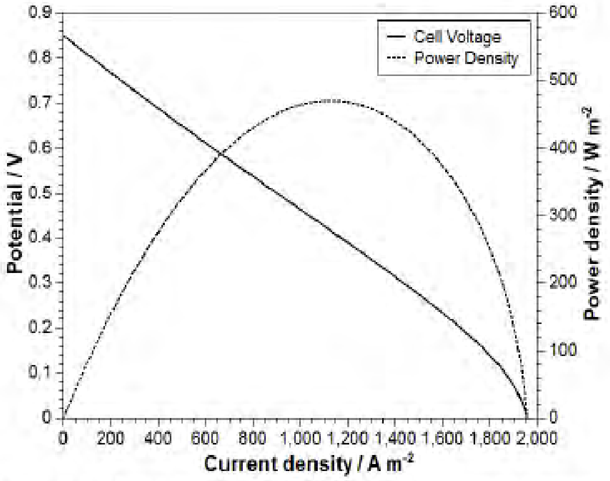

Figure 1. Predicted effect of operating current density on the cell potential difference and power density for a Sn(*l*)-SOFC at 900 °C.

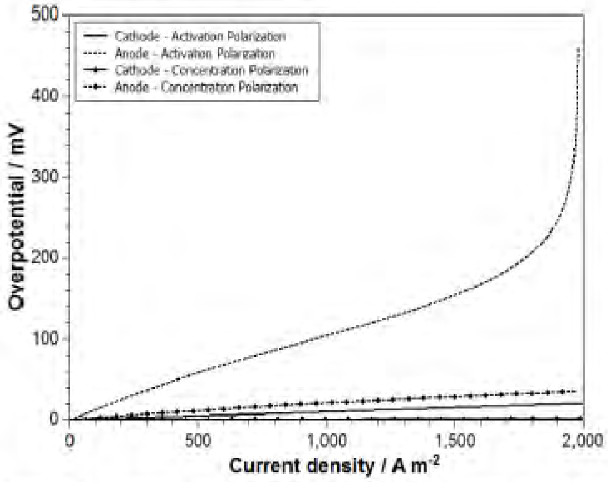

Figure 2. Predicted dependences of anode and cathode concentration and activation polarizations on operating current density in a Sn(*l*)-SOFC at 900 °C.

Acknowledgements

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Development of a Non-Pt Anode Catalyst for Alkaline Anion Exchange Membrane Fuel Cells

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With the high cost and limited availability of platinum, much effort has gone into the reduction of catalyst loadings in fuel cell electrodes. Platinum is the most effective catalyst for both the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR) in acidic polymer electrolyte fuel cells (PEM), but the vastly improved kinetics of the ORR in an alkaline medium opens up the possibility of utilizing cheaper catalysts for alkaline anion exchange membrane fuel cells (AAEM).

However, in the alkaline environment, the kinetics of the HOR are an order of magnitude slower on Pt than in acid (though Pt remains the best catalyst in both media). Therefore, in order to take advantage of the more facile ORR kinetics in alkaline, anode catalyst development and cost reduction is required. Anode catalyst development is often overlooked but is necessary for commercial realisation of AAEM fuel cells.

Rotating disk electrode (RDE) studies, along with *in situ* fuel cell testing, have shown a novel, high-efficiency low cost catalyst to have activation properties matching that of Pt, when used in alkaline conditions. The performance of the low cost catalyst in an AAEM is also similar to that of an AAEM made using commercially available Pt electrodes, suggesting a potential route for future reduction of cost and platinum use in fuel cell electrodes.

Advanced Diagnosis for Proton Exchange Membrane Fuel Cell Stacks

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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 order to make further improvements to the key performance metrics, it is important that we know as much as possible about the way the fuel cell is working in space and time. Electrochemical impedance spectroscopy (EIS) is a powerful in situ diagnostic technique for monitoring fuel cell performance; however, its use has been mainly limited to single cells using costly potentiostat hardware. Here we present a low-cost multichannel impedance analyser developed using a commercial data acquisition hardware and LabVIEW software[1]. This novel diagnostic system is applied to a commercial Intelligent Energy air-cooled open-cathode 5-cell PEMFC stack.

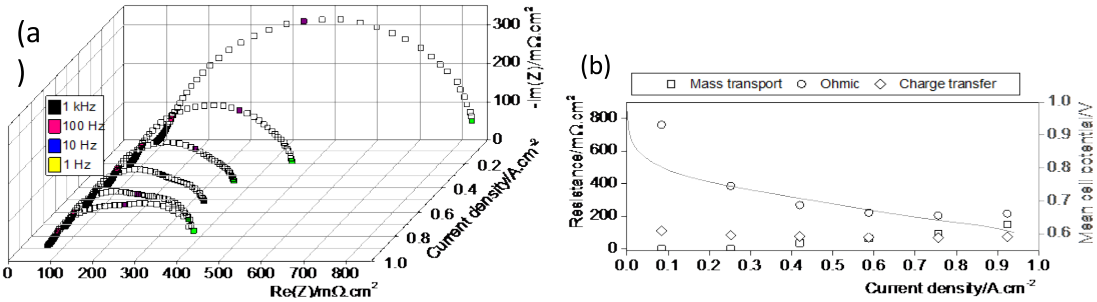

Figure 3. Nyquist plots from 0 to 1 A.cm^{-2} and associated fit results of cell 1.

The system is capable of simultaneous measurements and data fitting of all five cells in the stack. Measurements across the polarisation curve, and data fitting (Figure 1) revealed an increase in mass transport resistance and drop in charge transfer resistance from 0 to 1 A.cm^{-2}, coherent with an increase in hydration level due to higher currents. Infrared thermal imaging has been performed to study the heat distribution at the edges of the stack, with fans operating in different modes; revealing a 30°C temperature difference across the cathode inlet and outlet of the stack. A combination of impedance and infrared thermal imaging has been used to characterise the operations of the stack in through flow and dead ended anode operations.

Preliminary work using a current and temperature sensing plate promises to shed further information on the performance of the internal workings of a single cell.

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Applications of Metal Oxide Nanotubes for Solar Cells

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Elongated metal oxide nanostructures (such as synthetic titanates, vanadium pentoxide or natural silicates nanotubes) have attracted a great attention over the last decade due to their unusual phisico-chemical properties and potential use in many applications including conversion and storage of solar energy. Titanate nanotubes (TiNT) are of particular interest due to their direct applications in dye sensitized solar cells (DSSC) and lithium batteries [1, 2]

In case of DSSC, nanotubular morphology of TiNT and anionic nature of the surface can provide some advantages of improved current collection efficiency in dye sensitised collar cells due to increased adsorption of the dye resulting in reduced thickness of the light absorbing layer. Additional shift of the flat band potential of TiNT can also increase power efficiency of DSSC but would require to search for new dyes.

The interaction of several cationic dyes including Rodamine and Cyanine types with nanotubular titanates has been studied using the methods of steady state and time resolved fluorescence spectroscopy. It has been found that despite very strong interaction between negatively charged TiNT and positively charged dye, the coupling of wavefunctions between them strongly depends on the nature of the dye resulting in the difference in efficiency of electron injection from dye to semiconductor.

Strong adsorption of some cationic dyes is also accompanied with the reduction of their radiative lifetime without quenching of luminescence. This can be attributed to Förster resonance energy transfer (FRET) between the dye molecules [3]. Our early studies indicate that titanate nanotube decorated with organic fluorophores can be used as nanoscale light harvesting antennas, which can be utilized in dye sensitized solar cells or fluorescent solar collectors.

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ELECTROCHEM
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Speaker Abstracts

Electroanalysis at Gold Nanowire Electrode Arrays: Assessment of Required Inter-Electrode Distance Towards Sensing Applicability Enhancement

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Typically, nanowire electrodes demonstrate enhanced performance, when compared to microelectrodes, due to improved mass transport occurring at the nanoelectrode [1, 2], thereby offering the potential for faster and more sensitive electroanalysis. Further enhancements are expected at nanowire electrode arrays. However, a critical factor in the design of nanowire electrode arrays is the inter-electrode distance and hence the objective is to assess the separation required between adjacent nanowires to maximise the electrochemical response. To this end, 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, see Figure 1. To date, to the best of our knowledge, this has not been previously reported in literature and work is now on going to explore these phenomena.

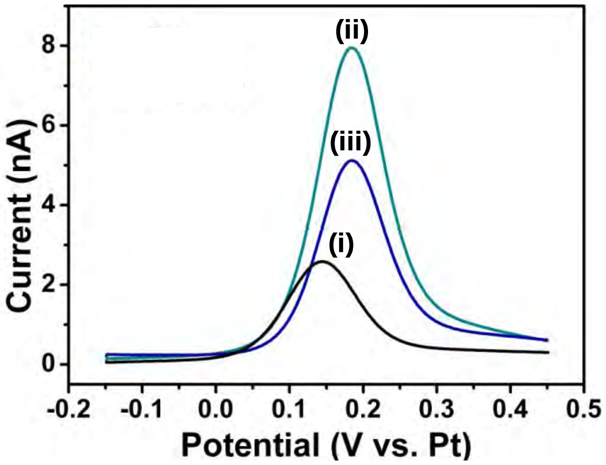

Figure 1: Typical square wave voltammograms of 5 mM FcCOOH in 10 mM PBS at (i) a single nanowire electrode, (ii) three nanowire electrodes in array separated by 5 µm and (iii) three nanowire electrodes in array separated by 15 µm.

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Electrochemical Detection of TNT at Gold Nanowire Arrays

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The detection of waste 2,4,6-trinitrotoluene in ground waters is an on-going concern for environmental and health reasons. TNT has linked with a variety of health risks such as anaemia, skin irritation and abnormal liver function. As well as this, the US Environmental Protection Agency has identified TNT as a possible human carcinogen. [1, 2] Current methods of TNT identification require expensive lab-based equipment and highly trained personnel so it is clear that a user-friendly and portable solution is required. Optical lithography allows for the reproducible fabrication of gold nanowire devices on a silicon substrate which lends itself to further intergration.

Square wave voltammetry (SWV) has been used to identify the reduction potential of nitro groups in TNT and similar nitroaromatic compounds (dinitrotoluene, nitrotoluene, dinitrobenzene). Subsequently, the magnitude of this electrochemical response was used for the generation of a calibration curve which allowed for the quantification of trace levels of the explosive compound.

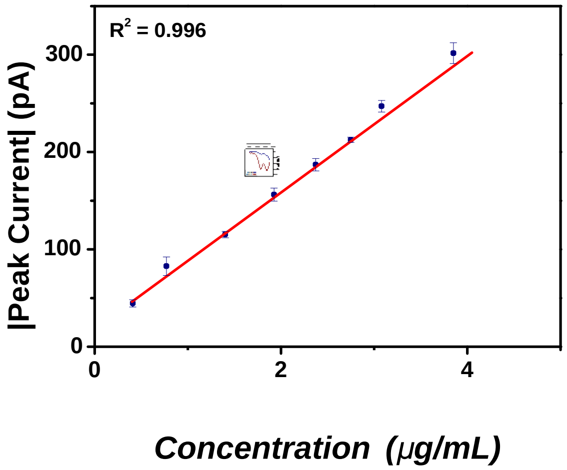

Figure 1: Calibration plot of TNT obtained using peak currents measured at -671 mV. Inset: SWV voltammograms obtained for 0.40 and 3.8 μg/mL, respectively

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Copper Alloy for Direct Detection of Amino Acids in Ion Chromatography

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The aim of this work is to present a novel pulsed amperometric detection of amino acids aimed specifically to apply after the chromatographic separation and using copper alloys as electrodes. Amino acids detection with the use of copper electrode dates from 1970s[1]. Even though almost 40 years have passed no further evolution has been achieved on this field, still gold working electrodes are employed. The principal detection type for amino acids is the spectrophotometric detection with ninhydrin. However, the highly alkaline media in which the separations occur must be considered. In order to maintain the system working, regular maintenance is needed. This work will present a technique that ally different properties of material to a specific developed pulsed technique allowing copper to work in these extreme alkaline conditions.

At first, a comprehensive study of how the amino acids would react with copper in alkaline solution was held. In agreement from the literature, amino acids present mix behaviour, on lower potential range (from 0.0 to 0.5V *vs* Ag|AgCl in 3 mol L^{-1} KCl), they form complexes with the copper hydroxide presented over the electrode. However, at higher potentials (from 0.5 to 0.8 V)[2], amino acids suffer oxidation over the electrode, leading to a measurable signal. At this point it is interesting to discuss about the substitution of pure copper by a copper alloy that allows a higher life time of the electrode, as the alloying elements form more resistant materials in the areas of interest. In the present case, the electrode has to be more resistant to corrosion in alkaline solutions when the production of oxide is needed up to be controlled.

Regarding the electrochemical technique, the development of a pulse involve the formation of the oxide with catalytic effect, and the restructuration of the electrode surface in order to achieve a life standing electrode. In Figure 1 it can be seen a chromatogram of BCAA (Branched-chain amino acids), obtained with the copper alloy electrode.

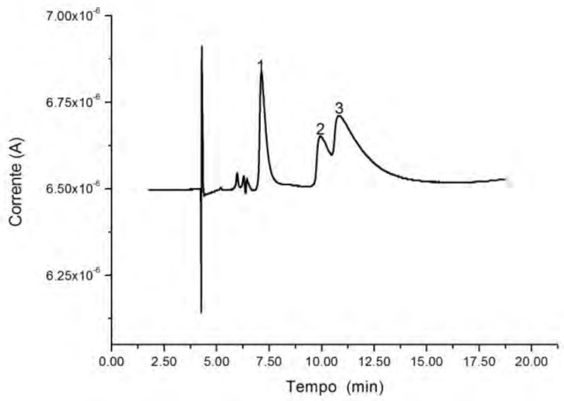

Figure 1 Chromatogram of BCAA sample obtained with a Carb1 Column. Flow Rate of 1 mL min^{-1} of 0.15 mol L^{-1} NaOH with 0.10 mol L^{-1} NaOAc as eluent. PAD detection with a brass working electrode. Peak 1 represents Valine, 2 Leucine and 3 Isoleucine.

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The Redox Behaviour of Diazepam (Valium®) using a Disposable Screen-Printed Sensor and Its Determination in Drinks using a Novel Adsorptive Stripping Voltammetric Assay

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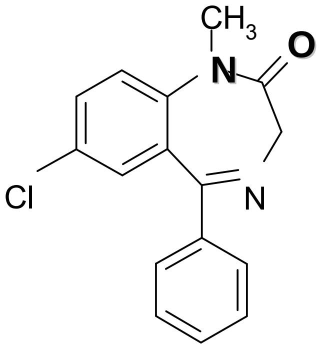
In this study we investigated the possibility of applying disposable electrochemical screen-printed carbon sensors for the rapid identification and quantitative determination of diazepam (i) in beverages. This was achieved utilising a previously unreported oxidation peak. The origin of this peak was investigated further by cyclic voltammetry and gas chromatography/mass spectroscopy. At pH 6 the voltammetric behaviour of this oxidation process was found to involve adsorption of the drug, on to the sensor surface, allowing for the development of an adsorptive stripping voltammetric assay. Experimental conditions were then optimised for the determination of diazepam in a beverage sample using a medium exchange technique. It was shown that no elaborate extraction procedures were required.



(i)

Detection of Sub-Femtomolar DNA Based on Double Potential Electrodeposition of Electrocatalytic Platinum Nanoparticles

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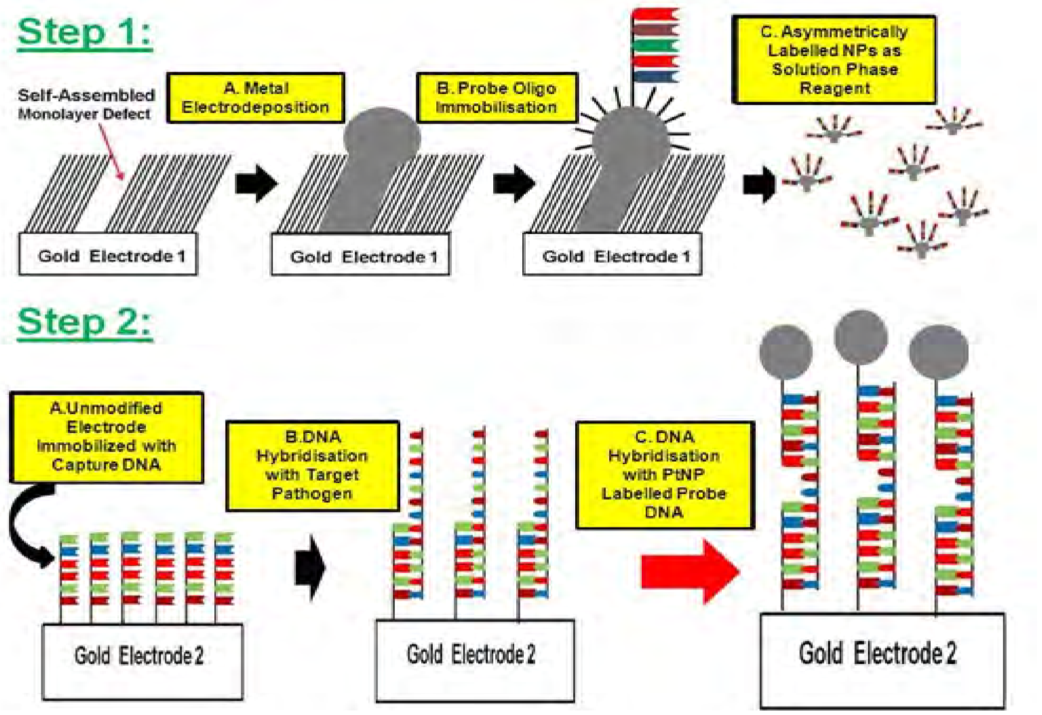
As illustrated in Scheme 1, an approach is described where electrodeposited nanoparticles within a dodecanethiol monolayer can be regioselectively functionalized with thiol terminated probe strand DNA. The size of these nanoparticles can be controlled to optimize their catalytic activity, by using a double pulse potential electrodeposition technique, which involves a nucleation pulse and a growth pulse. A current step is applied to melt the nanowire connecting the hemispherical nanoparticle to the electrode causing rapid desorption of the DNA functionalized PtNPs electrode while retaining the functionality of the bound nucleic acid. These DNA labelled electrocatalytic particles are then used in a hybridization assay to determine the concentration of the target DNA sequence from the specific strain of *S. aureus* that causes mastitis (mammary gland inflammation) by measuring the faradaic current associated with reduction of peroxide in solution. Significantly, beyond the ability to successfully create regioselective functionalized platinum nanoparticles (upper surface only) with DNA while the remainder of the particles surface is unmodified allowing efficient electrocatalysis to occur, we have also demonstrated that these particles are capable of detecting DNA with high sensitivity and selectivity at atto-molar concentrations. The assay is characterized by a wide dynamic range, high sensitivity, a low detection limit and an excellent ability to discriminate against interferences. This approach can easily be extended to reduction of water, which, in the case of biological samples, can come from the sample itself.



Scheme 1. Platinum nanoparticle formation and regioselective DNA functionalisation.

DNA Mediated Immobilisation of Electrocatalytic Nanoparticles in Gold Nanocavity Arrays

Elaine Spain, Tia E. Keyes, Robert J. Forster*
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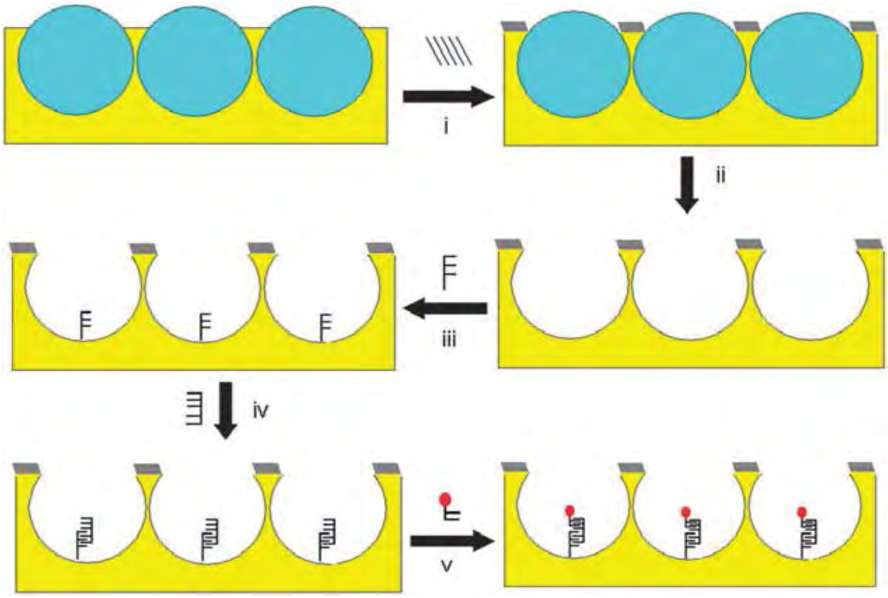
As illustrated in Scheme 1, an approach is described where platinum nanoparticles, PtNPs, functionalised regioselectively with probe strand DNA, have been immobilised within the interior of gold nanocavity arrays via DNA hybridisation. DNA hybridisation selectively confines the electrocatalytic platinum nanoparticles only on the walls of gold nanocavities while the upper surface remains unmodified. The use of DNA allows the separation between the nanocavity surface and the nanoparticle to be controlled which is important for maximising the interaction of the nanoparticle and cavity fields. Moreover, the DNA mediated immobilisation of a highly electrocatalytically active nanoparticle within a cavity opens up the possibility of highly sensitive DNA detection due to the significantly higher currents for the reduction of hydrogen peroxide than uniformly functionalised particles.

SEM reveals that after hybridisation with a target strand DNA and probe strand DNA modified with the PtNPs, nanoparticles can be clearly seen within the cavity at a high occupancy rate ~97 %. Significantly, negligible particle binding occurs outside of the cavity, indicating that the blocking monolayer of COOH-C11-SH at the top surface inhibits DNA adsorption. Electro catalytic sensing shows that nanocavity arrays containing bound platinum nanoparticles that have been regioselectively, or uniformly, modified with probe strand DNA generate a significant reduction current following the addition of hydrogen peroxide. The sensitivity of the assay is further enhanced when using the regio-selectively decorated PtNPs on which the two functions, i.e., molecular recognition and electrocatalytic sensing, are physically separated. Moreover, irrespective of whether the nanoparticles are functionalised regioselectively or uniformly, the electrocatalytic current as well as SERS signals of the bound DNA measured is approximately two times higher when they are captured within nanocavities compared to a planar surface.



Scheme 1. Fabrication of the gold nano-cavity arrays: (i) deposition of a self-assembled monolayer on the top surface, (ii) dissolution of the templating spheres, (iii) selective modification of the cavity interiors with capture strand DNA, (iv) hybridisation of the target with the immobilised capture strand DNA and (v) capture of the electrocatalytic platinum nanoparticles mediated by target–probe DNA hybridisation.

A Cholesterol Biosensor Based on the NIR Electrogenerated-Chemiluminescence (ECL) of Water-Soluble CdSe/ZnS Quantum Dots

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The burden of high cholesterol levels on healthcare services worldwide is becoming an increasing problem due to the global obesity epidemic. Hypercholesterolemia, usually caused by a diet high in saturated fat, results in the accumulation of this cholesterol on artery walls, leading to their hardening, thinning and chronic inflammation (atherosclerosis)[1]. This then becomes a risk factor for a number of diseases including ischaemic heart disease[2] and stroke[3]. Detection of elevated cholesterol levels is therefore key in implementing a strategic health plan to reduce total cholesterol blood concentrations, minimising the risk of progression to one or more serious diseases. The requirement for cheap, quick and simple biosensors for cholesterol detection is therefore of clear clinical significance.

In this work, we have developed a cholesterol biosensor based on the co-immobilisation of 800nm quantum dots (QD) and cholesterol oxidase (COx), in a Nafion film, onto a glassy carbon electrode (GCE) (Figure 1).

COx-catalysed oxidation of cholesterol in the presence of oxygen results in the release of hydrogen peroxide, which can act as a co-reactant in the production of ECL from QDs upon potential cycling. This enzymatic-based sensor allows reproducible detection of cholesterol at clinically relevant concentrations. ECL emission from the 800nm QDs lies outside the absorption range of blood, minimising sample preparation requirements and allowing further development of this sensor into a point of care device.

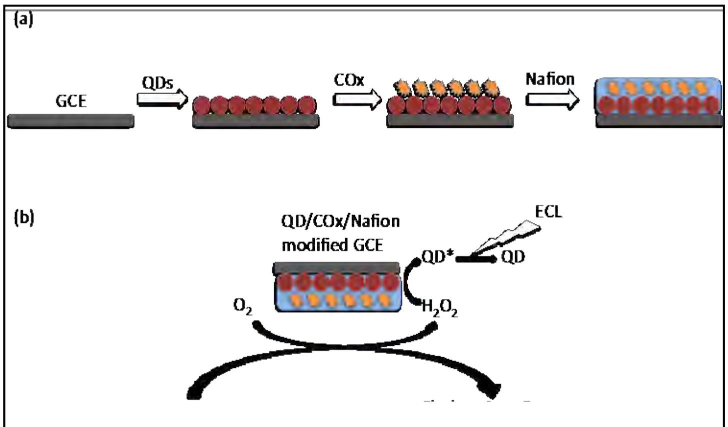

Figure 1 – (a) Preparation of the modified GCE through sequential binding of QDs, COx and Nafion. (b) Generation of QD ECL signal through interaction with H_2O_2 co-reactant, created in the COx-catalysed oxidation of cholesterol.

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Amperometric Gas Sensors: the Challenge of Low Concentrations

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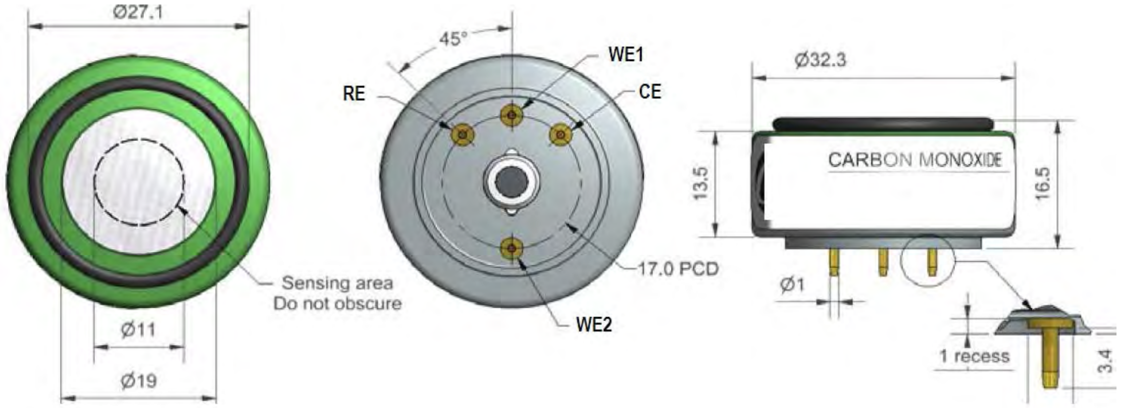
Amperometric gas sensors have been widely used for the detection of toxic gases for safety and process control for more than 40 years typically in the 10-10000 ppm concentration range [1-3]. Issues like pollution in urban areas and climate change have brought a new perspective to toxic gas monitoring and there is, certainly, today a growing interest at measuring lower concentration ranges (ppb levels). Indeed, it is not only the exposure to high concentrations of toxic gases that have a serious impact on health but exposure to traces can be significant on the long term too. The measurement of gases at low concentration by amperometric gas sensors would be a cost-effective alternative to existing technologies [4].

We propose, first, to introduce the issues involved in the use of amperometric gas sensors for measuring low concentration of gases, this will be illustrated by the determination of ppb levels of gas (e.g. formaldehyde) using a standard commercial sensor. Second, we will present new developments in sensor design to specifically address low concentration measurements. More specifically, sensors including two working electrodes (cf. Schematics below) show promising performances in the laboratory and in the field. Data obtained during a deployment of these sensors for air quality monitoring will be presented to illustrate possible applications.



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An Electrochemical Assay for the Detection of Methicillin Resistant Staphylococcus Aureus (MRSA)

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The ability to rapidly and sensitively detect the presence of antibiotic resistant bacteria would transform many aspects of modern healthcare. Electrochemical technologies are an extremely exciting approach for nucleic acid detection because they are very easily miniaturised, cheaply produced and in some instances capable of label-free detection. We have recently reported the development of an assay for MRSA based on electrochemical impedance spectroscopy (EIS) which is label free, can be used on screen printed electrodes and detects the clinically relevant MRSA *mec*A gene [1]. We have also reported an EIS based assay for three protein biomarkers of infection [2].

This presentation will highlight some recent advances in the development of the MRSA assay, which include enhanced sensitivity, improvements in time-to-result, data from different electrode types, the influence of sample pre-treatment on the EIS response and the fundamentals of probe-target interaction.

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A Label-Free Impedimetric Au-NPs Immunosensor for Amyloid Beta Peptides

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Alzheimer's disease (AD) is by far the most common dementing illness. Levels of Aβ peptides in some biological fluids are thought to be biomarkers for AD [1]. Development of simple, selective and sensitive tools for dection is very important to provide early diagnosis for AD. We present an impedimetric labeless immunosensor for Aβ. Label-free electrochemical detection of Aβ self-assembly has been reported [2]. Here, we Au-NP- modified screen printed carbon ink electrodes, following experimentation with NP sizes. Then, we modified the surface chemistry for immobilization of Aβ antibody (Fig 1).

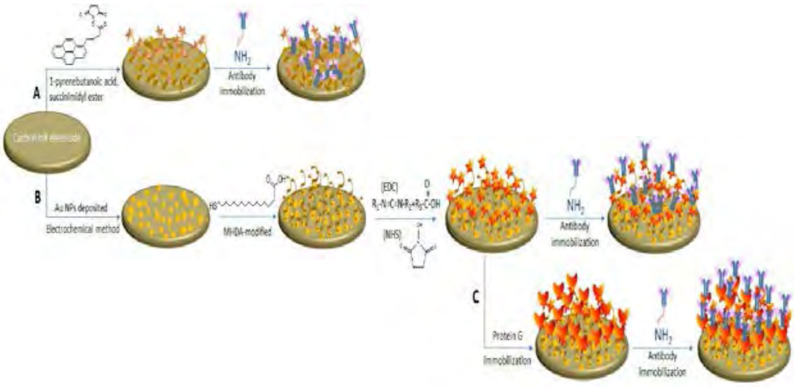

Fig. 1: Fabrication of an Aβ immunosensor on DEP chip using three methods; A: An electrode was modified using 1-pyrenebutanoic acid succinimidil ester; B and C: the electrode was modified by deposition of Au-NPs. In C, protein G was used to improve orientation the antibodies. Amyloid β peptides could be detected in the presence of bovine serum albumin (Fig 2).

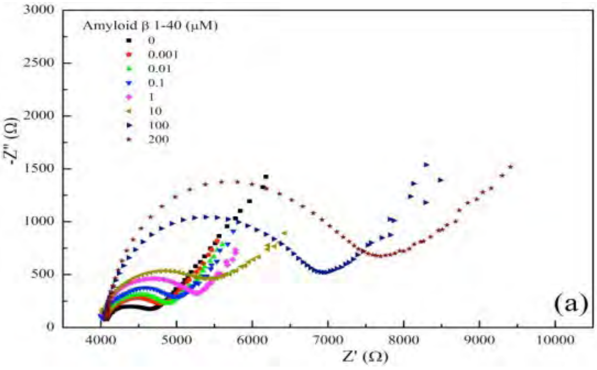

Fig. 2 Spectra of anti-Aβ/SAM/ AuNPs-modified electrodes exposed to a range of Aβ levels.

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An Activity Assay for the Detection and Quantification of Botulinum Toxin

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Botulinum Neurotoxins are one of the most potent toxins known to man. They are produced by a bacteria commonly found in soil and are often grouped with tetanus due to their similarity in action. There are four main causes of the disease botulism, infant botulism due to under-formed gut microflora being exposed to the bacteria, wound from contamination with the toxin which is common in drug users who share needles, foodborne from consuming contaminated with the toxin such as home canned products and finally iatrogenic botulism which is caused by errors in administering the toxin for cosmetic or therapeutic benefits.

Whilst botulism is so life-threatening the toxin does also have therapeutic benefits. As the toxin works by blocking nerve impulses it can be used to treat conditions such as muscle spasms and twitches. Due to its nature as a toxin and that it is a useful pharmaceutical product it is necessary to have an accurate assay for determining the concentration of a produced batch.

Currently the toxin is tested using the LD50 assay. This assay involves injecting a population of mice and measuring the mortality over 72 hours. This method is not standardized between manufactures due to different buffers and strains of mice used. On average 50-100 mice are used per batch of the toxin

SNAP-25 has been successfully immobilised onto a gold substrate utilizing the cysteine region of the protein to form covalent bonds to the gold producing a self-assembled monolayer. These layers have been examined *via*, cyclic voltammetry, electrochemical impedance, and UV-vis spectroscopy.

ELECTROCHEM
2013
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Yumi Yoshida, Kyoto Institute of Technology, Japan

Predominance Diagrams for U and Pu in LiCl-KCl

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Predominance diagrams were developed by Roy Littlewood in 1962, they represent thermodynamic data in a diagrammatic form. They developed from Pourbaix diagrams and are very useful when studying complex metal-molten salt systems, such as Li-K-U/Pu-O-Cl for spent nuclear fuel pyroprocessening. In predominance diagrams, the free energies of the system are represented by potentials that are relative to the standard chlorine electrode. The composition variable is the negative logarithm of the activity of the oxygen ion in the melt, pO^{2-}. Therefore, the diagrams are E vs. pO^{2-} plots.

The standard Gibbs free energy change of a given reaction, ΔG, may be related to the electromotive force of the specific cell, E, by Equations 1 and 2, and by the Nernst Equation 3.

$$\Delta G^o = -nFE^o \qquad (1)$$

$$\Delta G = -nFE \qquad (2)$$

$$E = E^o - \frac{RT}{nF} lnQ \qquad (3)$$

Where, n is the number of electrons transferred in a reaction, F is the Faraday constant (96485.4 $Cmol^{-1}$) R is the universal gas constant (8.314 $Jmol^{-1}K^{-1}$), T is the operating temperature of the molten salt in Kelvin, and Q is the reaction quotient.

Thus, using Equations 1, 2 and 3, and the corresponding chemical reactions for the system, equations for the interface lines between all the different stable phase compounds can be derived.

The predominance diagram for U and Pu in LiCl-KCl is shown in Figure 1.

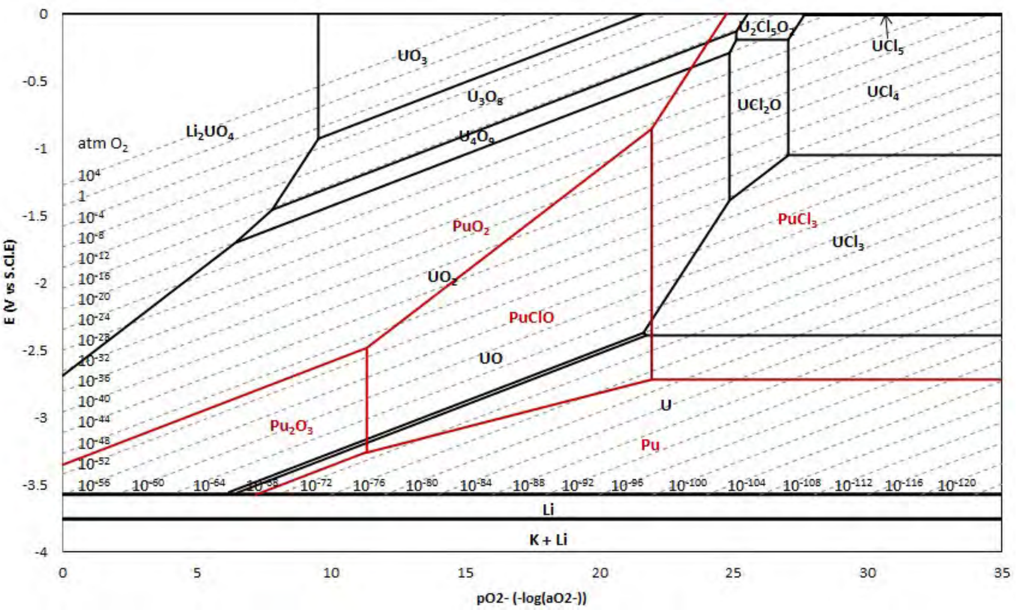

Fig.1. Predominance diagram for the Li-K-Pu-O-Cl and Li-K-U-O-Cl systems at 500˚C

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. The common property in these gases is the presence of charged species, which provide a conducting electrolyte that can be used to perform electrochemistry. A flame was used as an electrolyte to study electron transfer events at the solid/gas interface.

To date, redox reactions in the gas phase are commonly studied using photoelectron spectroscopic or related techniques, in conjunction with mass spectrometry for analysis of products and/or reactants.[1] Apart from experiments performed at specially designed interfaces, there were no examples of voltammetry in the gas phase at a true solid/gas interface.

We have previously established successful electrochemical measurements at the solid/gas interface by doping a flame plasma with different metal oxide salts[2] and recording distinct redox potentials as a function of concentration, surface area, scan rate and electrode identity.[3] The current-voltage signals we record are unique to the species we add to the plasma, and we believe the features are due to the reduction (electron attachment) of gaseous species present in the plasma medium: $A + e^- = A^-$.

Complex organic molecules present a different approach to what has been previously done and it relies on small differences in structure and/or groups. Organics based aliphatic and aromatic compounds have been added to the flame and the corresponding CVs recorded. Reduction signatures obtained probably originate from distinct breakdown products from the fragmentation (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.

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A New Family of Oligomeric, Redox-Active Metal Complexes as ‘Molecular Wires’

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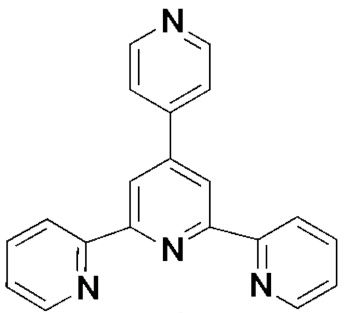
The ligand 4'-(pyridin-4-yl)-2,2':6',2"-terpyridine (1) has been used to synthesise octahedral complexes $[Co(1)_2]^{2+}$, $[Fe(1)_2]^{2+}$ and $[Ru(1)_2]^{2+}$ (as PF_6 salts). By using the relative inertness of Ru(II) and Ru(III) complexes with terpy ligands, well-defined linear oligomeric complexes $[(1)Ru(□L)Ru(1)]^{4+}$, $[(1)Ru(□L)Ru(□L)Ru(1)]^{6+}$ and $[(1)Ru(□L)Ru(□L)Ru(□L)Ru(1)]^{8+}$ (where ‘L’ is 1,4-di([2,2':6',2"-terpyridin]-4'-yl)benzene) have also been prepared and characterized. Scanning tunneling microscopy-based techniques have been employed to measure the electrical properties of metal | single molecule | metal junctions involving these complexes, using their terminal pyridyl groups as contacts. This paper will discuss the length dependence of the conductance of the Ru(II) oligomers and its implications for the conductance mechanism (tunneling or hopping?), and the electrochemical potential-dependent conductance of $[Co(1)_2]^{2+}$ (measured in ionic liquid).



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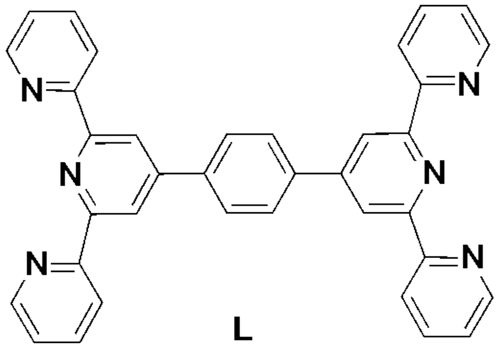

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Size and pH Dependent Redox Activity of Undoped Diamond Nanoparticles

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Diamond is a classic example of an inert, insulating material with a band gap of 5.5 eV. In contrast, nanodiamond (ND) boasts, amongst others, redox and catalytic properties. With approximately 20% of the atoms located on the surface, the chemical properties of ND are dominated by its surface chemistry.[1] Infrared spectroscopy of ND films [2] has shown the presence of a range of oxygen based surface functionalities (-OH and C=O groups). It has been suggested that different surface functionalities create surface states with energies that are distributed in the diamond band gap. These surface states can act as a sink/source for electrons and hence the origin of the observed redox/catalytic activity of ND particles.[3]

Given the intimate relationship between surface groups and redox activity of ND particles, it has been hypothesised that the redox behaviour would diminish on increasing ND particle size (smaller surface area to bulk ratio). Our work investigated different sized ND particles and their ability to promote redox processes in solution. Using ferrocenemethanol, we investigated how CVs differed when a boron doped diamond electrode was modified with different sized ND particles and the pH of the surrounding electrolyte was changed. The observed currents were found to have contributions from i) diffusion controlled redox process at BDD surface, ii) diffusion controlled catalytic cycle and iii) adsorption of the ferrocenium cation.

We demonstrate NDs ability to promote redox processes in solutions is dependent upon 1) the size of ND particles, 2) the redox potential of the redox species, 3) the pH of the external environment and 4) the interaction between the ND and solution redox species (whether chemical or electrostatic).

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Electrochemistry in High Pressure Carbon Dioxide

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The design of a reactor particularly suited for high-pressure electrochemical experiments in supercritical CO_2 ($scCO_2$) has enabled fundamental electrochemical studies in this unique media, as well as investigations of CO_2 reduction by electrochemical means at increasing CO_2 pressures. An overview of recent electrochemical studies in high pressure CO_2 are presented in which both macro and microscale electrodes are employed directly and in the presence of molecular catalysts.

The very low dielectric constant of the fluid still restricts the use of this solvent as an independent medium, but using organic co-solvents to dissolve highly lipophilic electrolytes can overcome the conductivity problems associated with the non-polar supercritical fluid, providing a fully supported single-phase for electrochemical investigation. Previously we reported the electrochemical oxidation and reduction of decamethylferrocene at a macroscale electrode in a $scCO_2$/acetonitrile medium [1]. Experimental and simulation results suggested that a quiescent liquid-like film of the co-solvent is formed at the electrode surface, leading to steady-state voltammetry at relatively high scan rates. Further studies of metallocenes have since been conducted using microelectrodes fabricated by novel means of parylene coating, the results of which are presented in this poster.

Instead of using a co-solvent for single-phase experiments, electrochemical studies can be performed in a biphasic arrangement of a water phase in contact with $scCO_2$. Direct reduction of CO_2 on a gold or copper electrode shows a current increasing linearly with pressure, indicating an increasing concentration of CO_2 in the water phase. Rather than reducing CO_2 in the bulk of the water phase, the interface can be used as reaction locus mediated by aqueous soluble catalyst, such as nickel cyclam [2]. In a previous study Ni-cyclam was suggested to catalyze CO_2 reduction more efficiently at the water-$scCO_2$ interface. Preliminary results using a microelectrode in the water phase, have given a scanning electron microscopy (SECM) type approach curve that indicates an enhanced catalytic current with the working electrode close to the interface (less than 70 μm).

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Sol-Gel Synthesis of Solid and Porous Functional Metal Oxide Films

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$BaTiO_3$ is a perovskite-structured ferroelectric characterised by a reversible spontaneous polarization and nonlinear dielectric behaviour [1]that is used for capacitors, non-volatile memories [2] and microwave electronic components [3]. We aim to produce porous $BaTiO_3$ films with well-defined pore structures and dense pore walls for incorporation into composite materials. TiO_2 and $BaTiO_3$ films have been prepared using sol-gel methods by dip-coating various sol compositions on silicon substrates and optimising the water contents, annealing times and reaction times. Film crystallisation was monitored by X-ray diffraction and the thickness and surface morphology by SEM. Titanium speciation in sol mixtures has been studied by ^1H and ^{13}C NMR and electrospray mass spectrometry.

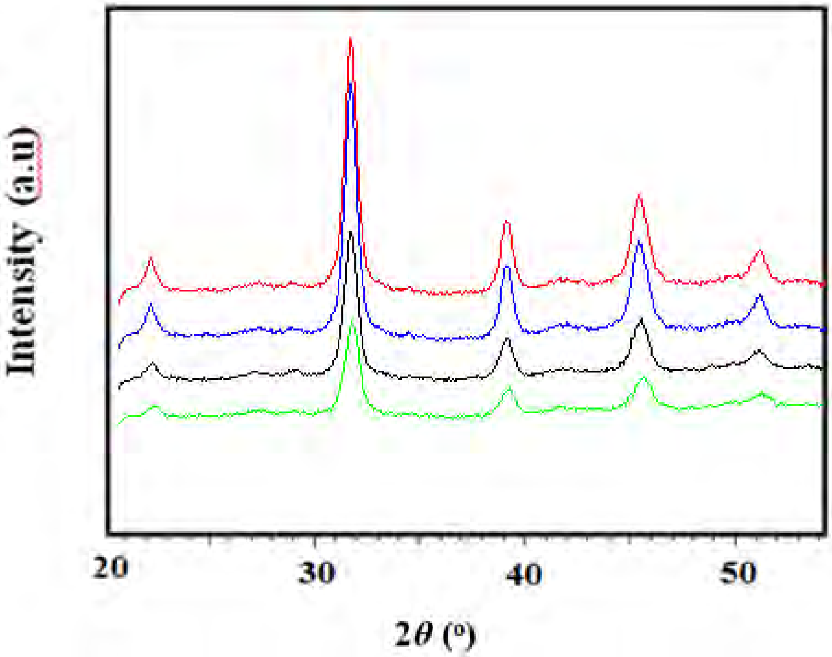

Fig.1 XRD patterns of $BaTiO_3$ films deposited on silicon and calcined at 750 °C for 5 (bottom), 10, 20 and 60 (top) minutes.

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ZnO Nanorods on Glass and Plastic Based Substrates for Various Energy Applications

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Synthesis of numerous ZnO nanostructures has recently attracted significant interest due to their promising applications in solar cells, transparent conducting films, ultraviolent-protection films and gas sensors. In particular, ZnO nanorods have received extensive attention in photonic electronic, optoelectronic and electrochemical devices due to ease of fabrication at ambient conditions. Unlike glass based substrates, 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 glass based rigid and flexible substrates and using such electrodes to construct various energy conversion devices is one of the key research interests in material processing. [1]

ZnO nanorods were deposited on FTO glass based and ITO-PEN plastic substrates at low temperature by chemical bath deposition.[1],[2] Before the growth of nanorods, the substrates were coated with seed layers at different thicknesses using sputtering and aerosol assisted chemical vapour deposition techniques. The samples were characterized by X-ray diffraction and it confirmed the deposited ZnO has the wurtzite crystal phase. The scanning electron microscopic (SEM) images illustrated the successful growth of the nanorods at all various seed layer thicknesses. The photoelectrochemical characteristics of the glass based ZnO nanorod electrodes have been measured. Also the ZnO nanorods grown on various seed layer thicknesses were used as photoanodes to construct flexible DSCs. The effect of seed layer thickness on the DSC performance was evaluated.

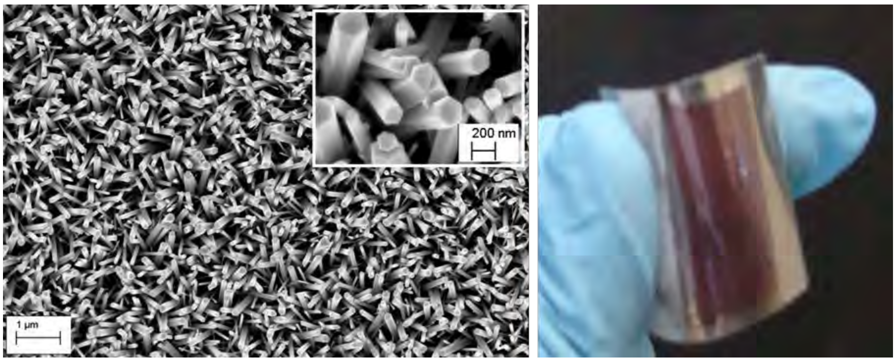

Figure 1: Top-view FEG-SEM images of surface topography of ZnO nanorods grown on 500 nm seed layer thickness to the left (the inset illustrates the respective magnified image) whereas flexible DSC image to the right.

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Diamond-Like Carbon for Oil and Gas Applications

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In more extreme oil extraction conditions, such as greater depth or where large volumes of abrasive rock are present, materials with superior performance characteristics are required. Diamond-like carbon coatings offer a highly desirable combination of properties including; low coefficient of friction, high hardness and they can give excellent corrosion resistance.

The goals for this project are to research the performance characteristics and failure mechanisms with a view to this material being used for coating valves, pumps and potentially the inside of transmission pipelines.

Diamond-like carbon coatings produced by a PECVD method were deposited on API-5L X65 steel. The coating was then characterized using SEM, Raman spectroscopy, EDX and AFM then subjected to simulated oilfield conditions. The coatings were tested using electrochemical impedance spectroscopy and potentiostatic polarization in sweet conditions. Some of the samples were damaged prior to testing to simulate damage that can be sustained in service. This damage includes abrasion simulating rock or sand particles wearing the coating and ball bearing impact simulating larger rock fragments striking components in the pipeline such as valves. SEM, AFM and electrochemical methods were used to work towards elucidating the failure mechanism of the coating.

Typical performance of these coatings under such conditions is demonstrated including possible key failure mechanisms. Such data will give greater confidence in the use of such materials in demanding applications.

Electroplating Nanowires from Supercritical Fluids

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We have developed a versatile and generally applicable method for metal electrodepostion from a single supercritical phase[1]. By judicious choice of electrolytes, metal precursors, plating conditions and (where appropriate) co-solvents we have been able to electrodeposit copper[2], silver, iron, cobalt, platinum and germanium[3] from supercritical fluids. Furthermore we have demonstrated that this highly mobile solvent can be used to electroplate metals into high aspect ratio nanopores.

We are currently developing new electrolytes, metal complexes, nanoporous templates and high pressure cells to better help us exploit the unique properties of supercritical solvents for electrochemisty.

We believe that supercritical fluid electrodeposition (SCFED*) will prove to be a genuinely disruptive materials deposition technology that will enable the production of three dimensionally nanostructured materials of a complexity (and with properties) that are currently unachievable.

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*The SCFED Project (www.scfed.net) is a multidisciplinary collaboration of British universities investigating the fundamental and applied aspects of supercritical fluids.

The Development of Nanopore-Based Electrochemical Biosensors

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For the past decade, the detection, separation and sequencing of DNA for diagnostic and screening applications using nanopores have sparked a tremendous interest [1, 2]. Detection using nanopores has numerous advantages over conventional techniques (e.g. gel electrophoresis) which includes label-free detection, low sample volumes and the ability to extract single molecule information. A nanopore can be either formed on a biological membrane or fabricated on a solid-state microchip. Solid-state nanopores have been proposed as an alternative to biological pores and been proven to be a powerful platform for an exclusive detection. The next for the nanopore based biosensing should be to increase its utility by constituting an engineered device which can perform multiple tasks within the capability of a single chip. Towards personalized medicine, the near future will possibly witness the miniaturization of many biosensing devices into intelligent mobile devices for point-of-care diagnostic applications. Furthermore, with an understanding on the physics of the biomolecule, these devices would also open up new possibilities to study the dynamics of the molecule in real time.

Here, we present a novel fabrication method for the integration of a nanopore within a microfluidic channel for electrochemical detection of DNA at single molecule level. A silicon nitride chip with a nanopore down to 30 nm in diameter is compacted into a PDMS microfluidic device with a channel of 75 µm depth; the translocation of 48.5 kbp DNA at both steady-state and continuous fluid flow has been achieved successfully. The figure a shows the schematic of the device where the microfluidic channel is well-aligned onto the channel. With a custom-made detection platform, the channel and the back side of the nanopore platform is filled with an electrolyte solution and the system is connected to a patch clamp amplifier via electrodes. Upon the application of the electric field, an ionic pathway is created from the channel to the back side of the device through a single nanopore. This is recorded as a stable current trace due to the passage of the electrolyte ions.

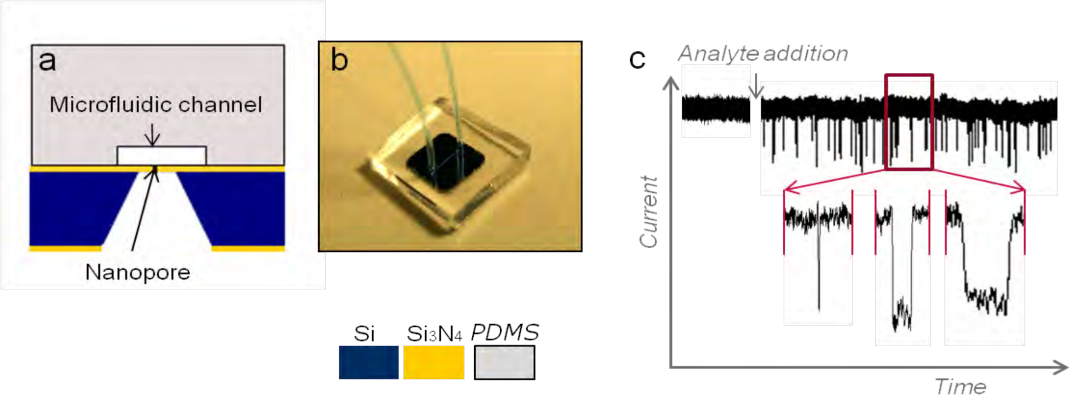

Figure. a. Schematic of the device. b. An image of the integrated chip. c. a representative biomolecule translocation data

Once DNA is added to the channel, DNA blocks the pore for certain time and current blockage events are observed, referring to individual DNA translocations. In figure b, a representative data for the translocation is shown. The shape of the events changes depending on the charge, conformation and size of the molecule inside the pore. What makes the research novel is that the detection has also been achieved under hydrodynamic flow conditions. We consider that the ability to qualify and to quantify biomolecules under continuous flow conditions using such a compact device would provide us with the potentials of continuous detection of different species while they are processed for any biological purposes.

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Spectroelectrochemical Studies on Graphene Modified with Lignosulphonate

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We have successfully modified a silicon ATR-IR prism with a single layer of graphene. We have also shown that this layer of graphene can be utilised as an electrode, which can also be modified electrochemically with lignosulphonate. Additionally, in situ spectroelectrochemical studies, including the effect of pH variance, on this layer were conducted.

Lignosulphonate is derived from lignin, which is a naturally occurring, amorphous biopolymer that binds together cellulose fibres in plant cells. It is most commonly obtained from wood and commercially available lignin is usually a by-product of the paper/pulp industry.[1-3] It has been found that various electrodes, such as gold and glassy-carbon, can be modified electrochemically with lignin and lignosulphonate.[3-5] Modified electrodes such as these can potentially be used for various electrocatalytic and bioelectrochemical sensing purposes. Lignosulphonates are available in the form of sodium salts, which are usually produced via acid sulphite pulping processes.

Previous studies on lignin and lignosulphonate-modified electrodes have shown them to affect the redox kinetics of various compounds and electrochemical probes, such as ferrocyanide, sodium nitrite, NADH and ascorbic acid.[3-5] We envisage that the graphene-modified ATR-IR prism setup can be employed to conduct in situ analysis of the behaviour of such probes in the presence and absence of lignosulphonate and other classes of modifiers. Indeed, there is potential for the system to be used to study a range of electrochemical systems.

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Electrodeposition and Characterisation of Ni-B Thin Films

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Surface degradation processes such as wear, oxidation, and corrosion are serious problems in many engineering applications.[1] Hence surface treatment of materials to inhibit these processes is vital. Nickel coatings have wide applications in decorative applications such as car bumpers and other vehicle parts, and functional applications as hard, corrosion resistant surfaces.[2] Electrodeposition is an important metal surface coating technique as it can smoothly coat large and complex objects in a convenient and economically viable way.[3] Boron is often incorporated into electrodeposited Ni using the standard Watt's bath for Ni electrodeposition (nickel chloride/nickel sulphate/boric acid) and adding dimethylamine borane as the source of boron. To prevent electroless deposition the electrolyte solution requires controlled temperature and pH.[4] We are examining the microstructure of electrodeposited Ni and Ni-B films using a variety of X-ray diffraction techniques and scanning electron microscopy. Introduction of boron into electrodeposited Ni films results in a large decrease in the crystallite size. Meanwhile the lattice strain is increased by the addition of boron to the Ni matrix, but reduced by increasing the thickness of the films and the amount of B. Thin (0.5 µm) Ni and Ni-B films on sputtered gold were observed to possess 111 preferred orientation, whilst in thicker (5 µm) Ni films the orientation switched to 220. This change was not observed in the case of Ni-B deposition.

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Method of Metal Powder Production, using Vibrating Electrode and Ammonia Chloride Electrolytes

Valery M. Lipkin, Alexandr A. Naumenko, Alexandr S. Misharev, Elena A. Rybalko, Nikolay. A. Lytkin, Vasily G. Shishka*

An increasing productivity of electrolytic method of metal powder manufacturing is very important for a lot of application. A perspective way of this is combination of electrolysis with cathode vibration. Using vibrating cathode, one can obtain metal powders from dilute solutions, including electrolytes, sintering by anodic dissolution of metals and alloys. Such a possibility provides many electrolytes, but ammonia based is much of interest. Copper powders, obtaining from anodic synthesized electrolytes, has an average particle size according to Microtrac analyzer data of about 8-10 micrometers (fig. 1)

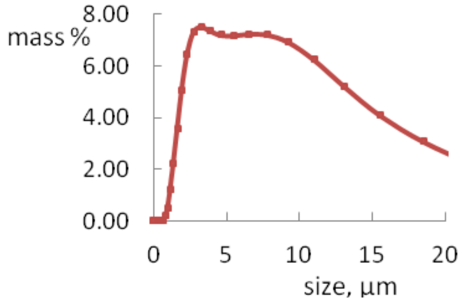

Fig. 1 Particle size distribution of copper powder, obtaining from anodic synthesized electrolytes, initially 1M NH_4Cl

A productivity of copper powders in ammonia chloride electrolyte is 0.064 g/sm^2 per hour, that is much higher, than from sulphate one. We assume this is due to reduction of copper from $[Cu(NH_3)_2]^+$ complex, which equivalent mass is two times higher. It is interesting, that in ammonia electrolytes there is a way of copper powder formation near insoluble anode, such as graphite or platinum. This reaction is possible due to Cu(I) complex disproportion or generation of hydrazine by ammonia anodic oxidation.
The shape of copper particles is polyhedral (Fig. 2) with dendrite nano-wiskers.

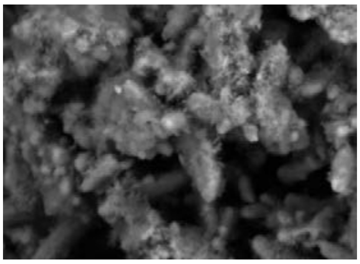

Fig. 2 SEM pattern of copper particles, obtaining from anodic synthesized electrolytes, initially 1M NH_4Cl

A method of electrolysis with vibrating cathode and anodic synthesized electrolyte was applied for iron, nickel and cadmium powders. Nickel spherical particles was obtained (Fig. 3), iron powder production efficiency was 90%

Fig. 3 SEM pattern of nickel particles, obtaining from anodic synthesized electrolytes, initially 1M NH_4Cl

All synthesized powders exhibit high activity in powder metallurgic processes and as electrode active materials of nickel-cadmium secondary cells.

Au Electrodeposition on Graphene and Highly Ordered Pyrolytic Graphite

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Graphene has generated much interest owing to its many superior properties, chiefly its great strength, transparency and high conductivity.[1] Functional materials are sought that take advantage of these; in particular, decoration of graphene with Au nanoparticles is ideal for use in catalysis, plasmonics and sensors. The control offered by electrodeposition allows small nanoparticles with narrow size distributions, required for such applications, to be achieved.

Whilst Au electrodeposition on glassy carbon (GC) and highly ordered pyrolytic graphite (HOPG) has been studied, the process is still poorly understood.[2-4] Au electrodeposition on mechanically exfoliated graphene or that grown by chemical vapour deposition (CVD) has yet to be reported.

Cyclic voltammetry and chronoamperometry were performed to carry out Au electrodeposition on HOPG and CVD graphene electrodes. A micropipette/micromanipulator setup was used, where a <100 µm diameter droplet positioned on the electrode serves as the electrochemical cell. This allowed the terraces of the HOPG to be addressed separately from the edges, for comparison with the graphene basal plane.

Conditions were varied, including pH, precursor concentration and electrochemical parameters, with the aims of elucidating the mechanism of Au deposition, and to optimise the electrodeposition process.

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Electrochemical Characterisation of Edge-Carboxylated Graphene Nanoflakes

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Graphene has attracted an enormous amount of interest ever since it was first synthesised in 2004 [1]. This two-dimensional, one-atom thick sheet of sp^2-hybridised carbon exhibits remarkable properties, such as a large surface area [2] and high charge-carrier mobility [3]. These properties make graphene a candidate for a range of potential applications ranging from energy storage [4] to biological sensing [5]. Pristine graphene contains few defects, making it less useful for electrochemical applications [6]. On the other hand, defects in graphene materials such as reduced graphene oxide disrupt the aromatic carbon network, which leads to reduced conductivity [7]. Edge-carboxylated graphene nanoflakes (GNF), a novel nanomaterial combining low internal defect density with oxygen-containing functional groups, have recently been prepared [8]. The flakes have an average diameter of 30 nm, and are well defined in terms of location and identity of functional groups.

GNF are used to modify a boron-doped diamond electrode surface and the electrochemistry in the presence of different redox probes is studied compared to the clean boron-doped diamond. Changes in the pH and the ionic strength of the supporting electrolyte can greatly alter the electron transfer kinetics at GNF-modified electrodes. The role of the functional groups in the electrochemistry of the flakes is investigated, and the functionalised flakes are compared with carbonised samples of the same size. 3D self-assembly of the flakes is also explored and the electrochemical properties of the resulting structures are studied. In addition, spectroscopic techniques are used to study the stability of GNF in aqueous solutions to find out if prolonged contact induces changes in the structure of the flakes.

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Characterisation and Behaviour of Particulate Material in PWR Primary Coolant

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Corrosion products are known to form in the primary water circuits in nuclear power plants by corrosion of structural materials. These corrosion products were first observed at the Chalk River plant, and were hence given the name CRUD (Chalk River Unidentified Deposit). CRUD causes a reduction in heat transfer within the primary circuit, as well as increasing radiation dosages by transporting activated nuclides around the circuit. It is for these reasons why CRUD has been investigated over the years, so measures can be taken to minimize its formation.

The structure and composition of particulate material in primary coolant is not well known. It is necessary to investigate these parameters to better understand CRUD behaviour. The stability of corrosion products in solution is determined by their zeta potential, ζ. The zeta potential is a measure of the electric charge at a particle's surface, and higher values of ζ indicate greater particle stability. At the Iso-Electric point, where the surface charge is zero, particles become unstable and tend to aggregate together and precipitate out of solution [1]. This leads to deposition of corrosion products onto surfaces. This project aims to characterise the structure of CRUD in solution using complementary spectroscopic and microscopic techniques such as Scanning Electron Microscopy and X-ray Diffraction. The stability of CRUD will be investigated by measuring the zeta potentials and deposition/release rates from surfaces of particulate material. By simulating the conditions found in a PWR using an autoclave, it is possible to recreate primary coolant conditions and analyse particulate material that forms at operating temperature and pressure

Reference

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Material Characterization of Ruthenium Oxide-Based Cathodes Exposed to Hydrogen Evolution in Alkaline Media

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Ruthenium dioxide, RuO_2, or mixtures of RuO_2 and other metal oxides (TiO_2, IrO_2, etc.) deposited on a titanium support, have successfully been used as catalytic and durable coatings for decades in different industrial processes like chlorine or oxygen gas production. These types of electrodes are often referred to as dimensionally stable anodes (DSA®). RuO_2-based coatings have also found practical applications as a catalyst for hydrogen evolution in chlor-alkali production and alkaline water electrolysis [1]. Regarding RuO_2-based cathodes that are exposed to hydrogen evolution in alkaline media there is a debate concerning coating stability and duration [1]. To shed light on this question we have performed material characterization on RuO_2-coated nickel cathodes before and after exposure to hydrogen evolution in 8 M NaOH (90°C).

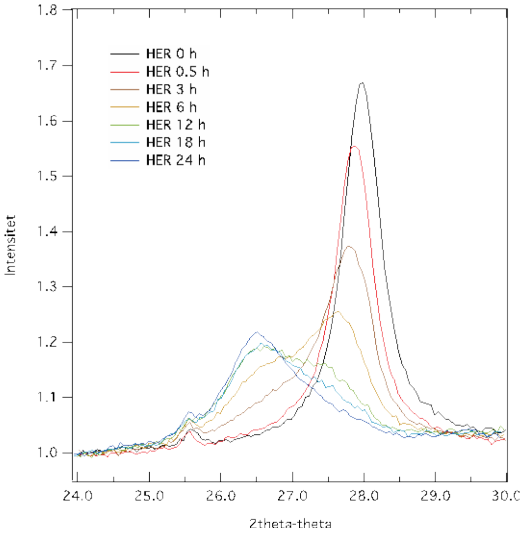

Figure 1. High resolution XRD in the rutile

High resolution X-ray diffraction (XRD) shows (figure 1) that RuO_2 transforms from the rutile phase into another phase that previously has not been identified, although it has been observed in an earlier study. [2] To identify the new phase we have employed the chemical specific and local geometry sensitive high resolution X-ray photoelectron spectroscopy (XPS).

The material characterization suggests that the observed phase is ruthenium oxyhydrate, $RuO(OH)_2$. However, the XPS measurements show that during prolonged exposure to hydrogen evolution the formed $RuO(OH)_2$ phase is consumed further into $Ru(OH)_3$, which is amorphous and thus not detectable by XRD. Additional studies show that the formation of $RuO(OH)_2$ and $Ru(OH)_3$ do not reduce the catalytic activity and are stable during hydrogen evolution in alkaline media.

The present study shows that RuO_2-coatings transform into $RuO(OH)_2$ and $Ru(OH)_3$ when exposed to hydrogen evolution in alkaline media. This transformation will, most likely, affect the properties of the cathode employed in industrial processes like chlor-alkali production or alkaline water electrolysis.

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Synthesis and Characterization of Ordered TiO2 Nanostructures

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TiO_2 is one of the most studied transition-metal oxides due to its biocompatibility and promising ionic and electronic properties. These properties can be explained on the basis of its wide bandgap (3eV), which enable this material to be used in solar cells and for photocatalytic applications [1].

In the present work, several TiO_2 ordered structures were synthesized and characterized. Their electrical and photo-electrical properties were evaluated by performing cyclic voltammetry, impedance spectroscopy and measurements of photocurrent and electrical capacitance. The prepared samples were also morphologically characterized by SEM analysis.

First of all, TiO_2 nanotubular structures were prepared by electrochemical oxidation of Ti sheets in different fluoride-containing solutions of organic solvents, following the procedure described elsewhere [2]. The influence of the organic solvent in the structure, electrical and photo-electrical properties was evaluated, finding that the electrodes synthesized in glycerol possessed a more ordered nanostructure than those oxidized in the presence of ethylene-glycol.

Next, hybrid electrodes were synthesized by the electrochemical functionalization of TiO_2 nanotube arrays with polyaniline (PANI). The addition of PANI was performed using two different approaches: 1) directly on the TiO_2 nanotube layer; 2) after the functionalization of the TiO_2 structure by a diazonium salt. The influence of both the functionalization procedure and the time of PANI electro-polymerization, were evaluated.

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Test Structures for Bath Development and Deposit Characterisation

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Nickel-iron alloys have useful magnetic properties that are of interest for use in micro-electromechanical systems (MEMS) [1]. In the fabrication of MEMS devices electrodeposition can be used as a rapid method for the deposition of thick films, however the resulting alloys can exhibit high levels of stress. Film characterisation by the use of suspended rotating structures (figure 1), electrical test structures (figure 2) and X-ray fluorescence has been previously developed to map the stress, composition and electrical properties of deposited films [2]. By applying these techniques in 100 cm^3 volume experimental baths comparisons can be made for films deposited under varying chemical and electrochemical conditions. The use of small volumes allows the rapid and cost-effective assessment of varying electrolyte composition and aids in the development and characterisation of new deposition electrolytes.

REACH legislation may soon limit the use of boric acid due to potential health effects [3]. In this work, we have used a combination of electrochemical methods and test structures to develop a new boric acid free NiFe deposition bath. The deposited films have been shown to display similar characteristics to films deposited from a boric acid based bath.

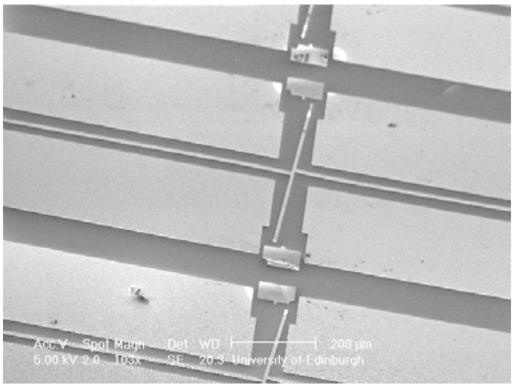

Figure 1, SEM image of rotating arm test structure for film characterisation.

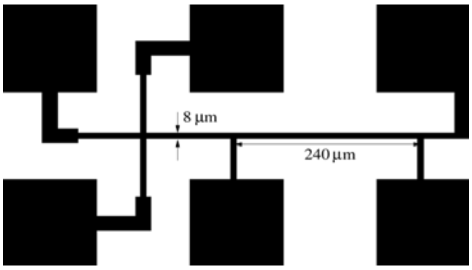

Figure 2, Layout for electrical line width test structure.

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A Study of the Fluorescent-Electrochromic Enhancement of Latent Fingerprints using 3-(pyrrol- 1-yl)Propylamine ($PyNH_2$) by Neutron Reflectivity

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Most fingerprints at crime scenes are "latent", i.e. non-visible, so they must be treated chemically to make them visible. Despite all the methods available the success rate for metallic items is very low. The electrochromic enhancement of latent fingerprints is an effective means of visualizing latent fingerprints.[1,2] This method is complementary to traditional enhancements, which require chemical or physical interaction with the fingerprint deposit, as it exploits the fingerprint deposit as an insulating mask blocking electrochemical processes, such as polymer deposition. This results in spatially selective deposition of the polymer on the bare metal surface in between the ridges of the fingerprint. Subsequent visual contrast manipulation can then be performed by cycling the potential of the polymer in monomer free electrolyte which changes its oxidation state causing a change in colour (electrochromism). A survey of fingerprints exposed to various environments shows this approach to be superior to traditional methods for some forensically challenging scenarios.[3]

Here we describe an extension of the electrochromic concept, in which the capability for emission (fluorescence) is added to that for absorption to novel combination of fluorescent and electrochromic enhancements of latent fingerprints.[4] This provides a second means of visual contrast with emission, rather than absorption, of light. The challenge is that fluorophore- functionalised monomers are not polymerizable, almost certainly for steric reasons. The solution we have begun to explore involves the polymerization of a monomer (here, 3-(pyrrol-1-yl)propylamine, Py- NH_2) functionalised with a large leaving group (here, 9- fluorenylmethoxycarbonyl, FMOC). After film deposition, the amide-bound FMOC is hydrolysed out, to leave nanoscale voids into which the fluorophores can be diffused, to bind with the polymer spine. The ease in which the bulky fluorophore moiety can penetrate into the film will determine the intensity of emission that can be achieved, and hence the improvement in visual contrast.

Neutron reflectivity was used to probe the structure of these films during these reactions. It measures the intensity of reflected neutrons as a function of either wavelength (time of flight mode) of angle of incidence (monochromatic mode) to yield a reflection profile. The shape of the profile gives information about the film spatial structure. Kinetic measurements performed on INTER (ISIS) show how the depth profile of the polymer alters during the hydrolysis in real time and static measurements performed on FIGARO/D17 (ILL) and OFFSPEC (ISIS) show the change in reflectivity after the subsequent reaction with a fluorophore. This allows us to map the total penetration depth of the fluorophore into $PPyNH_2$ films with and without free volume generated by FMOC hydrolysis.

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Electron Transfer Reactions on Insulating Materials

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It is well known that insulating materials (*e.g.* polystyrene) can undergo contact electrification. However, the mechanism by which these materials accumulate charge has been subject to extensive debate. All the proposed mechanisms can be separated into four main categories: electron transfer; ion transfer; material transfer; and the formation of mechanoradicals. These mechanisms are not exclusive, and can be any permutation of the aforementioned mechanisms. [1] In our recent work, we have focused on exploring the electron transfer model.

Utilising techniques developed for characterising nanodiamond surface functionalities [2], we have discovered and studied the presence of redox properties on the surface of various insulating materials via a combination of electrochemistry, spectroscopy and nanotechnology. More specifically, we have exploited the high surface area to volume ratio of nanoparticles to enable us to perform electrochemistry on these redox active surface sites. Currently, we have determined the presence of, and characterised, such sites on nanodiamond particles (d = 5-1000 nm), polystyrene particles (d = 20-900 nm) and human hair fibres. Results demonstrate the presence of surface groups that are able to gain or lose electrons, unlike the bulk material itself, which provides evidence suggesting an electron transfer mechanism for contact electrification cannot be ruled out, and opens the door to a new range of applications for insulting materials.

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Electrochemistry of Iron-Nickel Sulphides for CO2 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 envisioned to interact with carbon dioxide, electrochemically reducing the carbon dioxide and producing small molecule products which may be the first building blocks of life. Thus if such concept is plausible, iron sulphides may be the next catalyst to consider for the electrochemical reduction of CO_2.

Successful CO_2 reduction on iron sulphides 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 themselves. Hence in order to establish the CO_2 reduction mechanism on these surfaces, the redox mechanism of the mineral surface itself must be first understood.

Synthetic iron and iron-nickel sulphide nanoparticles are used in our study, employing electrochemical and spectroscopic techniques to work towards understanding and identifying the surface reactions. Preliminary results showed differences in their electrochemical behaviour in the presence and absence of CO_2.

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Chromium Electrodeposition using a Novel Type IV Deep Eutectic Solvent

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Chromium plays an important role in a number of fields of modern industries, for example as a protective material in automotive and planes as well as for decorative purposes. A novel Deep Eutectic Solvent (DES) can be formed between $CrCl_3 \cdot 6H_2O$ and urea (Fig. 1). A eutectic was formed from variety compositions, and the phase diagram behaviour of the system was studied. It has been well recognized that, in general, DES suffer from low fluidities and low conductivities, this has restricted their use as an electrolyte for electrodeposition process, especially for large scale applications. These systems are excellent candidates for electrochemical applications, such as hard chrome electrodeposition, as determined by EDAX and hardness testing. The physical properties of these systems have been characterised and it was noted that their viscosities were lower and the conductivities were found to be larger than for other reported DES systems.[1,2] Generally it was shown that these liquids are simple to synthesize and they help to avoid the use of Cr^{VI} and its compounds, which are toxic and classified as carcinogenic.[3]

Figure 1: The new DES and its two solid components.

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EIS Analysis of a 40Ah Lithium Ion Battery

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A rapid method for assuming the viability of lithium ion batteries on the production line is rgently required. To this end, we report studies using Electrochemical Impedance Spectroscopy on two sealed 40 Ah, automotive batteries selected as being viable and non-viable (i.e. the latter having an unacceptable self-discharge rate).

The batteries were investigated at constant temperature as a function State Of Charge (SOC), and at constant SOC as a function of temperature. The data so obtained were fitted to those produced by an equivalent circuit (EC) modelling the electrochemical processes taking place in the batteries, and the EC optimised by an iterative method. An example of the data and the fit provided by the optimised model represented by the EC, are shown in the Nyquist plot in fig. 1. Fits to the data using the viable and non-viable cells were excellent with $\chi^2 \leq 10^{-3}$. By careful data manipulation, it was found that the viable and non-viable cells could be straightforwardly and rapidly discriminated on the basis of a number of parameters extracted from the model, and the likely chemistries taking place elucidated.

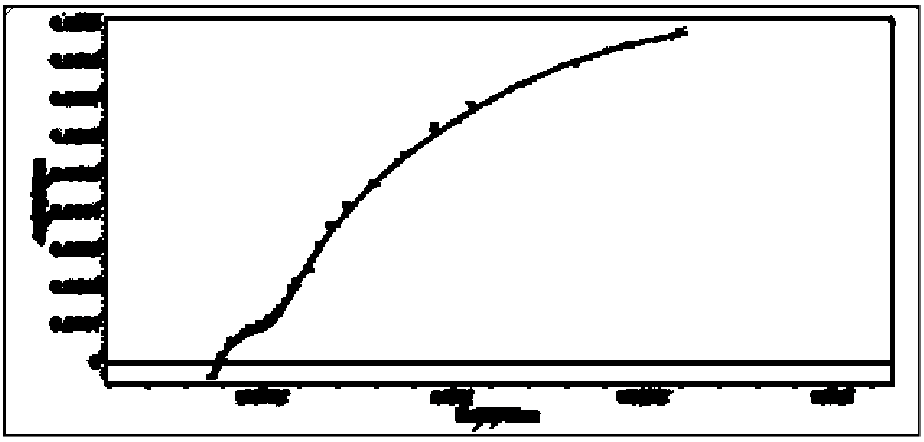

Fig. 1.Iimpedance spectrum obtained at 0 % SOC, 15˚C as well as the fitting curve from the designed EC model

Immersion Gold Coatings from Deep Eutectic Solvents: The Effect of Speciation on Coating Morphology

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This work shows that speciation in a deep eutectic solvent (DES) can be altered through the inclusion of highly coordinating ligands, such as cyanide, and that this can have a dramatic effect on the electrochemical behaviour of these compounds. DESs are a novel class of ionic liquids (ILs) that have generated widespread interest in both academic and industrial areas. This is due to their unique solvation properties when compared to both molecular solvents and conventional ionic liquids. The solvation behaviour arises due to the high salt concentration in DESs (ca 6 M) as well as the presence of polar, hydrogen bond donating, molecules such as ethylene glycol and urea. As a consequence DESs have seen considerable investigation in the metal processing area.[1] A number of groups have investigated the speciation of metal salts in DES by methods such as FAB mass spectrometry and EXAFS showing that speciation is often very varied compared to that of comparative molecular media,[2] although very few have linked this to the corresponding behaviour in electrochemical systems. Here we present an EXAFS study of the speciation of the gold compounds AuCl (1), AuCN (2), and $KAu(CN)_2$ (3) in the DES Ethaline 200, indicating that they all form $[Au(XY)]^-$ type anionic complexes with either 2 chloride ions in the case of AuCl, a mixed chloro/cyanide species for AuCN or a dicyano species for $KAu(CN)_2$. The electrochemical properties of these salts show an evolution from diffusion limited to kinetically limited behaviour with increasing cyanide content. Immersion Au onto electroless Ni is an important surface finish in the electronics industry and as such the immersion coating properties of these three systems has been investigated.[3] Quartz crystal microbalance (QCM) study shows the rate of deposition decreases with increasing cyanide content. In addition, the coating morphology was found to be remarkably varied with 1 producing a rough, poorly adherent brown coating. In contrast, both 2 and 3 produce uniform bright, adherent, gold coloured deposits which can be visualised from the SEM images in Figure 1. This difference in morphology can be explained by the relative kinetics of the Au deposition process where AuCl has comparatively fast kinetics compared to that of the cyano containing salts.

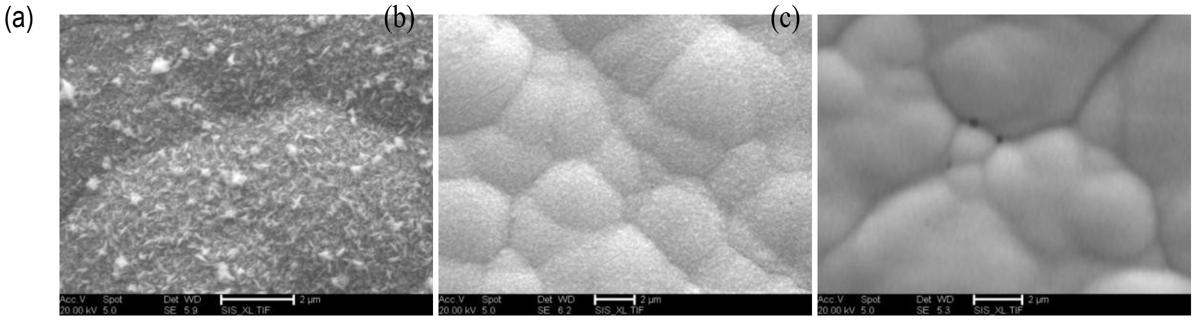

Figure 1: Immersion Au deposits onto electroless Ni substrates from 5 mM (a) $[AuCl_2]^-$, (b) $[AuCl(CN)]^-$ and (c) $[Au(CN)_2]^-$ solutions in the DES Ethaline 200

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Electrochemical Formation/Reduction of PtO on Bulk Pt Electrode at Elevated Temperature in Concentrated H3PO4

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High temperature fuel cells with proton exchange membrane (HT PEM FC) represent viable compromise between high temperature and low temperature fuel cells (LT FCs). They are much less sensitive to catalyst poisoning than LT FCs and their operating temperature of 150-200 °C does not restrict their utilization to rather stationary applications. Most common PEM membranes used in HT PEM FC's are based on polybenzimidazole doped with concentrated orthophosphoric acid (H_3PO_4). However, combination of elevated temperature and H_3PO_4 can under certain conditions lead to a gas diffusion electrode (GDE) degradation. It can be expected that rate of such degradation will increase in the case of HT PEM FCs compared to LT PEM FCs due to higher operating temperature. GDE usually consist of precious metal (Pt) nanoparticles dispersed on various forms of high-surface carbon. Detailed information on the GDE degradation in HT PEM FCs is still missing in literature. In principle the degradation can proceed by various mechanisms. One of them is Pt sintering due to Ostwald ripening (anodic Pt dissolution and redeposition) or Pt nanoparticle migration and coalescence. Extend of Pt sintering will most likely depend on the state of the Pt nanoparticles surface. Thus, it will depend on the presence and properties of surface oxide layer.

Aim of this work was to determine kinetics of PtO anodic formation and cathodic reduction on the bulk Pt electrode in concentrated H_3PO_4. Voltammetry experiments were performed in 3-electrode arrangement in Teflon cell heated to required temperature. Working and counter electrodes were made of Pt. As reference electrode served calomel electrode saturated with KCl. To simulate conditions present in polybenzimidazole membrane based HT PEM FCs at 160 °C a 99% H_3PO_4 was used as electrolyte. Electrochemically active surface area of pre-annealed Pt working electrode was followed by means of hydrogen underpotential deposition method in 0.5 M H_2SO_4.

Results showed that at elevated temperature H_3PO_3 anodic oxidation originating from H_3PO_4 reduction within the preceding potential scan interferes with the studied electrode reactions. Therefore electrode potentials in vicinity of hydrogen evolution, where H_3PO_4 is being reduced to H_3PO_3, has to be avoided to prevent its generation. Thickness of anodicaly formed PtO layer is increasing with increasing electrolyte temperature. This is documented by increasing number of PtO monolayers formed at elevated temperature. Kinetic parameters of PtO formation/reduction at 160 °C are estimated by fitting the experimental voltammetric curves. Emphasis during fitting was placed on value of current density plateau of oxide formation, equality of anodic and cathodic charge and position PtO reduction peaks.

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Ultrasonically Enabled Low Tempertaure Electroless Plating

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One of the most advantageous features of the electroless copper process is that it enables the metallisation of non-conductive substrates. For this reason it has been employed in the electronics industry for decades since it has enabled the plating of ‘through holes’ and ‘vias’ in printed circuit boards (PCBs) whilst also finding extensive use in the Automotive and Aerospace sectors. The non-conductive substrate must first be catalysed (or ‘activated’) and this is normally achieved using a palladium based solution. There has been much work performed on the effect of ultrasound on the electroless process and this was the subject of a recent review by the author [1] and suggested that sonication generally produced a significant increase in plating rate [2-5]. However, few studies take into account the catalysation stage despite the fact that this is a critical part in the process. One notable exception to this are the papers published by Touyeras et al [6-7]. They showed that if relatively high frequency ultrasound (530 kHz) was introduced to the catalyst bath then an increase in the subsequent electroless copper plating rate could be obtained. Indeed, by applying ultrasound in both the catalyst and the electroless copper solution the plating rate could be almost doubled. These papers clearly demonstrated the importance of the catalysation step in the electroless process. For industrial applications the use of low frequency ultrasound is preferred due to cost, availability and its more uniform effects in a bulk solution. For this reason this paper details the results of a study into the effect of applying low frequency (40 kHz) ultrasound in catalysed electroless deposition processes. The results indicate that the effect of low frequency ultrasound on a catalysed surface must be understood if enhanced electroless deposition (plating rates, morphology etc) is to be achieved.

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Effect of Ultrasound on Mass Transfer during Electrodeposition at Electrodes Separated by a Narrow Electrode Gap

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Recently a micro-scale pattern transfer method, called the Enface technique, has been proposed for metal plating and etching. This method introduces the idea of bringing a patterned tool and a substrate in close proximity, i.e. within less than 500 microns, and passing a current or voltage which enables metal to be deposited or removed from the substrate. It has been shown that this process allows metal to plate or etch selectively, provided that sufficient agitation is maintained and appropriate electrolytes are chosen [1,2]. Although the technique has been shown to hold in a vertical flow channel reactor, the process has to be adapted for tank-type metal plating systems in order to be implemented in industry. However, current agitation means in tank type reactors cannot be easily used to improve agitation within narrow electrode gaps, such as those encountered in Enface. It is well known that ultrasound waves can enhance mass transfer during metal electrodeposition [3,4]. In this study we have investigated whether ultrasound is a suitable form of agitation to use for improvement of mass transfer within narrow gaps between electrodes.

Experimentally, copper reduction at a 1cm diameter copper cathode was used as a model electrochemical system. Mass transfer boundary layer thicknesses for this reduction reaction were estimated using the limiting current technique, which was measured using potentiostatic polarization data. Two electrolytes, a solution of 0.1M $CuSO_4$ and an acidic electrolyte of 0.1M $CuSO_4$ with 0.1M H_2SO_4, were used. The ultrasound equipment used was a SONICS Vibra-Cell VC505 processor connected to an ultrasound probe; 13 mm in diameter operating at a frequency of 20 kHz, and was placed above the working electrode in a side-on orientation. The intensity of the ultrasound power was varied from 9 – 29 W/cm^2. The distance from the center of the electrode surface to the probe ranged from 1cm and 3cm. The inter-electrode gap was varied from 0.15cm to 1cm. At an inter-electrode gap of 1cm, the limiting current was found to increase from -57 to -130 mA/cm^2, as the intensity of ultrasound power was increased from 9 – 29 W/cm^2. The diffusion layer thickness was reduced by approximately a factor of 10 with ultrasound agitation. The thinnest diffusion layer thickness observed, using an inter-electrode gap of 1cm, was 12μm. These results show that ultrasound agitation considerably improves mass transfer of Cu^{2+} ions to the electrode surface. Currently, experiments with inter-electrode gaps less than 0.15cm are being studied as well as current distribution modeling of the cell.

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Microelectrodes for Molten Salt Analysis

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Molten salts are an ideal medium for the development of a wide variety of electrochemical processes with industrial application. However, there is a real need when optimising and controlling such processes for techniques to be developed which are able to sense and analyse the properties of redox active species in the extreme conditions found in molten salts. This talk will describe our work in developing microelectrode systems and will demonstrate for the first time the application of such systems to the measurement of the redox behaviour of a variety of species in the LiCl-KCl eutectic molten salt. The enhanced characteristics of these microelectrodes will be highlighted in comparison to equivalent macroelectrode measurements and the application of these systems in molten salt analysis discussed.

Electropolishing of Ni based Superalloys using Deep Eutectic Solvents to Remove Surface Oxides and Selectively Modify Surface Structure

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Here we describe the use of deep eutectic solvents (DES) as a novel alternative electrolyte for electrolytic etching of superalloy castings used in the aerospace industry. An homogenous etch can be achieved by careful selection of potential applied as well as the formulation of the DES. DESs are novel ionic media formed by complexing a quaternary ammonium salt with a hydrogen bond donor.[1] They exhibit good electrolyte properties and have been shown to be a promising alternative electrolyte media for many metal finishing processes, such as electropolishing and electrodeposition.[2,3]

The electrolytic etching of superalloys is of huge importance to the aerospace industry because it allows for the removal of any surface defects without the need for mechanical processing. Often these superalloys are made from single crystals and mechanical etching/grinding can induce the formation of new crystal grains, which are more susceptible to failure. The conventional methods used to electrolytically etch the surface employ toxic and corrosive acids, such as sulphuric/nitric/phosphoric and perchloric acids, these are highly hazardous, both environmentally and to the operator, and can cause uneven dissolution as well as deep pitting of the surface.

The DES Ethaline 200 (1 choline chloride: 2 ethylene glycol) has been used to electrolytically etch the surface oxide scale from high Ni content superalloy castings for inspection purposes. [4,5] These Ni based superalloys, once cast and subsequently then heat treated, exhibit a waffle like structure that is comprised of two main phases, a γ' cube and a γ channel that resides between the γ' cubes. As a result, this work has shown that not only can this scale be removed using a relatively environmentally benign solvent, but it also has the ability to selectively remove one phase of the superalloy structure preferentially over the other, depending upon the potential applied. It can be seen that at lower potentials there is a large preference for the removal of the γ' cubes in the bulk structure, whilst leaving the γ channels relatively intact; whereas, at higher potentials there is a switch in the selectivity where the γ' cubes are left relatively intact and the γ channels are preferentially etched. Making slight changes to the formulation of the DES can also have a marked effect on both the selectivity of the phase preferentially etched and the manner in which the dissolution occurs. By altering the type and quantity of additive in Ethaline 200, it is possible to tailor the mechanism by which the γ' cubes are dissolved, either by preferential dissolution at the edges or focusing at the centre of these cubes instead. This is an interesting observation as it leads towards the possibility of being able to selectively and beneficially modify the surface of these superalloy castings.

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Encapsulation of Cr_3C_2 in Nickel Composites on Cu and Ni Substrates

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Nickel is a popular metal for electro-deposition because it has good ductility, it is relatively straight forward to deposit, has good anti-corrosion behaviour and wear resistance. Often particulates are incorporated into the nickel deposits to provide additional wear resistance and abrasion for high precision gas-tight seals in aerospace turbine engines. Such composite coatings are required to endure extreme conditions of mechanical and thermal stress and therefore are required to retain the intrinsic characteristics of the Ni whilst exhibiting good adherence to superalloy substrate.[1] Conventional methods for electro-deposition of composite coatings of Ni involve rather complex and cumbersome techniques for particle incorporation as well as an electrolyte based on a strong inorganic acid. As part of our continuing efforts to find environmentally sustainable electrolytes for metal finishing processes we have investigated the deposition of Ni composite coatings from choline chloride based deep eutectic solvents (DES).

Here we describe the electro-deposition of Ni, composite wear resistance coatings, through the incorporation of the abrasive particles of Cr_3C_2. These particles are hard materials, have good thermal conductivity, excellent wear resistance, good chemical inertness and are very stable at high temperatures (up to 1237K).[2,3] Ionic liquids (ILs) based on the DES have a wide range of properties which make them suitable for metal electrodeposition, such as their wide potential windows, high solubility of metallic salts, unique solvation behaviour and good conductivities.[4] We have previously studied the electrolytic deposition of nickel from Ethaline 200.[5] The work presented here extends on this preliminary study and we will show data relating to the deposit properties, thickness, composition and morphology as a function of electrochemical deposition regime and electrolyte composition.

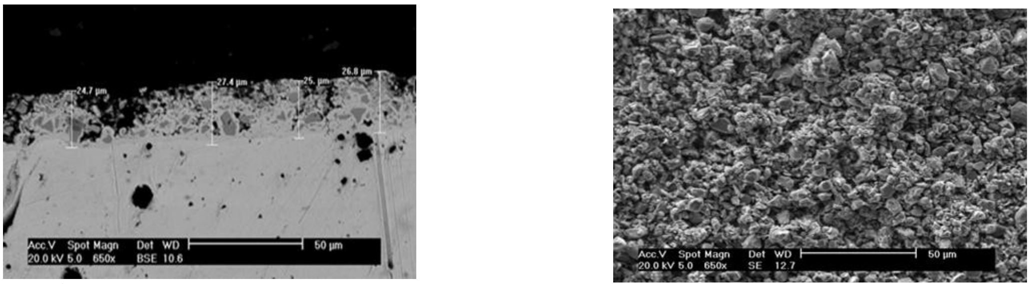

Figure 1: *SEM displays of the cross section and morphology of the first, second layer of Ni deposition and incorporated chromium carbide on Cu substrate.*

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Investigation of Supported IrO2 as Electrocatalyst for the Oxygen Evolution Reaction in Proton Exchange Membrane Water Electrolyser

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Indium tin oxide (ITO) was used as a support for IrO_2 catalyst in the oxygen evolution reaction. IrO_2 nanoparticles were deposited in various loading on commercially available ITO nanoparticle, 17-28 nm in size using the Adam's fusion method. The prepared catalysts were characterised using X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The catalysts were also used in a membrane electrode assembly (MEA) for electrolyser operation. It was found that crystallite size decreased with an increase in loading. The BET surface area of the support (35 m^2/g) was 3 times lower than the unsupported IrO_2 (112.7 m^2/g) and was proportional to the IrO_2 loading. The electronic conductivity increased with an increase in the IrO_2 loading. The bulk electronic conductivity and particle size also affected the electrode performance. The 90% IrO_2-ITO gave similar performance as the unsupported IrO_2 in MEA polarisation test which was attributed to a better dispersion of the active IrO_2 on the electrochemically inactive ITO support, giving rise to lower particle size catalyst and thereby higher surface area. Maintaining a network of conducting IrO_2 on the support was found to be the most important strategy in preparing the supported catalyst.

Electrochemical Treatment of Tannery and Electroplating Effluent

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Present study involves the treatment of tannery and electroplating industrial effluent by electrochemical process as an alternative to primary treatment by means of conventional coagulant-flocculants. The objective of this study is to bring the physiochemical phenomenon involved into perspective and to focus attention on those areas critically needing research. Electrochemical Treatment is a method of treating polluted water whereby the anodes corrode to release active coagulant precursors (usually aluminum or stainless steel cations) into solution. Accompanying electrolytic reactions evolve gas (usually as hydrogen bubbles) at the cathode. For homogenized tannery and electroplating effluent, present treatment mode has been employed to remove a wide range of contaminants. Both batch and continuous modes of treatment were studied. Further, the batch mode aims to optimize coagulant concentration, pH and current density at fixed treatment duration. Present study revealed that the current density is the most prominent factor in the suspended solids elimination followed in decreasing order of importance by coagulant-flocculant concentration. Physicochemical characterization of the effluent was done before and after the treatment to observe the prominence of overall treatment, included pH, Turbidity, conductivity, COD, suspended solids.

Electrochemical Reduction of Carbon Dioxide at Copper Oxide Catalysts in Aqueous Solution

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The emission of carbon dioxide into the atmosphere, released mainly by the burning of fossil fuels, is a serious problem with regard to the greenhouse effect. One of the most practical proposed electrocatalytic methods to maintain the concentration of carbon dioxide in the atmosphere is the electrochemical reduction of carbon dioxide to hydrocarbons and alcohols. These products can be further reacted to synthesize a variety of useful industrial supplies [1, 2].

Several studies about CO_2 reduction on metal electrodes have been conducted. The products of CO_2 reduction vary with the electrode material and the electrolyte solution used in the reactions [3]. Among these electrode materials, only copper and its oxides in particular have been investigated to reduce CO_2 to hydrocarbon production [3, 4].

The focus of my project is to study the possible use of copper oxides as catalyst for electrochemical CO_2 reduction and identify the optimum reduction conditions. Moreover, we aim to determine the selectivity for reduction products by various methods, to reach some conclusions about the catalytic mechanism and the importance of oxidation state of the Cu species.

In order to investigate the effect of Cu_xO materials on CO_2 reduction, a series of electrochemical methods are involved, such as cyclic voltammetry, electrocatalytic method and chrono amperometry. Nanoparticle catalysts were immobilized onto the working electrode under argon and CO_2-saturated atmosphere to understanding the catalytic mechanism. It may be concluded that selection of an appropriate operating conditions is essential to the reduction process. The lowest reducing potential is likely to be limited by the properties of catalysts. Therefore the process can be optimized.

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Are Deep Eutectic Solvents the Electrochemical Media of the Future? A Combined Optical- Gravimetric Study of DES Electrochemistry.

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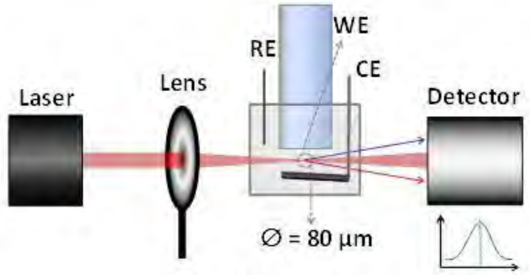
Chemistry of Deep Eutectic Solvents (DES) is a matter of current interest as the novel properties of these solvents make them a versatile medium for a variety of processes.[1] Due to their wide potential windows and high ionic strength they form an attractive media for exploiting the electrochemical properties of conducting polymer films as well as for the ionometallurgy. Metal plating is currently often conducted with the use of toxic compounds. DES based ionometallurgy allows for the use of more benign plating agents, thus creating safer alternatives to the current industrial practices.

The very different nature of DES compared to the conventional liquid electrolyte media requires detailed characterization of electrochemically driven ion transfers. In the case of redox switching of electroactive polymer films exposed to DES, the response is anticipated to be highly sensitive to the absence of molecular solvent. In the case of elemental metal deposition, metal ions speciation and transport are expected to be different in DES and molecular solvents.

In both instances, one requires technique that permits measurement of ion transfer at the electrode/electrolyte interface. Probe beam deflection (PBD) is an optical analytical technique based on the deflection of a laser beam passing very close (~50 μm) to the electrode surface. The deflection is caused by a concentration gradient that is generated by surface electrochemical processes and can be expressed (using a mathematical convolution tool) as a mass flux. In combination with the Electrochemical Quartz Crystal Microbalance (EQCM), PBD offers unparalleled sensitivity for the measurement of individual species attribution to the interfacial processes.

Implementation of the combined EQCM/PBD technique in DES media presents challenges associated with the viscosity of these solvents. In this presentation, we explore these issues and show how one can overcome challenges by appropriate choice of experimental conditions. We then apply the combined PBD/EQCM technique to characterize ionic fluxes occurring at the PEDOT conducting polymer/solvent interface upon film redox cycling [2] and to investigate mass transfer effects during the deposition and dissolution of metals from metal salts dissolved in DES.



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Corrosion of Metals in Deep Eutectic Solvents

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It has previously been shown that eutectic mixtures of quaternary ammonium salts when mixed with a hydrogen bond donor form fluids with properties which are similar to ionic liquids.[1,2] These so-called deep eutectic solvents (DESs) have been shown to have physical properties which would make them useful as lubricants. The liquids have high viscosity indexes, good thermal stability and are environmentally compatible.

To ascertain the applicability of DESs as lubricants it is important to characterise their compatibility with various metals. Corrosion studies of Fe, Al and Ni in four liquids were measured using both techniques linear sweep voltammetry and impedance spectroscopy. Linear sweep voltammetry was employed to measure corrosion rates wherein, the Butler- Volmer equation was employed to fit the data. In addition to pure liquids 1, 2, 5, and 10% water was added to see the effect of water on corrosion rates. The data shows that the Oxaline is the most corrosive liquid while; Glyceline, Ethaline and Reline show very slow corrosion rates. Addition of water in all cases increased the corrosion rates which may be due to the increase in mass transport in addition to its direct contribution to corrosion reactions. Impedance spectroscopy was also used to determine the influence of timing contact between these liquids and metals for long time. The Nyquist plot has been used to determine polarisation resistance for pure surface as well as for metals after immersion for up to 48 hours. The data show that in Reline all metals passivate over time whereas in Glyceline the rate starts low and remains constant. However in Ethaline each metal shows different corrosion behaviour. Oxaline shows a high corrosion rate for all metals and is unsuitable as a lubricant.

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Environmental Degradation of a Mg-Rich Primer: Comparison of Selected Field Environments with Laboratory Exposures

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Recently an organic coating system containing a Mg-pigmented organic primer (MgRP) for corrosion protection of precipitation age hardened Al 2024-T351 has been developed as a candidate to replace chromate-containing surface pretreatments and primers. Corrosion inhibition mechanisms of the MgRP [1] include sacrificial anode based cathodic protection of the aluminum as well as barrier protection by the primer and topcoat polymers. King and Scully [2] have shown this capability is mediated by the percent volume concentration of Mg and the conductivities of the organic polymers in the primer and topcoat. A test protocol was also developed [2] that could be extended to assess the degradation of the MgRP coating system throughout environmental exposure.

This poster reports on a comparison of field and lab exposures of MgRP in a non-topcoated and topcoated condition. Commercial MgRP was utilized for the corrosion protection of an AA2024-T351 substrate pretreated with PreKote™ surface pretreatment. Exposures were conducted in the field at a coastal marine site at Kennedy Space Center, FL, at an inland rural site at Birdwood Golf Course in Charlottesville, VA, in ASTM B-117 with 5% NaCl and the same standard test modified with ASTM Sea Water as well as in full immersion in ambiently aerated 5% NaCl solution. Mg pigment depletion rate, galvanic protection potential and coating barrier properties were tracked throughout exposure periods in both field and laboratory environments. Preliminary acceleration factors with respect to pigment depletion and residual barrier properties were developed. Analysis near and far from a scribe exposing bare 2024-T351 was performed. Post-mortem characterization with SEM/EDS was conducted to elucidate coating and scribe morphology, corrosion products present, corrosion of the AA2024-T351 substrate, as well as in an attempt to determine the "throwing power" of the MgRP coating system based on cathodic protection of a scratch exposing bare AA2024-T351. No blistering or similar macroscopic coating failure phenomena were observed in the MgRP or along the scribe lines after exposure in any of the studied environments. Additionally, in contrast to similar environmental exposures of earlier generation commercial products in the past, no indications of cathodic corrosion, as evidenced by narrow pinholes, or underpaint corrosion or anodic undermining, as evidenced by large areas of coating delamination above regions of Al corrosion, were visible at the coating/metal interface when viewed in SEM cross-section.

The differences in rate-of-change of Mg depletion from the coating upon environmental exposure was found to be related to differences in time-of-wetness and in rates of polymer degradation, specifically resistivity, due to environmental severity factors such as UV exposure and electrolyte pH. Differences in throwing power in lab and field environments, as elucidated by finite element modeling of current and potential distributions, were traced to differences in electrolyte geometries; continuous thin-layer in salt fog cabinet exposures compared to isolated droplets which do not form a connected path in field exposures.

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Electrochemical Study of Protective Oxide Films of Ferritic-Martensitic Steels, Formed by Vapor- Oxigen Treatment

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Corrosion resistance of oxide films, formed in high temperature vapor condition, is an important factor, determined rate of corrosion process. Protective properties of oxide films depend of their phase and elemental composition, thickness and porosity. Estimation of this properties is made now by SEM, X-ray, local element analisys and a lot of its versions. However, application of electrochemical methods in corrosion resistance measurements provides information about large scale properties of oxide films.

We proposed pulse chronopotentiometry, voltammetry and AC impedance technics as an appropriate methods for systematically estimation and prediction of corrosion resistance.

Using sequence of current pulse with uniform growing amplitude (Fig. 1*b*), one can obtain potential-time function (Fig. 1*c*), which indicate some important phases of mixed oxide film or its thickness. These cases differs by electrolyte type. Phase identification is based on electrochemical reduction of oxides in acidic electrolytes, whereas in alkaline solution this process indicate film thickness. In pulse chronopotentiometry we use clamping electrochemical cell (Fig.1*a*).

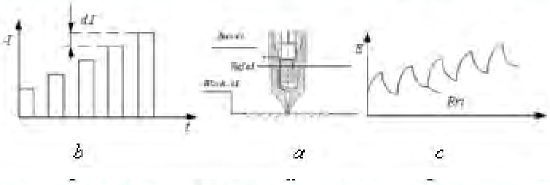

Fig.1 Clamping electrochemical cell (*a*), input signal (*b*) and output signal

After selection of potential values in absence of current, Er_i, one can identified phases of oxides (Fig.2). TiO, Ni_2O_3, Cr_2O_3, Fe_2O_3,CrO_3 were identified by this way. Obtained results were in a good agreement with elemental and X-ray analisys.

Maximum corrosion resistance of oxide films corresponds to the same elemental composition as in steel.

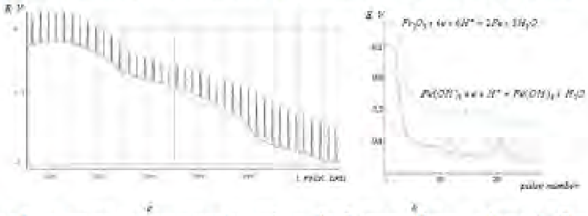

Fig.2 Output signal for electrochemical phase identification (*a*) and its treated form (*b*)

Voltammetry measurements give information about free surface portion of oxide films (Fig 3). This parameter can be calculated from current ratio at equal potential on film covered (j_f) and clear surface (j_c) of sample. A comparison of calculated and SEM data show, that voltammetry determined free surface portion indicates big cracks and transmittivity of pores.

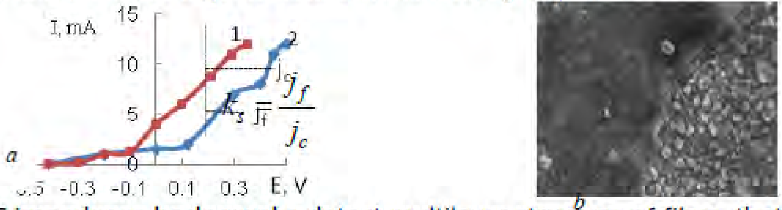

Fig. 3 Voltammetry determination of free surface portion of oxide films (*a*) and SEM pattern of the same film (*b*)

AC impedance hodographs detect multilayer structure of films, that is in agreement with SEM data (Fig. 4).

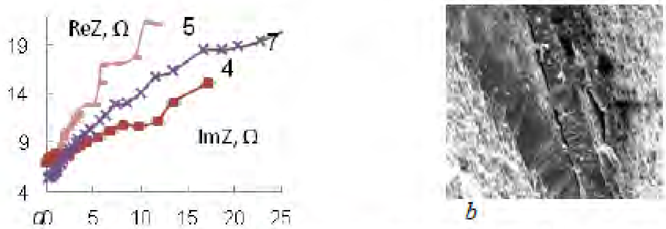

Fig. 4 AC impedance hodographs of different films (*a*) in 2M KOH and SEM pattern in cross-section (*b*)

Active conductivity of films in alkaline electrolyte at 45 kHz strongly correlate with corrosion rate. This means, that protonic conductivity of films play an important role in high temperature vapor corrosion.

Characterisation of Sn-Cu Intermetallic Growth in Electrodeposited Tin Films on Copper using Electrochemical Anodic Oxidation Techniques

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Electrodeposited tin on copper circuitry provides a surface with good solderability and resistance to corrosion and oxidation, however, whiskers may subsequently nucleate and grow producing localised degradation of the tin coating structure. Filamental whiskers are a common morphology, and are defined as single crystal metal filaments, typically between 1 and 500 µm in length and 1 to 5 µm in diameter (Fig. 1). Some whiskers can grow over 5 mm in length and are of significant concern in modern electronics as they can produce unwanted shorts within circuitry, with equipment failure.

Atomic diffusion of copper from the substrate into the tin coating causes the formation of vacancies within the substrate and intermetallic compounds (IMCs) within the tin coating itself. The formation of IMCs creates a positive expansion within the tin coating and it is this expansion and subsequent compressive stresses that are thought to be a major contributor to the nucleation and growth of whiskers. It is this connection between IMC formation and whisker growth that makes the IMCs, their rate of growth and distribution the focus of this study.

The effect of surface roughness was first eliminated by potentiostatically electropolishing the copper substrates. Tin was then electrodeposited from an acid sulphate proprietary bath. Formation of the Cu_6Sn_5 IMC at the tin-copper interface was studied with the use of sequential electrochemical oxidation, which allows the controlled stripping of metallic tin thereby permitting study by optical and electron microscopy. Variation in the time dependent growth of the IMC was predominantly dependent upon the grain orientation of the copper substrates. The initial growth of IMCs was sparse and non-uniform followed by a period of coarsening (Fig. 2) that eventually leads to a complete and uniform layer of IMC. The non-uniform distribution and growth rate of IMCs observed at specific locations across the interfacial layer demonstrated that growth is predominantly dependent on the roughness and grain orientation of the copper substrate and to a lesser extent by the tin coating morphology.

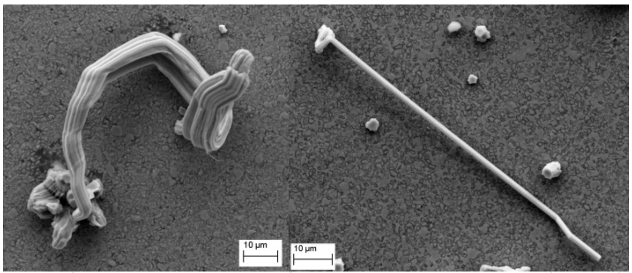

Fig. 1 SEM micrographs of tin whiskers on the surface of a 5 µm tin electroplate on brass after 160 days growth

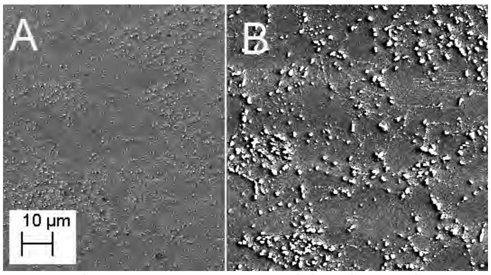

Fig. 2 SEM micrographs of Cu-Sn IMCs, after 1 day (A) and 17 days (B) growth

EQCM Monitoring of Growth of Polyaniline and Ion Exchange Characteristics of Polyaniline Films in a Deep Eutectic Solvent

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The modification of electrode surfaces with electroactive films is one of the largest areas of electrochemical research. A number of materials can be attached onto an electrode to achieve specific chemistry and applications in sensors, corrosion-protection, electrocatalysis, composite materials, electrochromic devices, energy conversion/storage and actuators. The modified electrode shows the chemical, electrochemical and optical properties of the surface species. Physical and chemical characteristics should be determined to improve the design and performance of the resulting films.

Conducting polymers have conjugated backbones allowing for a large degree of delocalisation of electrons for example polyaniline (PANI), polypyrrole and polythiophene. PANI has good redox reversibility and high environmental stability in aqueous solution. Recently, Deep Eutectic Solvents (DESs), which have melting points lower than both components, have been used in electrochemical applications because of their low volatility and high thermal and electrochemical stabilities. Spectroscopic, imaging techniques, reflectivity techniques, microbalance techniques (Electrochemical Quartz Crystal Microbalance -EQCM-) are used to characterize thin films. The aim of the characterization is to understand the correlation between the structure, spectroscopy and dynamics.

Here we describe various aspect of the behaviour of PANI films exposed to DES media in the potential range corresponding to p-doping. The effects of water during electropolymerization of PANI will be analysed with respect to film thickness, cycle numbers and potential scan rate. This involves a combination of electrochemical (cyclic voltammetry) and acoustic wave (EQCM) measurement. The EQCM allows the study of motion of mobile species populations between PANI film and DES via the related change in mass of a rigidly coupled film. The novelty of using a DES, rather than a molecular solvent such as water or acetonitrile, is that the fluid is entirely composed of ions. Consequently, questions relating to solvent transfer do not occur. The primary DES used for this process is Ethaline and these results would be compared to other DESs such as Glyceline and Propyline.

Electrochemical stability of PANI in DESs will also be explored. Electropolymerization of PANI and cycling with DESs will be supported by imaging of the films using SEM. The aim of these observations is to see porosity after electropolymerization and to relate film morphology to film stability and switching rate.

A Novel Approach Towards Designing Electrode-Electrolyte Interface for High Performance all- Solid-State-Supercapacitor

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We have developed a novel approach in the design of all-solid-state supercapacitor (ASSP) by impregnating polyaniline (PANI)-coated carbon paper with a polymer electrolyte, which in turn enhances the electrode-electrolyte interface of the resulting device. The design is simple, scalable and can be adapted to similar other energy storage systems. The designed interface of the device was confirmed by cross sectional elemental mapping and SEM images. The enhanced integrity of the electrode-electrolyte interface in the solid device helps it to perform as equivalent to its liquid counterpart. The device shows a specific capacitance of 647 F/g with an areal capacitance of 1 F/cm^2 at 0.5 A/g with a capacitance retention of 62 % at 20 A/g. The above values are the highest among the reported values of the ASSP's. The whole device shows a capacitance of 12 F/g. Higher integrity of the electrode-electrolyte as conceived through the strategy adopted here, helps the device to attain a very low ESR of 1 Ω. Apart from this, the device shows excellent stability of 10000 cycles with a columbic efficiency of 100 %. Energy density of the device is 14.3 Wh/kg with a significantly low leakage current of 16 μA. Therefore, the superior performance of the ASSP can be attributed to the enhanced integrity of the electrode-electrolyte interface due to the homogeneous intercalation of the electrode material and the solid polymer electrolyte, thereby mimicking the conventional liquid electrolyte-electrode interface.

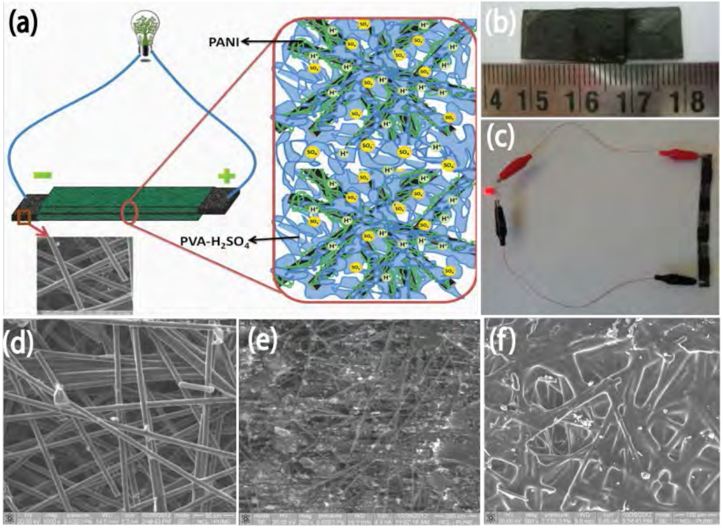

Figure 1.a) Schematic diagram of the all-solid-state-supercapacitor (ASSP); b) 1 cm^2 prototype ASSP c) LED powered by a four cell assembly which are connected in series. SEM image of d) porous carbon paper e) PANI coated carbon paper and f) intercalated gel-electrolyte inside the PANI/carbon paper

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Hot Compaction of Molten-Salt Electrodes and Electrolyte for Thermal Batteries

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Cold compaction is widely adopted to fabricate electrodes and electrolyte in thermal batteries for its lower manufacturing costs. The compacted electrodes and electrolyte, however, are so fragile that the handling of those thin disks requires troublesome cautiousness not to break them. Therefore, stiff materials such as FeS_2 for cathode, Li(Si) for anode and MgO for electrolyte, which have relatively abrupt elastic deformation before fracture, are coated with plastic molten salt, which has better coherence and smaller springback. In this study, hot-compaction process, simultaneous heating and pressing, has been used to reduce the porosity and defects and to improve the mechanical properties of the thin compacts. Hot compaction of molten-salt electrodes and electrolyte showed a marked improvement in strength compared to cold compaction and productivity compared to hot pressing. The enhancement of density uniformity and shape tolerance in final compacts relies mostly on the plastic deformation of lubricant molten salt and the rearrangement of hard materials at an elevated temperature. These results so far achieved make the hot compaction an ideal candidate process for thin powder compacts for thermal batteries with larger diameter.

Particle Size Effect of MS2 Cathode Materials on the Discharge Characteristics of Thermal Batteries

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Thermal batteries have been used as primary power sources for many military applications, such as guided missiles and torpedoes because of their inherent advantages of long shelf life, excellent performance and, high reliability. The Li(Si)/FeS_2 couple is the most popular electrochemical system adopted in thermal batteries. In this paper, we evaluated the material properties of iron disulfide (FeS_2) powder classified by particle size and the total polarization of single cells. Discharge performance of the smaller particle size (-325 mesh) cathode is increased by 15% compared to that of the larger one (-100 mesh to +140 mesh). In addition, we also evaluated the performance of single cells fabricated with MS_2 cathode materials such as nickel disulfide (NiS_2) and cobalt disulfide (CoS_2). Cobalt disulfide cathode showed the best performance on total polarization and practical run time.

Current Based Diagnostics of Ni-Cd Batteries

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State of charge diagnostics is very important problem for high power batteries, charging by constant voltage during long time. For many types of secondary cells, based on intercalation processes, a relation between capacity and current response on potential step can be obtain. This relation is direct proportional only in ideal case, but for real batteries a lot of different causes transformed this relation to more complex form. In this situation neural network models give some advantages. Proposed principle of diagnostics is based on applying se- ries of steps of voltage with information about battery's capacity appears in values of corresponding current steps. Three-step voltage was used therefore three values of current were availa- ble for calculating the value of capacity (fig. 1).

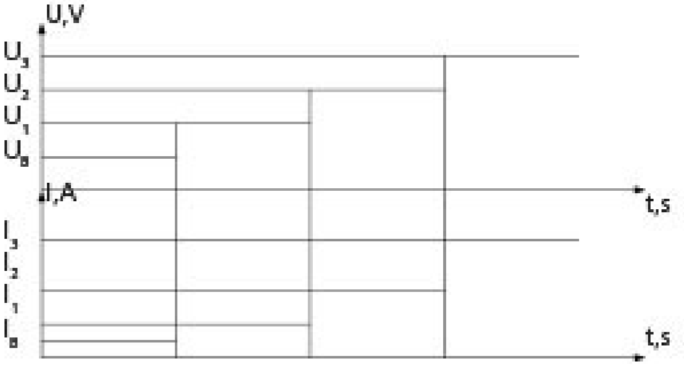

Fig. 1 Voltage steps and current steps of response

In this paper 24 batteries with capacities varying from 0.5 A/h to 1.2 A/h were used, so the raining set consisted of 24 three dimensional vectors of current values. Principal components analysis [1] has shown that capacity information (data variance in training set) is approximately evenly distributed over all three current values, therefore all of them can be directly used as an input for calculating value of battery's capacity. For such calculation feed forward neural network (ANN) with one hidden layer containing three neurons was used. Considering that speaking of battery's capacity lower prediction is much less critical than higher one results of ANN work can be shown on the following histogram (fig. 2).

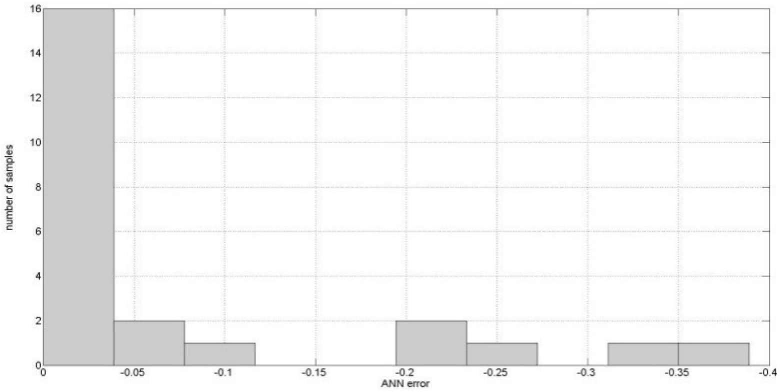

Fig. 2 ANN errors distribution

Thus, multiple voltage steps technique is multiparameter diagnostic, which provides determination on-line state of charge of secondary batteries. It is especially important for high power modules in the condition of complex history.

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Synthesis, Characterization and Electrochemical Studies of Functionalized Polypyridyl Ligands and their Ruthenium Complexes

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The design, synthesis, photo physical and electrochemical studies of polypyridyl based ligands and their corresponding Ru complexes are reported. The compounds were characterized by elemental analyses, electronic, photoluminescence, FTIR, ^{1}H and ^{13}C NMR spectroscopic techniques. The octahedral geometries proposed for the complexes are consistent with the spectroscopic analyses. The cyclic voltammograms of the ligands showed irreversible oxidation peaks. Electrochemical investigation of the complexes showed quasi-reversible and irreversible behaviour in some complexes while well defined reversible peaks were observed in others. Their voltammograms display the Ru(III)/Ru(II) couple at positive potentials and the ligand-based reduction couples at negative potentials. The overall outlook of the electrochemical properties showed that the ruthenium complexes possess good electroredox properties that are both single and multi-electronic in nature

Investigation of Water Sorption and Interaction with CO2 of Alkaline Membrane Electrolytes Using the Quartz Crystal Microbalance

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Fuel cells have for a long time been seen as one of the major contributors in the fight against climate change and the energy crisis. With the wide range of fuel cells available, the technology seems uniquely placed to cope with a large variety of applications.

Conventional low temperature polymer electrolyte membrane (PEM) fuel cells have an acidic membrane and operate below 100 °C. Their high efficiencies and high peak power densities make them extremely useful for applications from portable automotive power to large stationary power. However, issues pertaining to cost, reliability and durability hinder the technology's commercialisation.

Alkaline fuel cells (AFCs) which have more facile oxygen reduction reaction (ORR) kinetics than that of an acidic fuel cell are seen as an excellent alternative to PEM fuel cells as they can utilise cheaper non-precious metal cathode catalysts.

This work focuses on the performance of AFCs under a range of typical operating conditions. The water uptake and effect of CO_2 on the membrane are studied using a quartz crystal microbalance (QCM) able to detect nanogram changes in mass and / or viscoelastic changes in the material. How these factors affect the membrane is crucial to the optimum operation of the fuel cell. Whilst the membrane must be hydrated, the presence of water or carbonates in the electrodes or gas diffusion layers can prevent reactant access to the catalyst, reducing performance.

The experimental apparatus is shown in Fig 1a (controlled temperature and humidity block). Results have shown a clear increase in alkaline membrane resistance (with KOH) on exposure to CO_2. QCM impedance spectroscopy is used to show how operating conditions affect membrane viscoelastic properties.

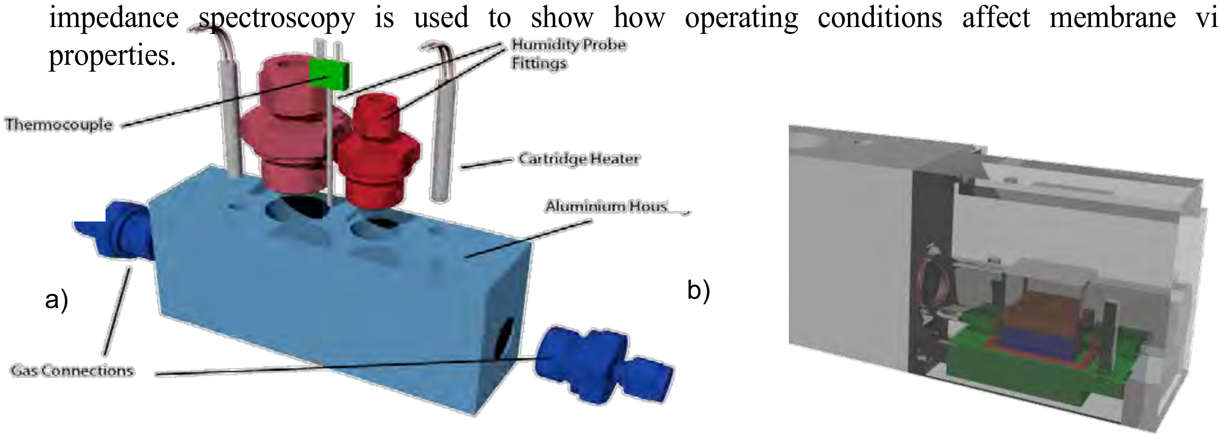

Fig 1 a) Rig setup overview b) internal view – showing QCM holder

The Oxygen Evolution Reaction at Manganese Dioxide Films in Base: Kinetics & Mechanism

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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 [1-3]. In practice, the efficiency of water electrolysis is limited by the large anodic over-potential of the oxygen evolution reaction (OER)[3] . 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 RuO_2 and IrO_2, since these oxides exhibit the lowest overpotentials for the OER at practical current densities [4]. However, the high cost of these materials and their poor long term stability in alkaline solution renders their widespread commercial utilisation both uneconomical and impractical[5]. In recent years manganese oxide films has been studied as an alternative anodic material for alkaline water electrolysis due to its relative low cost, eco-friendly properties and long term corrosion resistance in alkaline solution compared to RuO_2 and IrO_2 [6]. In the present work, we focus on the redox properties and electrocatalytic behaviour with respect to anodic oxygen evolution of manganese dioxide electrodes in aqueous alkaline solution. These films can be prepared simply via thermal decomposition of a manganese nitrate salt [7], Fig 1.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 substrate and annealing temperature using cyclic voltammetry. Interestingly, the voltammetric profile for the manganese dioxide film is strongly dependent on the nature of substrate and annealing temperature, as evident from Fig. 2. The kinetics of the OER at Mn_xO_y coated substrates have been studied using a range of electrochemical techniques including steady-state polarization and open circuit potential decay curves. In particular, Tafel slopes and reaction orders with respect to hydroxide ion activity are determined. Based on the available kinetic data, a reaction mechanism utilizing the active surfaquo group concep is proposed.

The Use of Graphene Oxide as a Support Material for IT-PEFCs

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The benefits of improved tolerance to impurities, higher quality heat and opportunities for lower catalyst loadings make the Intermediate Temperature Polymer Electrolyte Fuel Cell (IT-PEFC) a promising power generator in the future. Improving the intrinsic properties of the catalyst layer will enhance the performance of the membrane electrode assembly (MEA) and move this technology towards commercialization. This study looks at the optimization of the catalyst layer by the comparison of different catalyst-support conjugates/systems. The performance of Pt nanoparticles as electrocatalysts was compared on two different supports: (i) commercial Carbon Black (CB), (ii) reduced Graphene Oxide (rGO).

Pt/rGO has been reported to show increased CO-tolerance in Direct Methanol FCs (DMFCs) and a high Electrochemical Active Surface Area (ECSA) which should improve the catalytic activity towards oxygen reduction reaction (ORR) [1-5]. Depending on the technique employed to prepare catalyst-rGO system, it could be possible to attain higher ECSA and improved CO tolerance compared to conventional Pt/C [6]. Ex-situ electrochemical characterizations suggest that the Pt/rGO should give the best performance in the fuel cell. Testing has shown that the ECSA is much higher for Pt/rGO than for Pt/C [1, 5]. These characteristics are expected to be enhanced under HT-PEFC conditions, further improving the kinetics.

In this study, various electrochemical characterization techniques were used to study the kinetics and overall stability of the Pt/rGO and Pt/C systems. This was done by preparing rotating disk electrodes (RDEs) followed by potentiodynamic and chronoamperometry studies. MEAs were fabricated by using the same loadings of Pt/rGO and Pt/C and were tested by in-situ fuel cell measurements. Preliminary results indicate a lower ECSA value (15-20 m^2/g) of the Pt/rGO made by microwave reaction process. Initial conclusions indicate that there are severe mass transport limitations when employing the Pt/rGO system in a fuel cell MEA. Further studies will be reported that explore whether the formulation of catalyst ink can be fine-tuned to produce a better performing MEA.

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Transfer Function Analysis as a Novel Diagnostic Tool in Polymer Electrolyte Fuel Cells

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Fuel cells are a key technology in power production in the transition from a carbon-based economy to a sustainable, low carbon future. Polymer Electrolyte Membrane (PEM) fuel cells have a relatively high power density, low temperature operation, and produce no carbon emissions (depending on fuel source). However, there are limitations to the technology as PEM Fuel Cells have high catalyst costs, sensitivity to impurities and gaps in understanding of internal processes. In-situ diagnostic performance tests are essential to gain insight into the inner workings of an operational PEM fuel cell. This insight may lead to optimisation of durability and performance as well as more comprehensive models of fuel cell operation.

Electrochemical Impedance Spectroscopy (EIS) is a powerful diagnostic tool which can be used to identify various performance losses in a fuel cell. A small sinusoidal voltage is imposed on the fuel cell and the current response is measured. The phase shift and amplitude ratio between the voltage and current are dependent on the frequency of the imposed wave. These parameters, over a range of frequencies, can identify various resistances and capacitances in the system. In this work, similar cause- effect relationships are investigated to yield transfer functions which can infer other performance losses that are not accessible via EIS. The preliminary parameters for variation (causes) are:

- Thermal – varying temperatures will affect water management, reaction kinetics and can lead to mechanical failure
- Chemical – varying stoichiometry will affect reaction kinetics, catalyst degradation, and water management
- Mechanical – varying stress will affect water management, gas diffusion layer mass transport and membrane degradation
- Electrical – varying voltage and current will affect water management, temperature, and reaction kinetics
- Pneumatic – varying flow and pressure will affect mass transport properties
- Photo – varying light exposure to the catalyst may affect carbon monoxide poisoning processes.

The preliminary parameters for measurement (effects) are:

- Thermal – Sensible heat and radiation measurements using thermocouples and an infrared camera
- Chemical – Catalyst poisoning can be inferred from a CO sensor
- Mechanical - Strain can be measured using displacement sensors
- Pneumatic – Pressure and flow can be measured with pressure transducers and flow meters
- Electrical – Voltage and current can be measured with a potentiostat
- Acoustic – Acoustic emissions which show bubble rate can be measured with finely tuned hydrophones

The aim of these transfer function techniques is to develop a comprehensive set of diagnostic tools to identify faults, degradation mechanisms and general performance of operating systems.

Study to Obtain ZnSe Films to Photovoltaic Devices

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In this study, we have prepared a series of ZnSe thin films by electrodeposition from an acid bath (pH = 2) containing $ZnSO_4$ and SeO_2. The influence on band-gap and composition of the film was studied with different growth conditions, such as: potential and temperature of deposition, and annealing conditions. To characterize structural and optical properties of these films were used: cyclic voltammetric (CV), scanning electron microscopy (SEM/FEG), X-ray diffraction (XRD) and X-Ray Fluorescence (XRF) and optical absorption techniques (UV-Vis). The potentials to the sample's electrodeposition were chosen from the voltammetric study (Fig. 1A), which were: -0.748, -0.948 and -1.148 V (vs. SCE). The films were obtained on platinum substrates (0.9 x0.9 cm). The influence of the potential deposition in morphology of the films (Fig. 1 B-D) was studied and it was observed that at more negative potentials the were more dense and thickness, what can be related with the formation of ZnSe. The result is associated with XRD analysis where it was observed an increase in the characteristic peak of ZnSe when the deposition potential shift more negative values. XRF analyzes indicated that the films after annealing (400 ° C - 20 min - 1 mbar Argon) present a better ratio Zn/Se which was of 1.09. Films deposited at 60 ° C and no annealed shown a molar ratio of Zn/Se of 0.89 and 0.65 respectively. The annealing procedure decreases of thickness of the films and changed its morphology make it more compact. This results was also observed by the analysis of the XRD and XRF, where it was observed e a greater definition on ZnSe's peak counts and the decrease of film's thickness. The films thickness that were annealing presented the thickness of 691, 777 and 864 nm respectively. The band-gap of the samples was calculated by diffuse reflectance and the value obtained was close to 2.7 eV, indicating the formation of ZnSe under all experimental conditions studied. Thus, it was possible to obtain films of good quality ZnSe for applications in photovoltaic devices

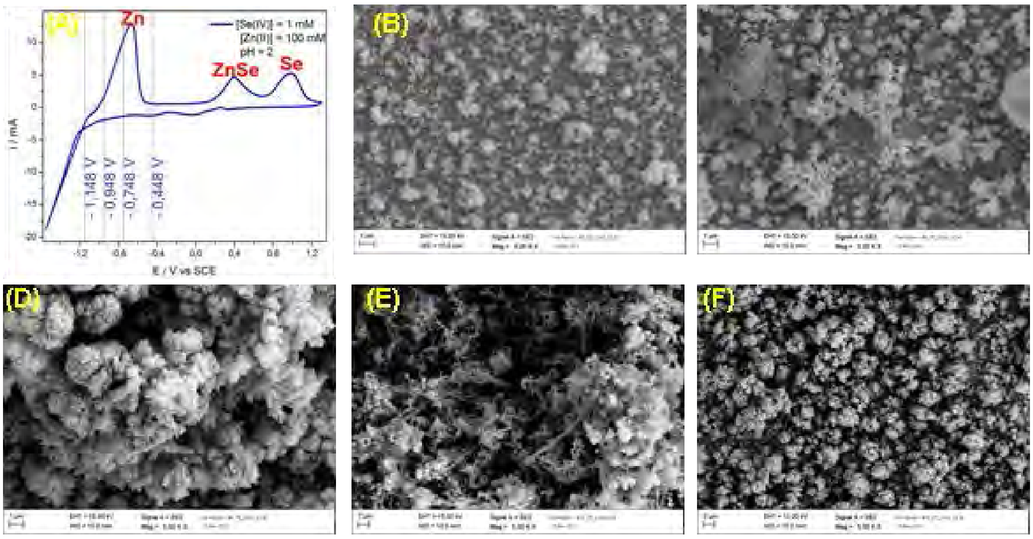

Fig 1. (a) Voltammetric cyclic on Pt of solution with Zn(II) and Se(IV) (100/1) pH = 2 and v = 100 mV s^{-1}, SEM micrographs of the samples under normal conditions (20 C - 60 min) E_{dep} (b) -0.748 V (c) and -0.948 V (d) -1.148 V (e) samples obtained at 60 C - 60 min and E_{dep} = -1.148 and (f) samples from 20 C - 60 min - annealing and E_{dep} = -1.148 V.

Pt-Cr Alloy Catalyst for Proton Exchange Membrane Fuel Cells

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Nafion stabilised nanoparticles of PtCr were synthesised using the sodium borohydride reduction method [1, 2]. The Nafion stabilisation was performed in order to protect these nanoparticles against dissolution and sintering. However, initial characterisation using transmission electron microscopy (TEM) coupled with energy dispersive spectroscopy EDS suggested traces of Cr in the system and no clear alloy formation. These catalysts were supported on Vulcan and graphene oxide (GO) for the possible use in Proton Exchange Membrane Fuel Cells (PEMFCs). Electrochemical studies show that the the Vulcan supported catalyst (25.36 m^2/g_{pt}) have slightly higher electrochemical active surface area (ECSA) as compared to GO supported PtCr nanoparticles (19.78 m^2/g_{pt}). This ECSA is very low as compared to the standard Pt/C catalyst (58 m^2/g_{pt}). The ECSA for the standard Pt/C catalyst obtained is in agreement with the literature values [3, 4]. However, the PtCr/C shows a three-fold increase in the specific activity and a slight increase in mass activity relative to the standard Pt/C catalyst. The PtCr/GO system also provides better specific activity and mass activity than the standard Pt/C catalyst, but not at the high levels obtained with PtCr/C. All these findings suggest that the PtCr stabilized with Nafion is a promising alternative in reducing the dependence on Pt for catalyst and increasing performance of the fuel cell. Studies are undergoing to increase the amount of Cr and forming an alloy by increasing the reducing agent concentration and investigating different reducing agents.

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Electronics Structures of the P3HT, PCBE and Rainforest Amazon Dye to be used as Potential Dye- Sensitized Grätzel Cells

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This work presents a theoretical electronics structures of the polymer composites P3HT and PCBE important for the manufacture of organic solar cells. Also we present some studies of electric field behavior inside the rainforest Amazon dye to be used as potential dye-sensitized Gratzel cells. The energy gap of the spectrum corresponding to the DOS was obtained using simulation base B3LYP/6-31G (d). Other results such as the UV-vis, density of states (DOS) and circular dichroism spectra were calculated using the base considered and interpreted their spectra to assess the main features of the molecules studied. These simulations were obtained spectra from DOS to verify the formation of the polymer.

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

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There is a substantial interest in the application of low cost steel as an alternative bipolar plate material for PEM fuel cells – currently the application of these materials is limited by their corrosion performance: The primary aim of the project is to study the feasibilities of mild steel and low carbon steel to be applied as bipolar plates (BPPs). The project is undertaken in collaboration with one of the largest steel producers in the world, TATA Steel. The ultimate focus is on the development of a novel coating solution that would be applicable to the selected TATA Steel substrates and would withstand the PEMFC environment. The candidate materials provided by the sponsor include Ni-coated mild steel, ECCS (electro-chromium coated steel), alloy coated mild steel and SS 316L which is used as a benchmark.

This project will involve the use of a suite of spectroscopy tools to examine their corrosion performance; initially, these materials have been screened through the ex-situ tests including, interfacial contact resistance measurements and corrosion rate measurements at varying temperatures and purging conditions. The materials have also been exposed to accelerated corrosion tests (including Electrochemical Impedance Spectroscopy) following which they are analysed using electron microscopy and other surface analysis techniques in order to gain an insight into the details of the degradation process and the corrosion performance of the candidate materials. Moving forward, these materials will also be evaluated in working fuel cell environments.

Nickel Based Alloy Nanoparticles as Electrocatalysts for the Hydrogen Evolution Reaction (HER)

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Hydrogen production via water splitting is an important process for clean-energy technologies. The hydrogen evolution reaction (HER) is commonly catalysed by platinum due to its high activity at low overpotentials. However, platinum is non-abundant, expensive and also catalyses the back reaction of hydrogen and oxygen to water,[1] therefore alternatives need to be developed. As a relatively cheap, abundant and readily available material, nickel is a promising alternative. Ni/NiO core/shell nanoparticles have been shown to be effective proton reduction catalysts on photocatalytic semiconductors, without catalysing the back reaction. However, there are longevity issues with this material.[2]

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 electrocatalytic activity for the HER. However, due to corrosion and leaching, the exact composition and structure of the active catalyst is often unknown.[3] 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.[4] Alloy nanoparticles of nickel with other inexpensive and abundant metals are being synthesised and their compositions analysed using powder x-ray diffraction, transmission electron microscopy and energy dispersive x-ray spectroscopy.

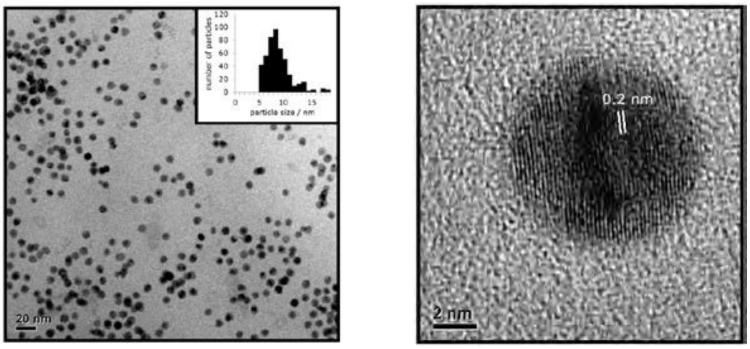

Figure 1. TEM images of $Ni_{0.5}Cu_{0.5}$ alloy nanoparticles at magnifications of 50,000 (left) and 800,000 (right) and histogram of size distribution (inset).

Electrocatalytic activity for the HER of nickel alloy nanoparticles will be described.

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Immobilisation of the Porphyrins onto Conductive Substrates

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Porphyrins are repeatedly found in natural systems with in different arrangements for mammals and plants, from oxygen transport to light harvesting. To understand their function both in solutions and immobilised on conductive surfaces has value in applications of broad interest from solar cells to artificial photosynthesis.

Examples of electrochemistry and spectroelectrochemistry of porphyrins in solution and on conductive substrates are presented in this poster. The properties of the porphyrins attached to titanium dioxide (TiO_2) were investigated for DSSCs. Immobilisation of porphyrins directly onto ITO were also studied in order to build organic photovoltaic devices that are nanostructured to maximise efficiency. In addition the incorporation of porphyrins into a protein matrix in solution or on conductive surfaces presented the opportunity to study an artificial photosynthetic system that harvests light, separates charges and transfers energy across an interface. Preliminary results to this end will be presented.

Amperometric Determination of High Density Lipoprotein and Total Cholesterol in Serum Using a Printed Biosensor

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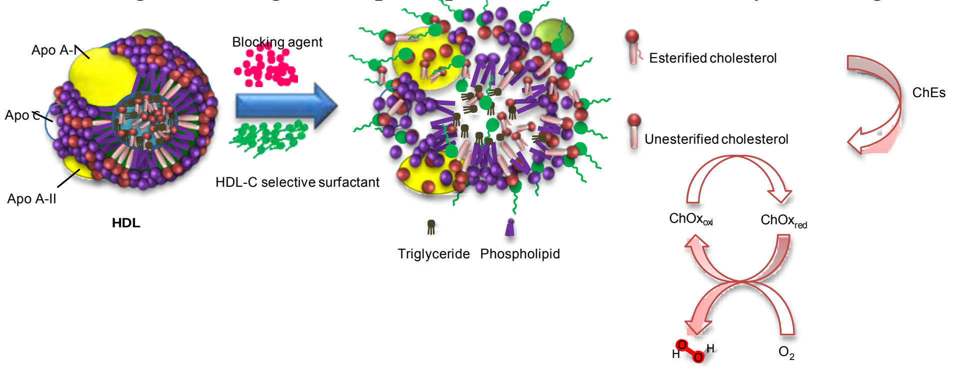
Since decreased levels of high density lipoprotein cholesterol (HDL-C) and elevated levels of Non-HDL-C are found to be the major risk factors associated with coronary heart disease (CHD), the importance of accurate measurement of both has been emphasized by the National Cholesterol Education Program (NCEP). [1] Since serum lipoproteins have unique physical and chemical characteristics, there are lots of different methods for determination of cholesterol in each specific lipoprotein. Among them, homogeneous assay showed a significant improvement in clinical measurement of HDL-C. [2]

It has been shown that polyoxyethylene tribenzylphenyl ethers allow HDL-C to be selectively dissolved to allow the enzymatic catalysis of HDL-C alone. The final step of measurement is typically based on the formation of hydrogen peroxide from cholesterol oxidase. A generalised approach to the selective detection of HDL-C using the homogeneous principle is shown schematically in the figure below.



This work investigates the application of homogeneous cholesterol assay strategies to the development of an electrochemical biosensor for the measurement of HDL-C using a novel inkjet-printed catalyst for hydrogen peroxide reduction. [3]

The effects of assay reagents such as surfactant, enzymes and serum on the electrode behaviour were assessed amperometrically in the presence of hydrogen peroxide solutions. The electrodes showed an increase in its catalytic activity toward H_2O_2 in the presence of polyoxyethylene tribenzylphenyl ethers. Despite the negative effect of cholesterol oxidase and serum components on electrode behaviour, the electrode response was linear from 0.5 to 4 mM HDL-C solutions and 2 to 10mM total cholesterol. Artificial sample with known concentration of HDL-C and total cholesterol was used for the real sample measurement.

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Towards Polypyrrole Self-Powered Drug Delivery System

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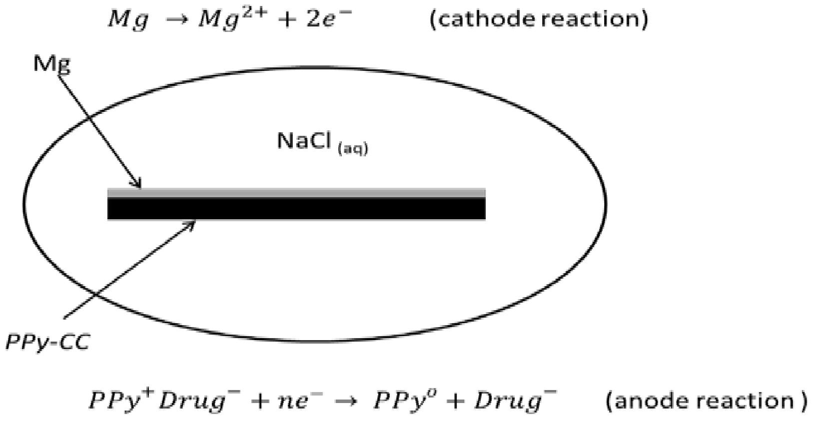
The unique properties of the conducting polymers (CP) which involve the ability of CP to undergo redox reactions by the application of a potential difference make them a suitable reservoir for accommodating and control releasing the active species. The first controlled release system developed in 1982 to deliver a small amount of the neurotransmitter dopamine, which is cathodically cleavable-bonded to the CP using cyclic voltammetry [1]. Since then, many researchers have sought to develop and to improve the use of CP as a controlled delivery and release system for drugs and other molecules. In spite of the interesting specifications that characterise CP for drug delivery systems and the on-going efforts made to develop them, they still suffer from limitations that prevent their extensive use in release systems. The capacity of CP films to store a drug is limited, and the amount of drug being released is very small. In addition, the drug is released from the CP film by applying an electrical potential to reduce it, using an external power source restricts its use in vivo. Recently, a self-powered drug delivery system based on the galvanic cell mechanism has been demonstrated. This system eliminates the need of an external power source and wiring. The CP film cathode is coated with a thin layer of active metal such as magnesium (Mg) which will be the anode as shown in figure 1[2, 3]. Figure 1: Self powered drug delivery system based on galvanic cell.



The galvanic coupling between the Mg layer and the CP film provide the driving force for the drug release. In the presence of electrolytes, the Mg metal electrode oxidises reducing the CP which causes the expulsion of the incorporated molecules. This work considers the chemical and electrochemical incorporation of a model drug and dye on polypyrrole (PPy) films on stainless steel and a cellulose acetate (CC) film. The effect of the use of TiO_2 nanoparticles and coating a thin layer of magnesium on one side of a PPy-CC composite film on the release of the incorporated molecules.

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Platinum Electrode Characterisation and Optimisation for Oxygen Consumption Measurements at Sub-Neuron Compartments

[3]*Martin Arundell,* [1]*Joanne Bailey,* [1]*John Chad,* [2]*Matthew Findlay,* [5]*Nandhini Sivakumar,* [3]Andrew Shevchuk*,* [1]*Vincent O' Connor,* [3]*Peter Smith,*
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The mammalian brain utilises a disproportionately high fraction of the total oxygen (O_2) consumed, ~20% of the O_2 inspired by the resting body. Although oxygen consumption has been measured from single neurons the metabolic differences between distinct neuronal subtypes, Glutamatergic and GABAergic, have not been compared. We therefore aim to investigate if different neuronal subtypes have different metabolic demands. To do this oxygen electrodes have been fabricated using 25 µm platinum wires and thermally sealed in glass capillaries using a laser puller resulting in electrodes ranging from a few hundred nm to µm dimensions. The electrodes have been characterised using outer-sphere one-electron redox couple $Ru(NH_3)_6$ calculated from the equation for the controlled limiting current at a microdisc. We have measured basal oxygen consumption and induced oxygen consumption using a potassium blocker 4-Aminopyridine (4-AP) to drive high frequency action potential activity. Electrode oxygen consumption rates are calculated and compared to known oxygen consumption rates from single neurons. Further work will be toward optimising the electrode fabrication process for better control of the electrode size and RG ratio so improving the reproducibility of the electrodes. In addition sub-micron electrodes, with RG ratios < 5, for good spatial resolution in order to probe different parts of a neuron, will be utilised to directly record synaptic oxygen consumption to investigate if the vulnerability of specific neurons and their synapses are related to their metabolic requirements. Synapses represent the communication points between neurons and as highly specialised structures are able to modify their activity levels for different functions. It is also part of the neuron which has been observed to degenerate early in the progression of neurodegenerative and psychiatric disorders such as Alzheimer's disease.

The Development of Electrochemical Sensors for Blood Ammonia

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Ammonia is found naturally in the body. It is produced from the deamination of amino acids in the liver, muscle and kidneys. It is neurotoxic, penetrating biological membranes such as the blood-brain barrier. It is detoxified by converting it to urea via the urea cycle in the liver and excreted by the kidneys as urine. The potential harm that ammonia can have on health is severe. A number of pathological conditions are associated with increased blood ammonia levels including liver disease, hepatic coma, Reye's syndrome and urea cycle disorders. Conditions like these can affect brain function and are often fatal. Healthy venous levels are approximately 30 µmol / L, an elevated level of 100 µmol / L or above indicates an abnormality in nitrogen homeostasis.[1] Routine blood ammonia measurement can be used to evaluate conditions, manage patient progress and prevent debilitating illnesses developing.

Many methods of ammonia sensing are used in the laboratory such as distillation, micro diffusion, ion exchange chromatography, enzymatic reaction and colorimetric titration. Some have found commercial success,[2, 3] although few are suitable for efficient point-of-care testing due to long reaction times and insufficient linear range.

The conducting polymer polyaniline has been identified as an ammonia-sensitive material.[4] The principle feature of polyaniline as a sensor material lies in its great affinity with ammonia due to a similarity of the coordinative roles of nitrogen atoms.

$$\mathrm{PANIH^+ + NH_3 \quad \leftrightarrow \quad PANI + NH_4^+}$$

The aim of my work is to fabricate a disposable point-of-care electrochemical sensor for blood ammonia. This research employs advanced functional materials to fabricate electrochemical sensors for blood ammonia using a combination of print methodologies such as screen printing and inkjet printing.

The effects of water and buffer were assessed impedimetrically in the presence of ammonia as ammonium chloride. Further method developments are to be carried out to optimise performance and make the sensors free from blood related interferences.

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Amperometric Detection of Hydrogen Peroxide at Prussian Blue Nanoparticle-Modified Electrodes

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Hydrogen peroxide (H_2O_2) is a very simple compound in nature but with great importance in pharmaceutical, clinical, environmental, textile and food manufacturing applications. In living organisms, besides its well-known cytotoxic effects, H_2O_2 also plays an essential role as a signalling molecule in regulating diverse biological processes such as immune cell activation, vascular remodelling, apoptosis, stomatal closure and root growth. Pathophysiological conditions often lead to increased hydrogen peroxide levels produced by inflammatory cell, e.g. neutrophils[1]. H_2O_2 is involved in several biological events and intracellular pathways and is the by-product of oxidases such glucose oxidase (GOx), cholesterol oxidase (ChoOx), *etc.* Conventional techniques for H_2O_2 determination such as titrimetry, fluorescence, chemiluminescence and spectrophotometry are complex, costly and time consuming. In comparison, electrochemistry can offer simple, rapid, sensitive, and cost effective means H_2O_2 is an electroactive molecule.

A large range of materials such as redox proteins, transition metals and redox polymers have been employed to perform electrocatalytic H_2O_2 detection. In recent years, ferric hexacyanoferrate or Prussian blue (PB) has been denoted as an "artificial peroxidase" because the reduced form of PB- Prussian white- is capable of catalyzing the reduction of H_2O_2 at low potentials, similar to peroxidase[2]. Nanomaterials have recently become one of the most exciting forefronts in analytical chemistry because of their desirable chemical, physical and electronic properties that are often enhanced in comparison to bulk materials.

This work explores the fabrication and application of sensors based on nanomaterial formulations of PB for the detection of H_2O_2. A number of PB nanofabrication methodologies and their deposition onto screen printed electrodes are explored. Sensors were characterised using physical and electrochemical methods and their use for the measurement of H_2O_2 optimised.

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An Automated System for the Analysis of Organophosphate Pesticides in Different Sample Matrices Based on a Disposable Acetylcholinesterase 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 environmental and food samples. The instrument incorporates an electrochemical biosensor array based on screen-printing technology allowing mass production at low cost1. The biosensors are comprised of a layer of AChE obtained from Drosophila 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 current2, forming the basis of the measurement. Studies were carried out on this array based on the wild type and mutant forms of AChE. Inhibition studies performed using the biosensor array provided sufficient 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 environmental and food samples; there were no false positive or negative results for the samples investigated. Following development, the components of this system have since become commercially available.

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Detection of Chloride Ion Concentration Based on Chronopotentiometric Sensor-Actuator System

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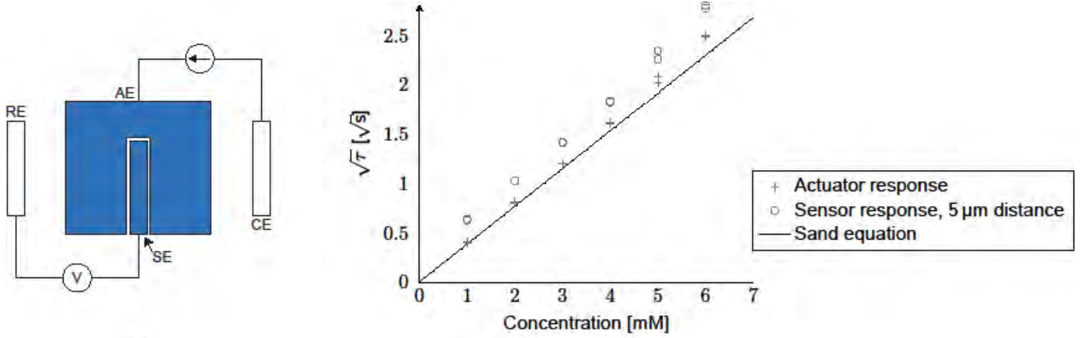
To accurately assess the durability of concrete structures, the detection of chloride ions is highly desirable [1]. Potentiometry is the existing technique for chloride ion detection in concrete [1], but this method is not suitable for long term measurements due to the lack of stability of conventional reference electrodes inside concrete structures.

This work presents sensor-actuator approach to measure Cl^- ion concentration using chronopotentiometry. In this technique, a stable reference electrode is not required [2], a bare Ag/AgCl electrode or a metal wire can be used as a pseudo-reference electrode. An anodic current pulse is applied to a Ag/AgCl actuator electrode (AE), which results in the formation of AgCl at the electrode ($Ag + Cl^- \rightarrow AgCl + e^-$). Due to this reaction, Cl^- ions deplete near the electrode surface which results in a potential change at the electrode [3]. The time at which the concentration of Cl^- ions at the AE becomes zero is called transition time (τ) and is characterized by the maximum of the first derivative (inflection point) of the ΔV response. The transition time can be calculated using the Sand equation [3].

In this system, the potential changes (ΔV), as a result of Cl^- ion depletion at AE, are detected at a separate Ag/AgCl sensor electrode (SE) placed near the AE (see Figure 1a). Measuring the transition time of the sensor electrode gives the Cl^- ions concentration in the electrolyte. The measured potential is not influenced by fouling of the electrode by AgCl and Ag_2O formation as a result of the anodic current pulse. Initial experiments showed a linear increase of the square root of τ at SE as predicted by the Sand equation, but with a constant offset (Figure 1b).



(a) (b)

Figure 1: (a) Schematic representation of the measurement setup with separated sensor and actuator electrodes. RE=reference electrode, CE=counter electrode, SE=sensor electrode and AE=actuator electrode. (b) Calibration curve of the square root of transition time vs. Cl^- ions concentration, theoretical curve from Sand equation (solid line), measured transition time at AE (+) and at SE (o).

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Application of a Printed Electrocatalyst for H2O2 Reduction to the Determination of Cholesterol in Serum Samples

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Many current clinical disorders such as atherosclerosis, hypertension, cerebral thrombosis and coronary artery disease are associated with abnormal levels of cholesterol in blood. Therefore, the development of a reliable and simple method for cholesterol determination is essential in clinical diagnosis.

Electrochemical biosensors have played an important role in this field because they allow the rapid and accurate estimation of cholesterol without the need of sample dilution and they are suitable for mass production at low cost. Cholesterol oxidase (ChOx) is most commonly used as the biosensing element in the fabrication of cholesterol biosensors. Hydrogen peroxide (H_2O_2) is released as the end-product of the enzymatic reaction and its concentration may be used as an indicator in the progress of the reaction.

Recently, our group has reported a significant enhancement in the catalytic activity of silver screen printed electrodes (Ag SPEs) towards H_2O_2 reduction after exposure to a mixed surfactant/salt solution.[1] The electrodes modified with a inkjet printed solution of dodecylbenzenesulphonic acid (DBSA) and KCl exhibited up to 40-fold higher amperometric responses to H_2O_2 at -0.1 V vs. Ag/AgCl, pH 6.8.

In the present work, the H_2O_2 formed via the enzymatic reaction of cholesterol and cholesterol oxidase was measured using DBSA/KCl modified Ag SPEs. Encapsulated electrodes allowed sample volumes as small as 10 µl. A chitosan membrane was then investigated to both diminish matrix interference effect and assist on the enzyme immobilization. The device was then assessed for the quantitative determination of cholesterol in serum.

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A Consideration of the Deswelling of an Inorganic Polymer; a Possible Biochemical Response Meter Indicating the Characteristic Angular Variation for Different Entities

Grayeff, S.G.

The swelling and deswelling reactions of inorganic polymers such as vermiculite are extremely interesting. Sometimes unexpected reactions occur. For example, n-buty lammonium vermiculite may swell to three times the original volume and n-lysine mono hydrochloride may cause medium grade vermiculite to five times the original volume, (this experimental value is in agreement with the work of Ballard et al, for one gram atom of polymer.)The amino acid n-lysine is a straight chain amino acid; thus when it is ion exchanged with aqueous medium grade vermiculite the original amino acid structure appears to be maintained. The thin film formed from the swollen polymer is impervious to water. This physical property may be explained by the formation of hydrogen bonding between two lysine entities. Thus the chirality of the molecule is retained. Further n-lysine mono hydrochloride appears to be yield a singular reaction, namely the formation of a water impermeable film; butyl ammonium chloride can also form such a film.)It was found that in the case of other amino acids, such as histidine, the thin film formed could be hydrated and the geometry was retained in the film but in the presence of an aqueous or combination solution the complete film was not retained. It is possible that chiral asymmetry has occurred.

Theoretical Interpretation of Thin film formation.

Let F= Formation factor of film which is a function of the aqueous entity.

Let E = Energy of formation of film.

Let SR = Swelling ratio of film formation.

Let Ch = chirality factor.

Let Z = number of interactive centres.

Let z =- cyclization factor.

Thus,

$\sum F = (\Pi Z) E^{+/- (SR).Ch}$

Where, the energy of formation of the film is an interaction parameter of the swelling of the inorganic polymer,

For an aqueous double layer where the energy has been shown to be (70.02MeV)

$\sum F = (70.02)^{+/- (SR)(Ch)}$

If $(70.02)^{(SR)} = (70.02)^5$ for SR = (5.0), in the case of two free functional positions.

In this case Ch= (1.0) and (Z) = (1.0).

For a negative swelling reaction $\sum F = (70.02)^{-(SR)(Ch)}$

When SR = - (1.0) ; also $\mathrm{Tan}^{-1} (\alpha) = 1.0$

$\sum F = (70.02)^{-(1.0)(Ch)}$ for an interacting free functional position as in an amino acid such as histidine.

If the energy of the formation of a water insoluble film is a ratio alogorithm of these two factors, then

$\sum F_1 / \sum F_2 = \Pi \Omega = 4.0$

Where (4.0) = κD,

Where D= distance between the inter layers.

Where κ = closest distance of approach of the charged species.

The following can be noted,

If N = number of carbon atoms in the aliphatic chain, then for maximum swelling F = (n-2) = 4.0, where (n= 6.0)

If n= (5.0), F = z (3.0) where z = cyclic factor possibly equal to (-1), and also z may have the following values (-1.0....1.0).

In the case of butyl ammonium chloride, (n= 4.0) and F = (4.0-2.0 where (n= 6.0).

If the inverse swelling ratio, (1/SR), where SR is the swelling ratio, then $(SR)^{-1} = (0.25)$,

$\Omega / (SR)^{-1} = (70.02 \times 4.0) = 4\pi^2 n = (280.08)$.

Further, 2.0 x5.0 n = Ω,

Where n = number of nodes in the swollen entity.

Also 2d =17.5.2 =35.0, where d = 17.5 could be the c axis reflection of the matrix.

Thus $2d.\kappa D/2 = \Omega$,

Where D = distance between the silicate layers.

In this case the theoretical swelling angle of tilt of an included entity = 400.0/280.0 = Tan^{-1} 1.4286 = $(55.0\ )^0$ and (90.0-55.0 = 35.0).

Various angles of response for the plane of the zig-zag hydrocarbon chain have been determined by x ray analysis , such as $(50.0 \dashrightarrow 51.34)^0$ for 6-aminohexanoic acid vermiculite.

Further, (5.0/12.0 = 0.4167) = Tan^{-1} (0.4167) = (22.62^0).Indeed an angle of $(25.0)^0$ is predicted for an amino acid vermiculite from IR results.

Development of a Screen-Printed Glutamate Biosensor, Fabricated using Modified Screen Printed Carbon Electrodes, for Cell Metabolism Studies.

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The purpose of the present investigation was to develop a glutamate biosensor for application in cell toxicity studies. A screen printed carbon ink electrode was modified by the addition of either Meldola's Blue (MB) [1] or Meldola's Blue Reinecke Salt (MBRS) [2] to act as electro catalysts for NADH oxidation. The resulting screen-printed electrodes act as the base transducer for biosensor construction.

Voltammetric studies were performed with these devices in the presence and absence of NADH to characterise their redox behaviour under various solution conditions. The results indicated that a suitable oxidation peak could be obtained for NADH which was a pre-requisite for the operation of the proposed biosensor. In order to fabricate a glutamate biosensor, this transducer was coated with glutamate dehydrogenase.

Studies are underway to optimise the conditions for operation in culture medium.

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Recovery of Cu and Ni from Dilute Solutions using Bioelectrochemical Systems

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The demand for mineral and energy resources is increasing rapidly due to the growing world population and rising economies. Industrial, municipal and agricultural wastewater is potential sources of metals and chemical salts, acids and bases, and energy from oxidising organic matter in wastewater. Their recovery is however hampered significantly because of their low concentrations in a highly complex mixture. Conventional methods, e.g metal recovery technology from wastewater using chemical precipitation, filtration and solvent extraction, have low efficacy, high start-up or operating costs, and low metal selectivity.

In bioelectrochemical systems (BES), living microorganisms convert the chemical energy from organic waste into electricity or hydrogen or other chemical products in Microbial fuel cells (MFC), or microbial electrolysis cells (MECs) (Fig. 1).

In the present work, BES has been investigated for metal recovery, copper and nickel in particular. It is demonstrated that by connecting to a bioanode, copper was recovered from the mixed solution without an electrical energy input by reduction on a graphite cathode, and nickel was sequentially recovered by controlling the cathode potential to be -0.6 V (vs. Ag/AgCl). The MEC for Nickel recovery powered by a single MFC is also investigated. This emerging technology can provide the solution to combine waste treatment and resource recovery with positive impacts on the environment and society.

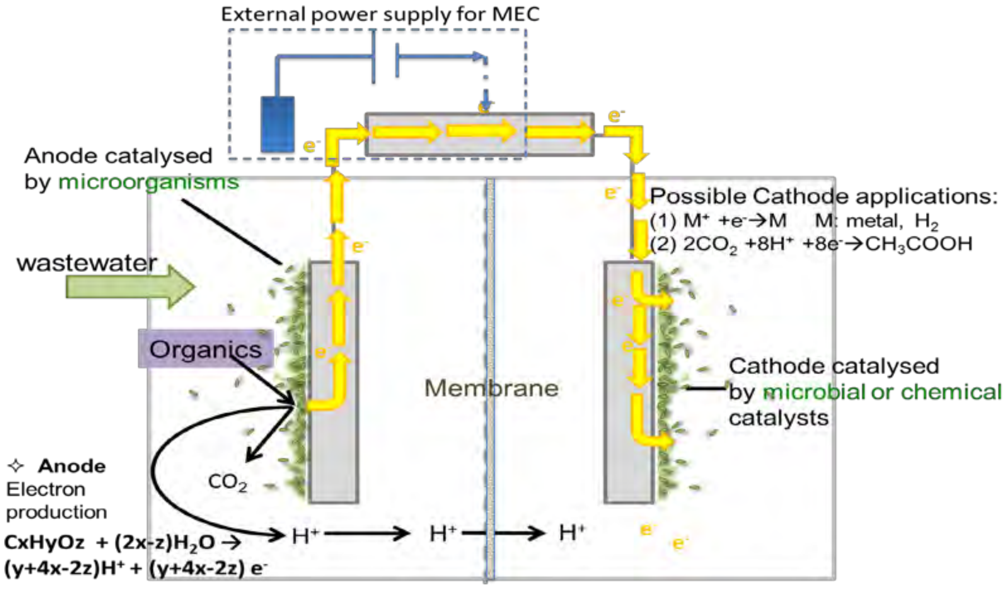

Fig 1. Schematic demonstration of a bioelectrochemical system.

Principles of Electrochemical Nondestructive Alloy Analisys on the Base of Intercalation Processes

Semen M. Lipkin, Andrey V. Sedov, Mikhail S. Lipkin, Svetlana A. Pozhidaeva, Dmitri A. Onyshko*

An analisys of alloy directly on surface example is interest- ing for many applications. Electrochemical methods, used in solving this problem, provide variability, low cost, minimal ex- ample treatment and informational content of analytic signal. All the advantages of electrochemical nondestructive alloy analisys can be realized by using appropriate electrode processes. We assume that intercalation is one these processes due to its high sensitivity to host structure composition. It was shown, that pulse chronopotentiometry is the most appropriate method for different intercalation processes.

Use of intercalation process type is determined mainly by nature of analyzed component. So, for metals with high overpotential it is convenient to use anodic intercalation in alkaline electrolytes (fig.1) or reduction of anodic oxide (fig 2).

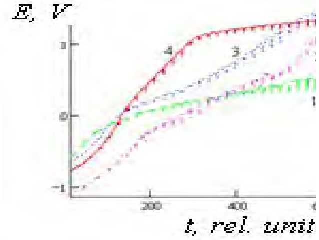

Fig.1 Anodic pulse chronopotentiograms in 5M KOH, 0,01M phenol: 1 – Mo; 2 – Mo16Ni; 3 – Fe; 4 – Ni

For metals with low overpotential (Au, Cu, Ag, Pt) inter- calation of water and anions in anodic part of polarization give easy reductive adsorbed complex ions and their inverse reduc- tion is displayed as a horizontal part on chronopotentiometry curve (Fig. 3). A length of such part is proportional to alloy com- ponent content, which provides analysis possibility.

Cathodic intercalation of lithium ions from acetonitrile electrolyte makes a basis of carbon determination in steels. Pulse chronopotentiograms of this process (fig. 4) have plato, which length change is proportional to carbon content

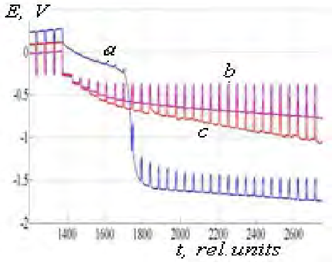

Fig. 2 Inverse pulse chronopotentiogramms of Ni in 8M NaOH(*a*); 1M H_2SO_4(*b*); 1MNa_2SO_4(*c*)

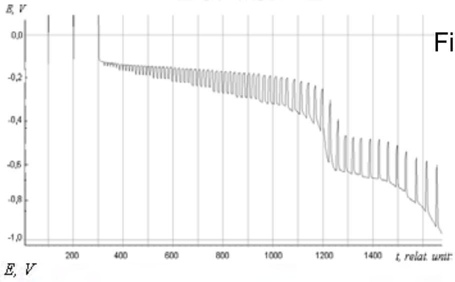

Fig. 3 Inverse pulse chronopotentiogramms of Pb16Cu in 1M Na_2SO_4

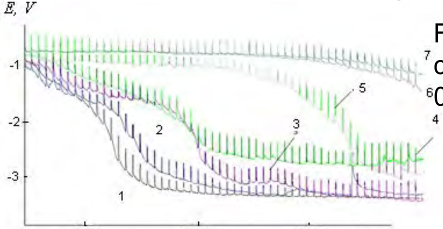

Fig. 4 Cathodic pulse chronopotentiogramms of carbonaceous steel with carbon content (%): 1 – 0,119; 2 – 0,205; 3 – 0,32; 4 – 0,43; 5 – 0,62; 6 – 0, 96; 7 – 1,0

Thus, electrochemical nondestructive alloy analisys on the base of intercalation processes is perspective adaptive method with a much of various tunning-up parameters.

A Novel Approach to Chronopotentiometry Data Treatment

Semen M. Lipkin, Andrey V. Sedov, Yuri Y. Gerasimenko and Dmitri A. Onyshko*

Significant number of electrochemical and contiguous problems are studied and solved via chronopotentiometry. So in [1] it was used to define the solution composition. Expanding this application chronopotentiogram can serve as a source of information about metal alloy composition if small part of alloy sample is passed into solution in three-electrode cell. According to this method alloy sample is attached to the cell as a working electrode and is oxidized by series of pulses of current. Parameters of these pulses are selected so that contents of elements in solution would be the same as in an alloy.

This solution is later reduced by series of pulses of opposite polarity current. Thus, obtained chronopotentiogram $E_j = [e_{j1}, ,e_{jn}]^T$ (fig. 1) consists of two stages: oxidation and reduction and its form depends on alloy composition.

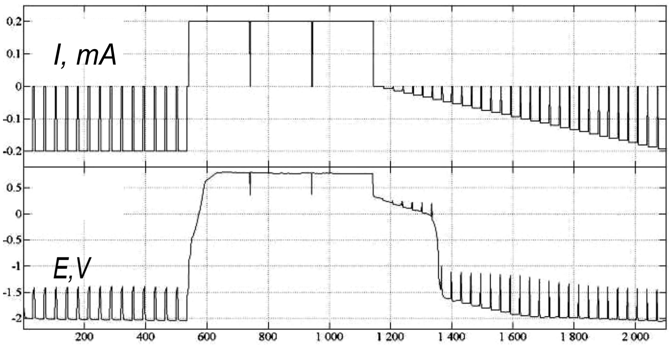

Fig. 1 Pulses of current and corresponding chronopotentiogram

However, as seen on fig. 1, obtained chronopotentiogram has a complex shape which doesn't allow defining alloy composition directly by potential values of E_j. Therefore chronopotentiometry data treatment comes down to extracting required information from potential values vector E_j. This extraction is often based on mathematical model of used electrochemical process with models like Poisson-Nernst-Planck system [2] and convolutions [3] being used. Proposed approach to chronopotentiometry data treatment is similar to convolutive modeling, except for weight functions V are defined not theoretically from analysis of used process but adaptively as eigenvectors of covariance matrix K of training set of chronopotentiograms $KV=V\Lambda$, where Λ - diagonal matrix of eigenvalues λ_l of matrix K . Extraction is made via the following conversion: $Y_j = V^T E_j$. And source chronopotentiogram can be recovered from Y via the following:

$$E_j = \sum_{i=1}^{m} y_{ji} \cdot V_i + Q_j$$

, where Q_j is constant bias vector.

As a result of application of this approach to chronopotentiograms of molybdenum alloys obtained potential values vectors $E_j = [e_{j,1}, ,e_{j,728}]^T$ were converted into vectors $Y_j = [y_{j,1}, ...y_{j,4}]^T$, i.e. chronopotentiograms dimension was 242 times reduced. In addition, this approach allows unification of chronopotentionmetry data treatment independently from analysed alloy composition.

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Synthesis of Au:Cu Core:Shell Nanowires and their Application in DNA Detection

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School of Chemical Sciences, Dublin City
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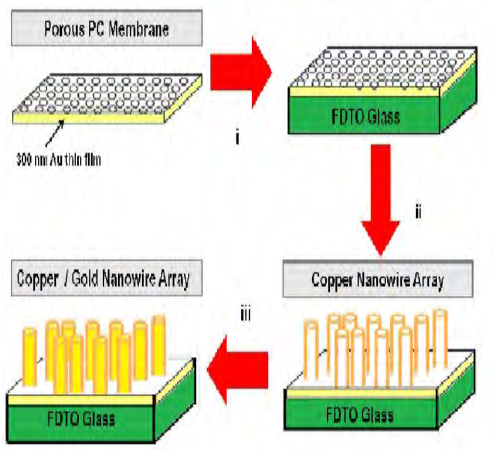
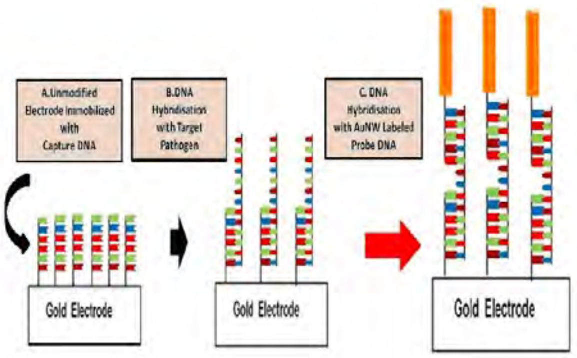
Hollow copper (Cu) nanotubes were successfully fabricated by electrodeposition within the pores of polycarbonate membrane filters (PC), 22 µm thick, by using template synthesis method. To fabricate the working electrode, a thin layer of Au (~300 nm thick) was coated on the reverse side of template to create electrical contact. It was found that the individual cylindrical copper nanotubes are hollow and continuous, with uniform diameters (70 ± 20 nm) along the entire lengths of the wires (3 ± 0.5 µm) and can be electrochemically filled with gold creating solid gold:copper core:shell nanowires.

Subsequently, the nano wires were selectively functionalized with single stranded probe DNA (5' thiolated) by immersing the nano wire functionalised membrane in a 1 µM solution of the probe DNA strand for 6 hours. The membranes were then dissolved in dichloromethane and the solid gold:copper core:shell nanowire/probe DNA was released into solution.

A second electrode was functionalized with a monolayer of single stranded capture DNA (10 µM) that has a sequence that is complementary to the pathogen, Staphylococcus aureus but leaves a section of the target available to bind the probe strand immobilized on the solid gold:copper core:shell nanowire. Following hybridization of the target and capture strands, the surface was exposed to the probe DNA labelled gold:copper core:shell nanowire.

Target binding was detected by monitoring the charge associated with the oxidation of copper via cyclic voltammetry before and after desorption of the copper. The magnitude of the charge is proportional to the amount of copper present, which in turn is proportional to the concentration of target DNA. The good biocompatibility of nanometer sized metals and the vast surface area of the nano wire structure make it ideal for adsorption of DNA for the fabrication of a biosensor. The detection of DNA was performed in 0.1 M H_2SO_4 and cycled at potentials from -0.2 − 0.6 V. The resulting biosensor exhibited sensitive response (7.46 μC^{-1}), with short response time of 3 minutes, linear range of 100 µM – 1 nM, and lower detection limit of 1 nM.





Strain Discrimination in Yersinia Pestis and Bacillus Anthracis Bacteria by using SERS Monitoring and Electrochemical Melting

Evanthia Papadopoulou[a], Sarah A. Goodchild[b], Nittaya Gale[a], David W. Cleary[b], Simon Weller[b], Tom Brown[a] and Philip N. Bartlett[a]*
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Yersinia pestis and *Bacillus anthracis* are pathogenic bacteria that can cause plague and anthrax respectively and could be used in bioterrorism. The development of low cost, rapid and sensitive methods for strain discrimination between pathogenic bacteria is therefore imperative. However, strain discrimination in *Y. Pestis* and *B. Anthracis* can be difficult due to genetic homogeneity.

We have recently developed a surface-enhanced Raman spectroscopy (SERS)-based platform for detecting and discriminating mutations and short tandem repeats in DNA sequences utilizing sphere segment void (SSV) surfaces.[1] In a typical DNA discrimination assay using SERS on an SSV surface, a modified DNA probe strand is first attached to the gold surface via a series of three di-thiol linkers. The surface is passivated by treatment with mercaptohexanol to prevent the non-specific adsorption. The probe strand is then hybridized with target DNA that is labelled with a Raman active dye. By applying an external driving force, the bound dsDNA is denatured and the SERS signal is lost. Plotting SERS intensity against potential yields SERS melting profiles that are dependent on dsDNA stability, we have successfully discriminated single nucleotide polymorphism (SNP) and short tandem repeats within unpurified long PCR products from *Y. pestis*. Assays on *Bacillus anthracis* are underway. In order to improve discrimination, different experimental parameters have been explored such as temperature and ionic strength. The technique used has many advantages over conventional methods due to speed of analysis and ability to be used in portable technologies including Raman-based systems.

Reference
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An Electrochemical Microbiosensor for Galactose for Monitoring Cell Metabolism Changes

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University of the West of England, Bristol,
Coldharbour Lane, Bristol, BS16, UK

An electrochemical biosensor for galactose was developed using a water-based screen-printing carbon ink formulation containing the redox mediator cobalt phthalocyanine (CoPC). The ink was screen-printed and then coated with a perm-selective cellulose acetate membrane which would permit hydrogen peroxide to gain access to the electrode whilst excluding interferences. The enzyme galactose oxidase, which produces H_2O_2 from galactose in the presence of oxygen, was deposited onto the cellulose acetate surface.

The resulting macroelectrode working area was converted into microband format by masking off a thin strip with Valox card, then applying commercial paint to act as a dielectric. Upon removal of the mask a narrow biosensor working electrode of microband dimensions was revealed.

Galactose microbiosensors fabricated in this way were tested as amperometric devices in buffer and in culture medium, pH 7.2, with added galactose. The analytical signal was obtained from the electrocatalytic oxidation of H_2O_2 via CoPC at an applied potential of +0.5V versus a Ag/AgCl reference electrode in a 3-electrode system. Steady-state current responses were obtained in quiescent solutions, and were monitored over a 4hr incubation period. The responses showed linearity up to 10 mM galactose. The microbiosensors were used to interrogate culture media at 37^{o}C, following a 24h incubation period in the presence or absence of HepG2 hepatocytes. The results demonstrated that the cells completely metabolised galactose over a 24h period from a starting concentration of 10 mM in a 15 ml volume.

The microbiosensors were then used to investigate the effect on cellular galactose metabolism, of the liver toxin paracetamol, at drug concentrations over the range 5 – 1000 micromolar. The results demonstrated that paracetamol inhibited galactose metabolism in a concentration-dependent manner. These microbiosensors have the potential for application in continuous monitoring of galactose in cell culture, and the effects of toxic drugs on its metabolism by mammalian cells.

Solid-state Nanopores as a Tool for Probing Protein-Protein Interactions

William H. Pitchford, Robin Leatherbarrow, Joshua Edel and Tim Albrecht*
Department of Chemistry, Imperial College London, UK

Inspired by the Coulter counter and the role transmembrane pores play in molecular transport within nature, since the mid 1990's there has been a tremendous amount of research into the use of nanopores as sensors.

The principle of detection behind this powerful technique is remarkably simple. A nanopore within an electrically insulating membrane connects two sides of an electrolyte. Upon immersion of non-polarisable electrodes either side of the membrane and application of a transmembrane potential, a steady-state ionic current is established through the nanopore. As a result of the potential gradient, charged analytes may be driven across the pore. The presence of an analyte within the pore usually lowers the flux of ions and therefore pore conductance resulting in a resistive pulse. It is these transient current blockages that provide single-molecule detection, where duration and amplitude relate to the size, shape and charge of the analyte. A wide range of human diseases, including Azheimer's and Parkinson's Disease, are associated with the formation of intracellular or extracellular fibrillar protein aggregates from a specific peptide or protein. The goal of this project is to develop a solid-state nanopore capable of studying fibril formation in such diseases. Interestingly, recent studies have indicated that oligomeric species formed prior to fibrils may be responsible for disease pathology. For instance, within Alzheimer's Disease it is the dimers of amyloid beta protein (the main component of the amyloid plaques which are a hallmark of the disease) which are the chief neurotoxic agent. [1] Nanopore-based sensing is an ideal tool for identifying and characterising the oligomeric species present during fibril formation.

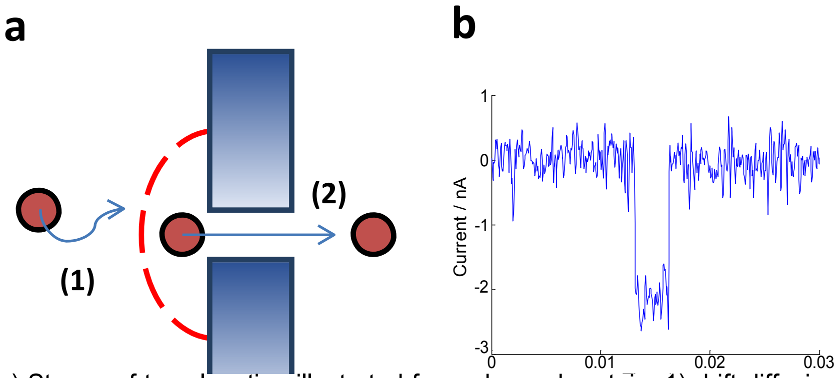

Figure 1. a) Stages of translocation illustrated for a charged protein; 1) drift diffusion 2) capture & translocation. b) Typical transient current blockage associated with a protein translocation event.

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Construction of a New Versatile Point-of-Care Testing Device with Electrochemical Detection in Paper Platform

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Departments of Analytical Chemistry, and INCT-Bio, Institute of Chemistry – UNICAMP, P.O. Box 6154, 13084-971, Campinas, SP, Brazil

In recent years, the paper has been used as microfluidic platform in analytical devices due to your analyte separation ability from complex samples (blood, for example), besides to present low cost, flexibility, high surface area, and more.[1] These devices, also called microfluidic paper-based analytical devices (*μ-PADs*), has been used for environmental monitoring and health diagnostics using many types of detection system, as colorimetric, fluorescence, electrochemical, and others.[2] Among the detection methods mentioned above, the electrochemical detection is the most promising because your high sensitivity and high selectivity (by the choice of applied potential and/or electrode material). However, the most of *Eμ-PADs* present hydrophobic walls, generally obtained by wax printing, and has some materials imprinted on paper platform (generally, high or noble metals) to obtain the electrodes system.[3] These modifications can difficult the recycling of the device and, many times, the noble metals used as electrodes (gold, silver and others), increase the cost of device and are discarded in the nature. In the present work we demonstrated the construction of a new point-of-care device that allows the use of paper without modifications, contributing for the green chemistry. The new device was constructed in an acrylic base with all electrodes included and putted only in contact with the paper platform (not printed) to make the analysis (Figure 1a). In this device the working electrode (WE) is mobile and can be removed and changed always be necessary for different applications, moreover, with the same device is possible the use of any kinds of paper as microfluidic platform. To demonstrate the application of the electrochemical device, Paracetamol (PA) and 4-Aminophenol (4-AP) were used as analyte and yours electrochemical detection was observed by chronoamperometry (using acetate buffer, pH 4.5, as eluent). A cationic exchange paper (Whatman P81) was used as platform for the separation and detection of PA and 4-AP simultaneously, as can be observed in Figure 1b. The separation of the analytes in this pH was possible just with the cationic paper, due to the PA is a neutral molecule and the 4-AP is a cationic molecule. These results show that this new device is versatile by the use of different kinds of paper as platform and different working electrodes, and these characteristics show that this device is very promising for the application in point-of-care monitoring and health diagnostics.

Acknowledgements: CAPES, CNPq, FAPESP, INCTBio and CsF.

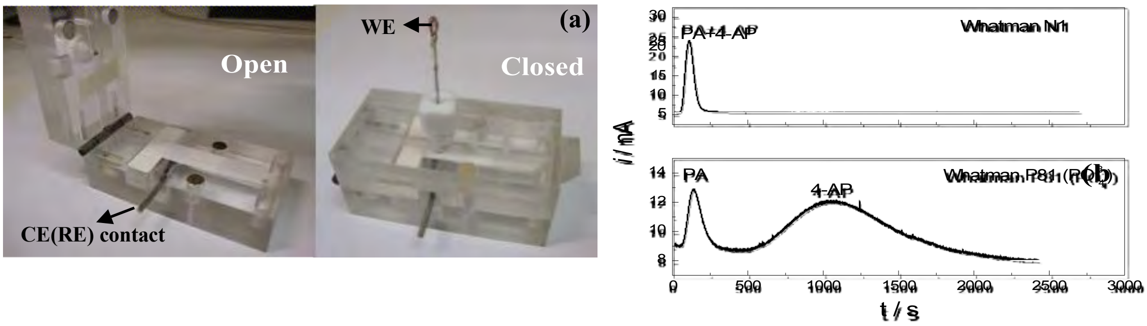

Figure 1. (a) The new point-of-care device and (b) separation and detection of PA and 4-AP.

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Electrochemical Impedance Spectroscopy can Detect the Clinically Relevant Pathogen P.aeruginosa in Artificial Sputum

Andrew C Ward[1], Nicholas P Tucker[2] and Patricia Connolly[1]*
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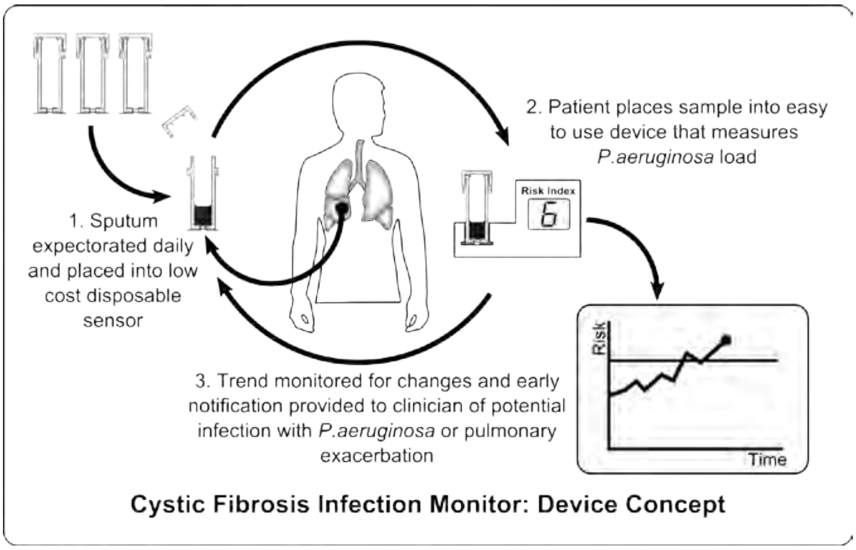
The bacteria *Pseudomonas aeruginosa* is widely regarded as the leading cause of morbidity and mortality in patients with the inherited condition, Cystic Fibrosis (CF). In the CF lung, these bacteria rapidly adapt and form so-called biofilms that are impossible to irradiate, leading to a permanent, chronic infection. Early detection of *P.aeruginosa* could help to improve patient prognosis by allowing interventions to help remove the bacteria to be started earlier, before the infection becomes established. Electrochemical Impedance Spectroscopy (EIS) is used in this study to show that it is possible to detect the presence of *P.aeruginosa* using a screen printed carbon electrode. Cultures of *P.aeruginosa* were grown in an artificial sputum media for three days, under conditions similar to those found in the CF lung, with a custom made chamber containing an in-situ electrode. Applying full impedance analysis of impedance modulus , phase angle and impedance normalisation revealed impedance signatures attributable to the *P.aeruginosa* that were not present in control samples, indicating that the system may have some potential as a diagnostic for infection. However as the patient microbiome will contain multiple species of bacteria then measurements in more complex environments are required. As an initial investigation a polymicrobial culture containing both *S.aureus* and *P.aeruginosa* was subjected to identical analysis. An *S.aureus* control did not induce a significant change in the impedance, whereas the polymicrobial culture resulted in a detectable change in impedance signatures with time attributable to the growth and domination of the culture by *P.aeruginosa*. The results from this study are encouraging and demonstrate how EIS could be used to detect a clinically important pathogen in a sample of media representative of that from a CF patient. Devices based upon this technique, if successful in detecting bacteria in real patient samples, could be deployed at low cost in a number of heathcare scenarios, including home use diagnostic devices.



A Flow Electrolysis Cell with a Thin Aqueous Phase and a Thin Organic Phase for the Absolute Determination of Trace Ionic Species

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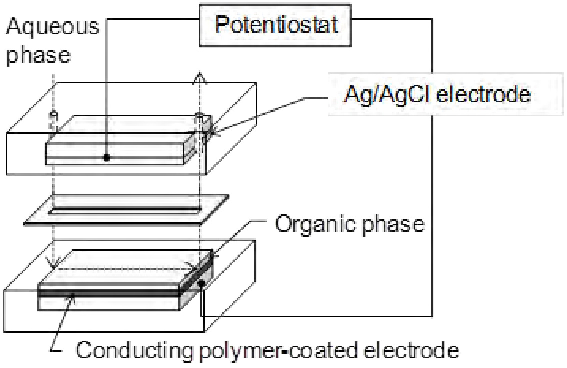
A novel thin-layer electrolysis flow cell based on ion transfer at the liquid | liquid interface was proposed for the absolute determination of a sub-nanomole ionic species. By using the conducting polymer-coated electrode as an electrode in organic phase, the flow cell was developed as a laminate structure incorporating a thin aqueous layer and a thin organic layer, which were set between an Ag/AgCl electrode and the conducting polymer-coated electrode. Its simple structure made it possible to miniaturize the flow cell, and to reduce the required sample volume to only 1 μl. In the present electrolysis cell, both quantitative extraction and quantitative back-extraction of total amount of the ionic species were achieved. This advantage was applied to two absolute determinations. One is that by flow injection method, and the other is that by pre-concentration into the thin Org and back-extraction of the species from the thin Org to the thin W (i.e., the stripping technique). In these methods, coulometrical determination of sub-nanomol ionic species was realized without a calibration curve.



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Maximum measurable current	±80 mA
Rise time	20 µs
Applied Potential Resolution:	1 mV
Measured Current Resolution	0.025 % of current range (1 pA on lowest current range)
Potential Accuracy	±0.2 %
Current Accuracy	≤0.5 % (current range dependent)
External inputs/outputs	- 5 Digital Input/Output pins [PIO 1, PIO 2, PIO 3, PIO 4, PIO 5] - 3 Analog Inputs multiplexing PIO 1, PIO 2, PIO 3 - 2 Analog Outputs (configurable I-out or E-out)
Indicators	LCD display in front panel
Dimensions	22.2 cm x 20.5 cm x 7.5 cm (L x W x H)
Weight	1.6 kg

Control Specifications			
General Pretreatment	Conditioning stage duration:	0 – 1300 s	
	Deposition stage duration:	0 – 1300 s	
	Equilibration stage duration:	0 – 1300 s	
General Parameters	Begin, End, Base, Vertex potentials:	-4.096 V to +4.096 V	
	Step potential:	1 mV to 500 mV	
	Pulse potential:	1 mV to 250 mV	
	Scan rate:	1 ms up to 1.3 s per step	
Specific Parameters	SWV	Frequency:	1 Hz to 400 Hz
		Amplitude:	1 mV to 250 mV
	DPV, NPV, NDP	Modulation time:	1 ms to 1300 ms
		Pulse time:	1 ms to 1300 ms
	ACV	Frequency:	2 Hz to 250 Hz
		Amplitude:	5 mV to 250 mV (RMS)
	Chrono. Methods (AD, ZRA)	Interval time:	0.1 s to 1300 s
		Run time:	Hours (65000 points)
	Fast Chrono. Methods (FA)	Interval time:	1 ms to 1300 ms
		Run time:	Hours (65000 points)
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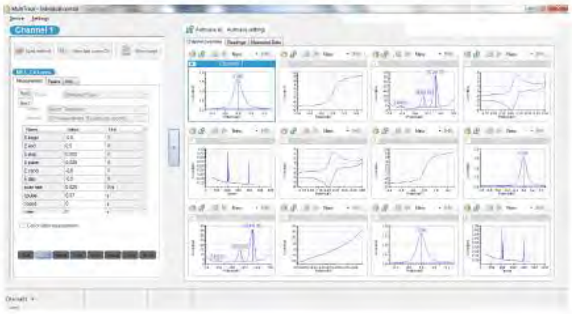

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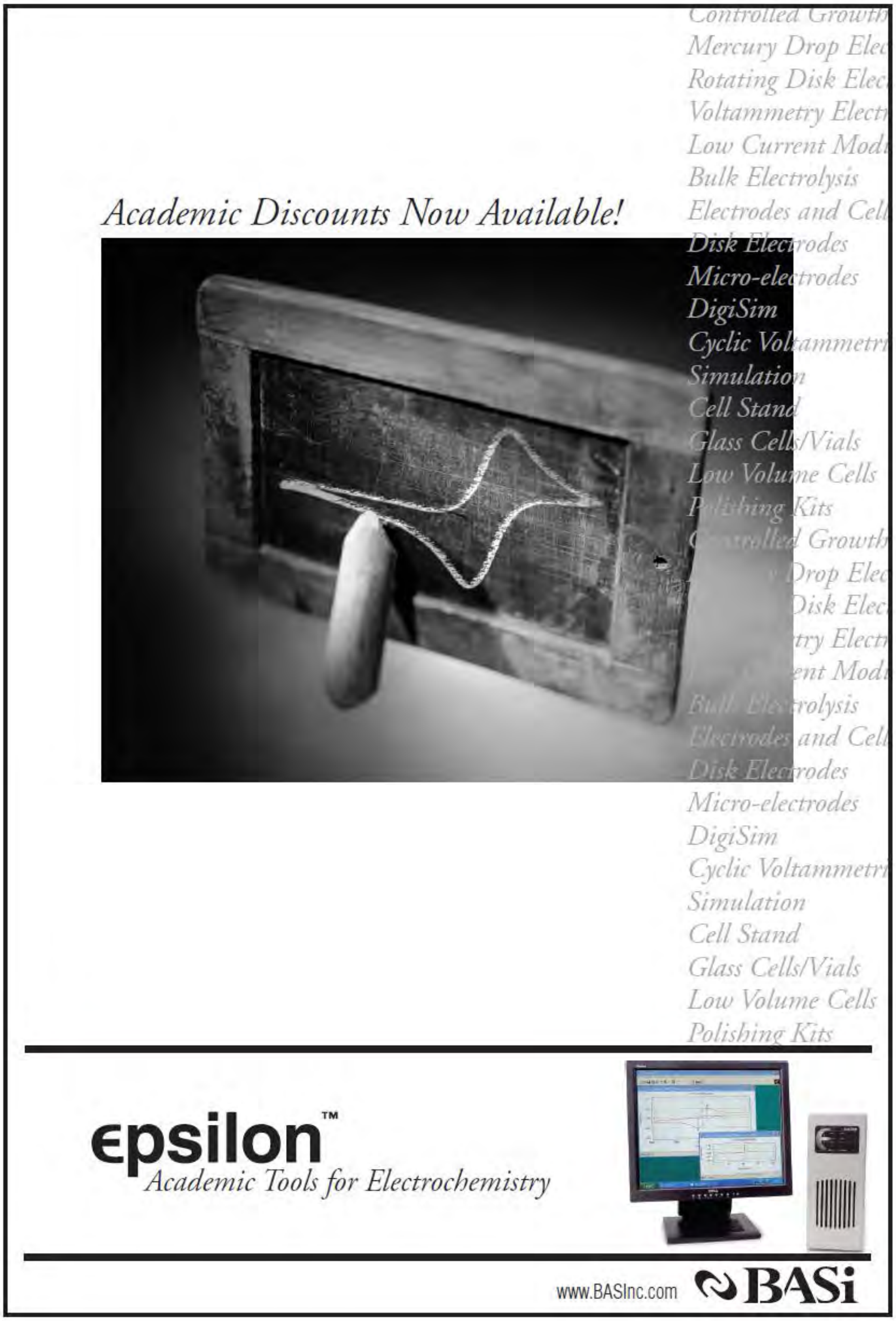

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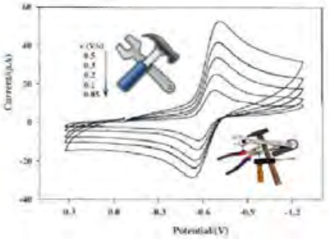
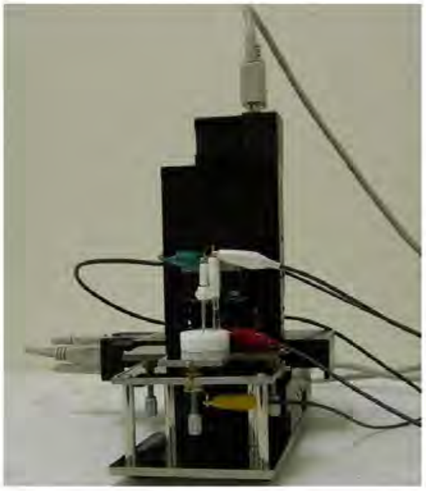

Current(μA)
60
40
20
0
-20
-40
v (V/s)
0.5
0.3
0.2
0.1
0.05
0.3
0.0
-0.3
-0.6
-0.9
-1.2
Potential(V)



General Adverts

Thin-film microelectrodes

Flow cell