

Electrochem 2017

BIRMINGHAM



Welcome from the LOC

Welcome to Electrochem 17 at the University of Birmingham!

We are delighted to welcome you to our University and our city. Birmingham is known for many things: its canals, the Birmingham Royal Ballet, the Birmingham Philharmonic Orchestra, the balti, Cadbury's chocolate, Staffordshire hoard, Jewellery Quarter and the Bull Ring, to name a few. Within the University we also have the Lapworth Museum of Geology, the Barber Institute of Fine Arts, the recently opened Bramall Music Building and the Winterbourne Botanic Garden. Matthew Boulton and James Watt lived and worked here and Soho House, the home of Matthew Boulton and sometimes meeting place of the Lunar Society, is now a museum open for visitors. Whilst the industrial heritage of our region is widely recognised, what is perhaps less well-known is a strong local tradition in the metal finishing industry. There are many small plating shops around the city and wider region, as well as one or two larger companies developing products for metal finishing. One of us has fond memories of an interesting summer student work placement in a local company over some years, helping to make corrosion inhibitors for paints, electroplating customers' samples and helping to test additives for anodising baths.

We also have a strong academic tradition in electrochemistry. John Randles carried out his work in the School of Chemistry here, making varied and important contributions to our field of work, both in the development of theory and in careful, rigorous experimental Physical Chemistry. 70 years ago this year, he published work on the cathode ray polarograph, which soon led to his equation for the peak current, the Randles-Sevcik equation. In this year he also published his analysis of the impedance of an equivalent circuit to represent an electrochemical cell, the Randles Equivalent Circuit. A little later came his work on the liquid|liquid interface. We hope that he would be happy that we are meeting here this year to share our work and our interest in Electrochemistry.

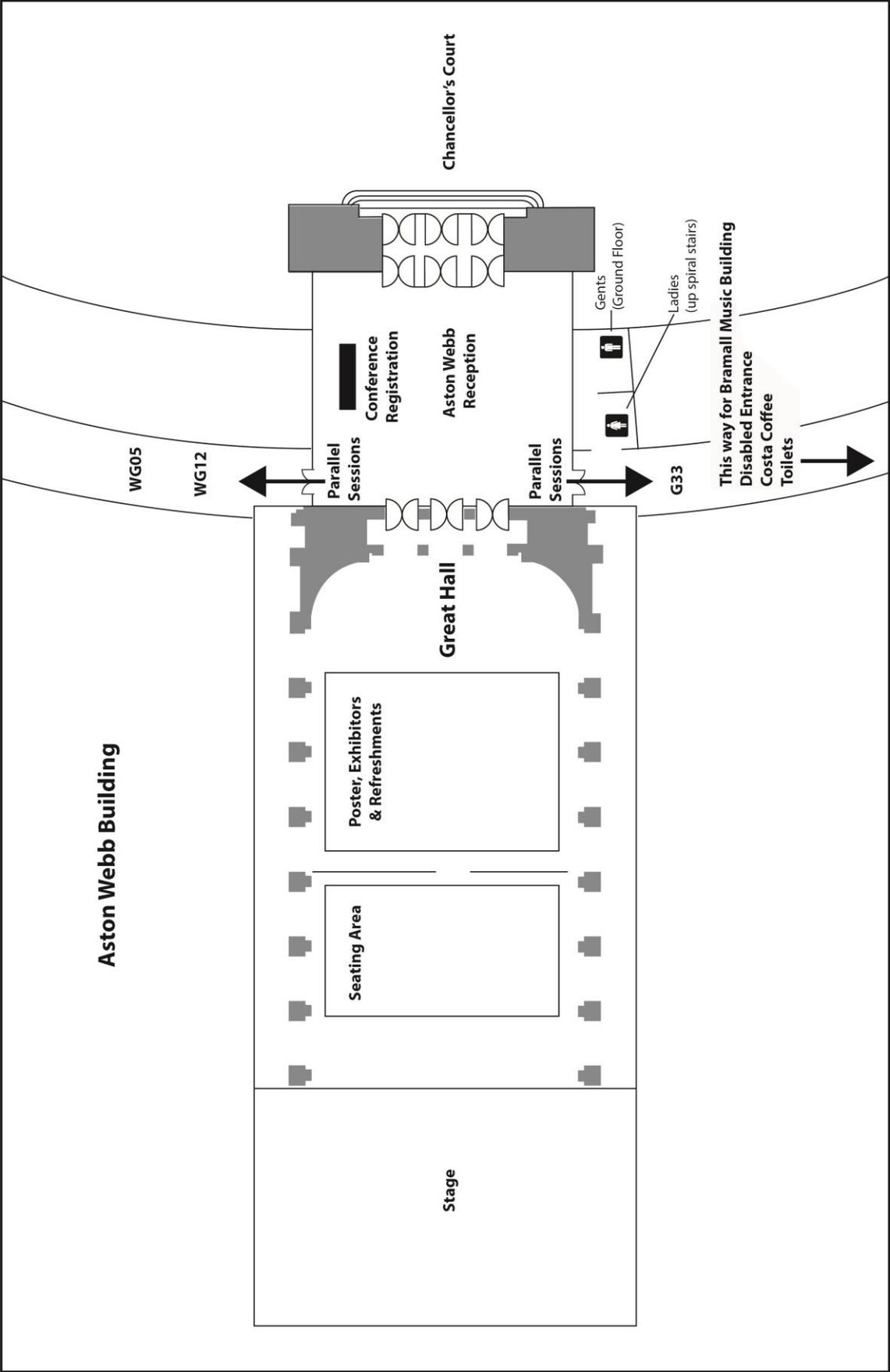
We very much hope you enjoy the conference and would like to thank you all for coming and for participating. We would also like to thank Elizabeth Harrison, David Oram and George Merriman, the University's Medical School Events Team, for their hard work in organising this meeting.

Dr Neil Rees, Dr Sarah Horswell, Dr Paramaconi Rodriguez, Professor Alison Davenport
University of Birmingham

Contents

Floor Plan and Campus Map	4-5
Delegate Information	6
Poster Prizes	7
Sponsors	8
Programme	10-15
Poster Abstracts at a glance	12
Oral Abstracts at a glance	13-15
Invited Speaker Abstracts	17-19
Faraday Medal: Marc Koper	17
Evans/Medal Sword: Hugh Isaccs presented by Mary Ryan	18
Fleischmann Lecture: Stephen Fletcher	19
Energy & Environmental Oral Abstracts	21-53
Keynote: Nuria Garcia-Araez	26
Keynote: Kylie Vincent	44
Sensors and Analytical Oral Abstracts	55-69
Keynote: Darren Walsh	61
Keynote: Tim Albrecht	66
Physical & Fundamental Oral Abstracts	71-84
Keynote: Gary Attard	76
Keynote: Katherine Holt	83
Corrosion Oral Abstracts	86-106
Energy & Environmental Poster Abstracts	108-120
Sensors and Analytical Poster Abstracts	122-129
Physical & Fundamental Poster Abstracts	131-139
Corrosion Poster Abstracts	141-142

Floor Plan & Campus Map



Edgbaston Campus Map

Index to buildings by zone

Red Zone

- R1 Law Building
- R2 Frankland Building
- R3 Hills Building
- R4 Aston Webb – Lapworth Museum (Reopening 2016)
- R5 Aston Webb – B Block
- R6 Aston Webb – Great Hall
- R7 Aston Webb – Student Hub (Opening September 2015)
- R8 Physics West
- R9 Nuffield
- R10 Physics East
- R11 Medical Physics
- R12 Bramall Music Building
- R13 Poynting Building
- R14 Barber Institute of Fine Arts
- R15 Watson Building
- R16 Arts Building
- R17 Ashley Building
- R18 Strathcona Building
- R19 Education Building
- R20 J.G. Smith Building
- R21 Muirhead Tower
- R22 Main Library
- R23 University Centre
- R24 Staff House
- R25 Munrow Sports Centre
- R26 Geography
- R27 Biosciences Building
- R28 Murray Learning Centre
- R29 Postgraduate Centre (under construction)
- R30 New Library (under construction)

Orange Zone

- O1 The Guild of Students
- O2 St Francis Hall
- O3 University House
- O4 Ash House
- O5 Beech House
- O6 Cedar House
- O7 New Sports Development (under construction)

Green Zone

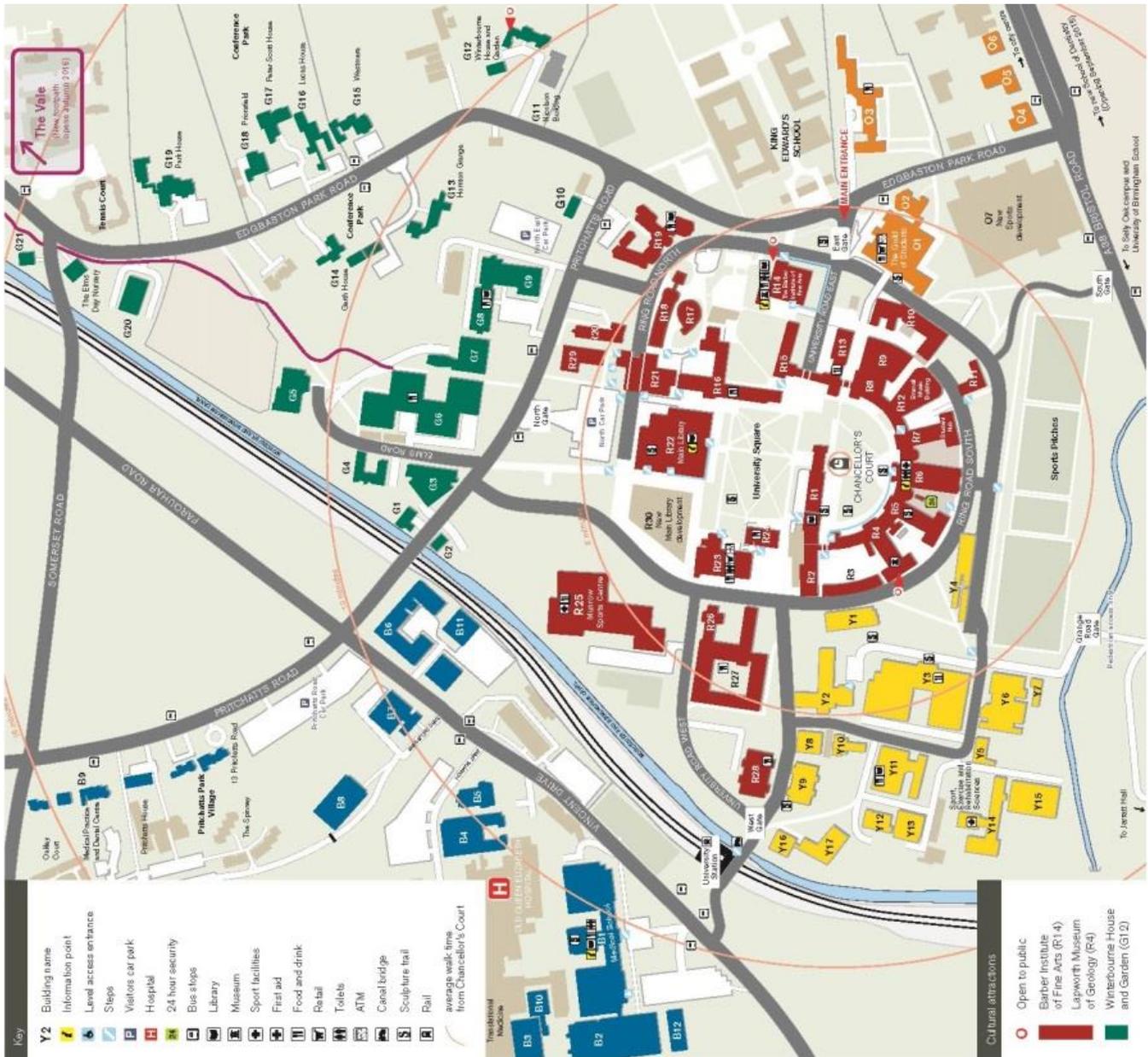
- G1 32 Pritchatts Road
- G2 31 Pritchatts Road
- G3 European Research Institute
- G4 3 Elms Road
- G5 Computer Centre
- G6 Metallurgy and Materials
- G7 IRC Net Shape Laboratory
- G8 Gasber Kapp Building
- G9 52 Pritchatts Road
- G10 54 Pritchatts Road
- G11 Nicolson Building
- G12 Winterbourne House and Garden
- G15 Westmere
- G18 Priorsfield
- G19 Park House
- G20 Elms Plant
- G22 Elms Day Nursery
- G23 Elms Conference Park
- G13 Hornton Grange
- G14 Garth House
- G16 Lucas House
- G17 Peter Scott House

Yellow Zone

- Y1 Old Gymnasium
- Y2 Haworth Building
- Y3 Mechanical and Civil Engineering Building
- Y4 Terrace Huts
- Y5 Estates West
- Y6 Maintenance Building
- Y7 Grounds and Gardens
- Y8 Chemistry West
- Y9 Computer Science
- Y10 Alta Bioscience
- Y11 Chemical Engineering
- Y12 Biochemical Engineering
- Y13 Chemical Engineering Workshop
- Y14 Sport, Exercise and Rehabilitation Sciences
- Y15 Civil Engineering Laboratories
- Y16 Occupational Health
- Y17 Public Health

Blue Zone

- B1 Medical School
- B2 Institute of Biomedical Research including IBR West
- B3 Wellcome Clinical Research Facility
- B4 Robert Aitken Institute for Clinical Research
- B5 CRUK Institute for Cancer Studies and Denis Howell Building
- B6 Research Park
- B7 90 Vincent Drive
- B8 Henry Wellcome Building for Biomolecular NMR Spectroscopy
- B9 Medical Practice and Dental Centre
- B10 Advanced Therapies Facility
- B11 BioHub Birmingham
- B12 Health Sciences Research Centre (HSRC)



Delegate Information

Conference Venue

Aston Webb
University of Birmingham
Edgbaston
Birmingham
B15 2TT

Campus Map – R6

Conference Registration is located in the Reception Area of the Aston Webb Building. Plenary Speakers, Posters, Exhibitors and refreshments will be in the Great Hall.

WiFi

Free wi-fi access is available throughout the conference.

Connect to 'WiFIGuest'

Open a browser and visit 'service.thecloud.net'

Click 'Get online at Edgbaston Campus'

Follow the on screen instructions to create an account.

Campus Accommodation

Chamberlain Halls
Birmingham
B15 3SZ

Internet access available in all rooms, please ask at reception.

Check out by 10am on date of departure.

Taxis – TOA Taxis – 0121 427 8888

BBQ

Sunday 10 September, 17:00

Venue: Duck and Scholar, The Vale Village Hub, Shackleton Hall

Conference Dinner

Monday 11 September, 19:00 – 23:00

Venue: Noble Room, 2nd Floor, University Staff House, R24 on campus map.

Drinks reception from 19:00, dinner served at 20:00.

Poster prizes



Many thanks to Royal Society of Chemistry for donating yearly e-subscriptions for Analyst and Analytical Methods journals for the two best poster abstracts.



Analyst publishes analytical and bioanalytical research that reports premier fundamental discoveries and inventions, and the applications of those discoveries, unconfined by traditional discipline barriers.



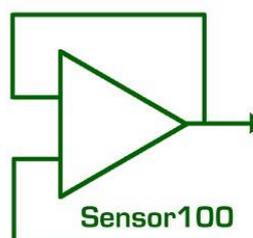
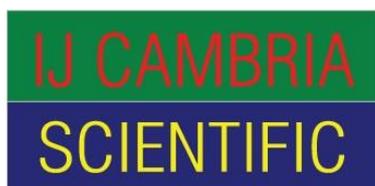
Analytical Methods welcomes early applications of new analytical methods with clear societal impact.

Analytical Methods requires that systems are demonstrated with real samples and that methods and technology reported in the journal are sufficiently innovative, robust and compared to other available methods for the intended application.

Developments are encouraged within the fields of global health, drug development, pharmaceutical analysis, Point-of-Care diagnostics, molecular diagnostics, applied microfluidics and nanotechnology, proteomics, metabolomics, environmental, neuroscience, biochemical and forensic analysis, agriculture and food science, and industrial process development.

Sponsors

Many thanks to the generous sponsors for supporting this event.



Programme

Programme overview

MONDAY		Energy & Environmental	Sensors & Analytical	Physical & Fundamental	Corrosion
	Room	Great Hall	WG12	G33	WG5
	08:40	Refreshments & Registration			
	09:10	Welcome & Opening Remarks			
	09:20	Plenary - Faraday Medal: Marc Koper			
	10:40	(EE1) Paramaconi Rodriguez	(SA1) Antonio Chaves Neto	(PF1) Frank Marken	(C1) Tiphaine Lutzler
	11:00	Refreshments, Posters and Exhibitors			
	11:30	(EE2) Cameron Bentley	(SA2) Adam Kolodziej	(PF2) Nikolas Antonatos	(C2) Khizar Sheikh
	11:50	(EE3) Sunyihik Ahn	(SA3) Mark McAuley , Trevor Davies	(PF3) Regional Prize Winner: Onagie Ayemoba	(C3) Andrew Cobley
	12:10	(EE4) Alexander Cowan	(SA4) Frankie Rawson	(PF4) James Behan	(C4) Sikiru Mohammed
	12:30	(EE5) Daniel Escalera-López	(SA5) Changhui Chen	(PF5) Robert Dryfe	(C5) Angus Cook
	12:50	Lunch, Posters and Exhibitors			
	13:00		RSC ECG AGM		SCI ECTG AGM
	14:00	(EEK1)	(SAK1)	(PFK1)	(C6) Petre-Flaviu Gostin
	14:20	Keynote: Nuria Garcia-Araez	Keynote: Darren Walsh	Keynote: Gary Attard	(C7) Joshua Owen
	14:40	(EE6) Andinet Ejigu	(SA6) Jacqueline Hicks	(PF6) Regional Prize Winner: Amelia Langley	(C8) Mohammed Majeed
	15:00	(EE7) Kathryn Toghil	(SA7) Lasse Murtomäki	(PF7) Richard Nichols	(C9) Jiejie Wu
	15:20	(EE8) Musbaudeen O. Bamgbopa	(SA8) Melanie Britton	(PF8) Mary Wood	(C10) Alex Nielsen
	15:40	Refreshments, Posters and Exhibitors			
	16:10	(EE9) Jianyun Cao	(EE12) Saranya Sriram	(EE16) Carlota Domínguez	(C11) Nofrizal Nofrizal
	16:30	(EE10) Tomas Bystron	(EE13) Robert Wilson	(EE17) Secil Unsal	(C12) Amir Shamsa
	16:50	(EE11) Aimee Jackson	(EE14) Wisit Hirunpinyopas	(EE18) Miguel Molina-García	Close
	17:10	Close	(EE15) Aondoakaa Nomor	(EE19) Sheelagh Campbell Memorial Prize Winner: Kent Griffith	
	17:30		Close	Close	
	19:00	Conference Dinner, Noble Room, University Staff House, R23 on campus map			

Programme overview

TUESDAY		Energy & Environmental	Sensors & Analytical	Physical & Fundamental	Corrosion
	Room	Great Hall	WG12	G33	WG5
	08:40	Refreshments & Registration			
	09:20	Plenary - Evans Medal/Sword (Great Hall)			
	10:40	(EE20) Gaurav Gupta	(SA9) Simon Reeves	(PF9) Sofya Danilova	(C13) Tianyang Lan
	11:00	Refreshments, Posters and Exhibitors			
	11:30	(EE21) Laura Allerston	(SAK2) Keynote: Tim Albrecht	(PF10) Scott Lewis	(C14) Yading Wang
	11:50	(EE22) Lina Troskialina		(PF11) Ifan Stephens	(C15) So Aoki
	12:10	(EEK2) Keynote: Kylie Vincent	(SA10) Ronan Baron	(PFK2) Keynote: Katherine Holt	(C16) Yong Hua
	12:30		(SA11) Andrew Lodge		(C17) Yuxiang Liu
	12:50	Lunch, Posters and Exhibitors			
	14:00	Fleischmann Lecture: Stephen Fletcher (Great Hall)			
	14:20				
	14:40				
	15:00	(EE23) Paul Kavanagh	(SA12) Regional Prize Winner: Sam Cobb	(PF12) Yara Aceta	(C18) Stacy Moore
	15:20	(EE24) Richard Bennett			(C19) Matthew Kitchen
	15:40	Refreshments, Posters and Exhibitors			
	16:10	(EE25) Bo Hou	(EE28) Priscila Valverde		
	16:30	(EE26) Micheál D. Scanlon	(EE29) John Graves		
	16:50	(EE27) Matthew Lawrence	(EE30) Richard Merrill		
17:10	CLOSE				

Poster Abstracts at a glance

NUMBER	ENERGY & ENVIRONMENTAL	
EE31	Michelle Browne	New Mechanical Route for Screening OER Catalysts
EE32	Martin Prokop	Electrochemical Behaviour of H ₃ PO ₃ on Pt Electrode in Hot Concentrated H ₃ PO ₄ Electrolyte
EE33	Xiaoting Chen	Electrochemical CO ₂ reduction and formic acid oxidation on Pd _{MIPt} (111) and Pd _{MIPt} (100) electrodes
EE34	Jose Alfredo Del-Oso	Control of Thickness and Morphology of Poly-(3,4-ethylenedioxythiophene) by Electrochemically Growth (E-PEDOT) and Manipulation of its Conductive State for Use as Anodic Buffer Layer in Organic Photovoltaic Cells
EE35	Carlota Domínguez	Synthesis of highly durable and methanol tolerant Pt catalyst for oxygen reduction reaction by ultraspray method
EE36	Luis F. Arenas	Versatile 3D-Printed Electrodes for Electrochemical Flow Reactors
EE37	Kasid Khan	Targeting the Electrochemical Activity of Biofilms
EE38	MD Khairul Hoque, James Behan	Capacitive Properties of Nitrogen Doped Amorphous Carbon Materials for Electrocatalytic Applications
EE39	Craig Armstrong, Kathryn Toghill	Transition Metal Coordination Complexes with Redox Non-Innocent Ligands for Flow Battery Energy Storage
EE40	Penny Whalley	Synthesis and Electrochemistry of Advanced Electrocatalysts Based on Ternary Metal Nitrides
EE41	Jo Humphrey	Catalytic Activity of Electrodeposited MoS ₂ Films for Hydrogen Evolution
EE42	Yasmeen AlZahrani	Developing magnetic resonance imaging (MRI) for studying batteries
EE43	Luis Andres Romeral Fernandez	An Electrochemical Impedance Study of the Oxygen Evolution Reaction at Nickel-Cobalt Oxides in Base

NUMBER	SENSORS & ANALYTICAL	
SA13	Kelly Westmacott	Voltammetric Analysis Of Vitamin B ₁ B ₂ & B ₆ Using Screen Printed Carbon Electrodes
SA14	Adrian Crew	Development of an Assay for the Beta-Agonist Salbutamol in Serum using Voltammetry in Conjunction with a Disposable Screen-Printed Carbon Electrode
SA15	Harry Sherman	Electrochemical Detection of Cellular Iron Reduction in Epithelial Cancer Cell Lines
SA16	Bongiwe Silwana	The Role of Electrochemistry in Understanding the Drugs Targeting Copper Complexation for Alzheimer's Disease
SA17	Edward Burgoyne	Detection of Biomarkers of <i>Pseudomonas aeruginosa</i> Bacteria by Electrochemistry at the Interface between Two Immiscible Electrolyte Solutions
SA18	Yousillya Bunga	Interactions of thiolated gold nanoparticles with lipid membranes
SA19	Abigail Thompson	Cellulose in Sensors and Logic Gates: Ionic Diode Phenomena Based on Surface Charges in Reconstituted Cellulose Films
SA20	Ammu Rosin Jose	Simultaneous Determination of Epinephrene and Homovanilic Acid on Bromophenol Blue Modified Glassy Carbon Electrode

NUMBER	PHYSICAL & FUNDAMENTAL	
PF13	Hasan Alesary	Electroplating of Aluminium from Novel Ionic Liquids
PF14	Lisa Rhodes-Martin	Development of an X-ray cell for electrochemical studies of ionic liquids on single crystal surfaces
PF15	Adam Kolodziej	Phosphate-mediated electrochemical adsorption of cisplatin on gold electrodes
PF16	Lena Reichenbach	Temperature dependence of Cu-UPD on Au(111) in 0.1 M sulphuric acid
PF17	Budi Riza Putra	Ionic Diode Characteristics at a Polymer of Intrinsic Microporosity (PIM) Nafion "Heterojunction" Deposit on Microhole Poly(ethylene-terephthalate) Substrates
PF18	Shi Xuan Leong	Microporous Heterocarbon Flakes as Catalyst for Ammonia Oxidation
PF19	Thulase Sivasothy	Microporous Nafion Composites in Electroanalysis
PF20	Luthando Tshwenya	A Polymer of Intrinsic Microporosity (PIM-1) in Electrochemical Membranes and Diodes

NUMBER	CORROSION	
C20	Khalid Mohammed	An experimental investigation into the effects of water condensation rate and surface temperature on top of line corrosion in a CO ₂ environment.
C21	Nikita Rathod	The Influence of Pulsed Electrical Charge on Electrochemical Remediation of Steel Reinforcement

Oral Abstracts at a glance

NUMBER	ENERGY & ENVIRONMENTAL	
EE1	Paramaconi Rodriguez	Role of the adsorbed oxygen species in the selective electrochemical reduction of CO ₂ to alcohols on copper single-crystal electrodes
EE2	Cameron Bentley	Scanning Electrochemical Cell Microscopy (SECCM): A Versatile Tool for Probing the Active Sites and Quantifying the Activity of Electrocatalysts
EE3	Sunyhik Ahn	Poly-amine Modified Copper Foam Electrodes for Enhanced Electrochemical Reduction of Carbon Dioxide
EE4	Alexander Cowan	Studying electrocatalytic CO ₂ reduction mechanisms with IR-Vis SFG spectroscopy
EE5	Daniel Escalera-López	Benchmarking the activity, stability and inherent electrochemistry of amorphous MoS _x thin films for the hydrogen evolution reaction
EEK1	Keynote: Nuria Garcia-Araez	Using redox mediators for Li-O ₂ and Li-S batteries and Li recycling
EE6	Andinet Ejigu	Electrochemical Exfoliation and Functionalisation of 2D-materials for Energy Storage Devices
EE7	Kathryn Toghil	Complexes with Tuneable Ligands as Redox Flow Battery Mediators
EE8	Musbaudeen O. Bamgbopa	Cyclable All-Iron Membraneless Redox Flow Battery Based on Multiphase Immiscible Liquid Electrolytes
EE9	Jianyun Cao	Two-step electrochemical intercalation and oxidation for mass production of graphene oxide
EE10	Tomas Bystron	Modification of Ti Surface as a Way to Reduce Excessive Surface Passivation During PEM Water Electrolysis Operation
EE11	Aimee Jackson	Platinum Decorated Manganese Oxide – Graphene Oxide sheets for Methanol Oxidation Reaction in Direct Methanol Fuel Cells
EE12	Saranya Sriram	Low Energy Intensive Electrochemical Reduction of Chromium contaminated wastewater and soil matrices
EE13	Robert Wilson	Development of a self-cleaning wall-jet flow cell for continuous quality monitoring in drinking water distribution systems
EE14	Wisit Hirunpinyopas	Desalination and Nanofiltration through Functionalised Lamina MoS ₂ Membranes
EE15	Aondoakaa Nomor	The influence of anions on the release of Ag(I) from silver nanoparticles (AgNPs).
EE16	Carlota Domínguez	Study of model carbon materials with graphitic-N sites for oxygen reduction reaction
EE17	Secil Unsal	N-Doped Carbon Aerogel Supported Cobalt Catalysts by Supercritical Deposition for Oxygen Reduction Reaction
EE18	Miguel Molina-García	Graphene doped with boron, nitrogen, phosphorus and sulfur as metal-free electrocatalysts for the oxygen reduction
EE19	Kent Griffith	Elucidating the Mechanism of High-Rate and High-capacity Lithium-ion Intercalation in Bulk Complex Oxides
EE20	Gaurav Gupta	Effect of different ionomers on the performance of alkaline exchange membrane (AEM) fuel cells
EE21	Laura Allerston	The Relationship Between Synthesis, Formulation and Performance of Low Cost Non Platinum PEM Fuel Cell Catalysts
EE22	Lina Troskialina	Effects of Sn anode-infiltration on direct-biogas SOFC's electrochemical performance
EEK2	Keynote: Kylie Vincent	Hydrogen energy in biology: learning from nature's electrocatalysts
EE23	Paul Kavanagh	Living electrodes: using microbes as electrocatalysts for a sustainable future.
EE24	Richard Bennett	Biopower and biosensors: aspects of enzymatic electrodes
EE25	Bo Hou	Solution-Processed Cascaded-Junction Quantum Dot Solar Cells
EE26	Micheál D. Scanlon	Photo-Induced Electron Transfer at Porphyrin Sensitised Water-Oil Interfaces for Solar Energy Conversion
EE27	Matthew Lawrence	Tuning the size and shape of novel nanoscale metal oxide photocatalysts using the cathodic corrosion method
EE28	Priscila Valverde	Effect of water on Cu electrodeposition from a water-containing deep eutectic solvent
EE29	John Graves	A New Procedure for the Template Synthesis of Metal Nanowires
EE30	Richard Merrill	Copper turmeric electrochemically deposited composite coatings

Oral Abstracts at a glance

NUMBER	SENSORS & ANALYTICAL	
SA1	Antonio Chaves Neto	Sensor using Molecular Dynamics of Drugs in Carbon Nanotubes Under External Uniform Electric Field
SA2	Adam Kolodziej	Electrochemical stability of thiols and disulfides assembled on gold in physiological medium
SA3	Mark McAuley , Trevor Davies	Electrochemical Detection of DNA Methylation: A possible method for detecting changes to health
SA4	Frankie Rawson	Fabricating Cellular Bioelectronic Systems by Combining Inkjet Printing with Bipolar Electrochemistry
SA5	Changhui Chen	Electrochemical characterisation and regeneration of sulfur poisoned Pt catalysts
SAK1	Keynote: Darren Walsh	How Ionic are Ionic Liquids? Measuring the Ionicity of Protic Ionic Liquids using Electroanalytical Chemistry
SA6	Jacqueline Hicks	Investigating Bacterial ROS with Tailored Carbon Nanotube Sensors
SA7	Lasse Murtomäki	SECM Study of Metals Extraction at the ITIES
SA8	Melanie Britton	MRI of electrochemical systems: batteries, corrosion and electroplating
SA9	Simon Reeves	The development of electrochemical online monitoring in nuclear pyroprocessing using in-house microelectrodes.
SAK2	Keynote: Tim Albrecht	Nanopore sensing for DNA fingerprinting and profiling applications
SA10	Ronan Baron	Performance characteristics of New NO ₂ and O ₃ Low Cost Air Quality Gas Sensors.
SA11	Andrew Lodge	Electrodeposition of Tin Nanowires into an Anodic Alumina Template from a dichloromethane electrolyte.
SA12	Sam Cobb	Development of a Boron doped diamond pH sensor for unbuffered media: The effect of Quinone surface coverage on pH response.

NUMBER	PHYSICAL & FUNDAMENTAL	
PF1	Frank Marken	Electrochemical Processes Leading to Ionic Diode Phenomena
PF2	Nikolas Antonatos	The Influence of Acetonitrile on Cu Under-Potential Deposition in presence of adsorbing anions
PF3	Onagie Ayemoba	Spectroscopic Evidence of Size-Dependent Buffering of Interfacial pH by Cation Hydrolysis during CO ₂ Electroreduction
PF4	James Behan	Combined Optoelectronic and Electrochemical Study of Nitrogenated Carbon Electrodes
PF5	Robert Dryfe	Electrowetting without Dielectrics
PFK1	Keynote: Gary Attard	The slowly-evolving picture of the Pt{110} electrode surface: Is there still something new to learn from single crystal platinum voltammetry?
PF6	Amelia Langley	Polymer of Intrinsic Microporosity (PIM) Film Coating Dampens Chaotic Copper Corrosion
PF7	Richard Nichols	STM Studies of Electrochemical Single Molecule Transistors and Molecular Wires
PF8	Mary Wood	Using X-ray and neutron reflectometry to monitor corrosion mechanisms at the angstrom-level
PF9	Sofya Danilova	Electroless Ni-B plating in a gradient magnetic field.
PF10	Scott Lewis	Proton conduction pathways in porous organic cage networks and functionalised silica ionogels
PF11	Ifan Stephens	Trends in oxygen reduction on a Pt-alloy single crystal: acidic versus alkaline media
PFK2	Keynote: Katherine Holt	Deprotonation of graphene nanoflake electrode edge groups studied using <i>in situ</i> IR spectroelectrochemistry
PF12	Yara Aceta	Study of Oxygen Reduction Reaction by Scanning Electrochemical Microscopy

Oral Abstracts at a glance

NUMBER	CORROSION	
C1	Tiphaine Lutzler	Improvement of sol-gel coatings and their anti-corrosion properties by doping with Titanium precursors
C2	Khizar Sheikh	AFM-SECM and Nanoelectric Liquid Imaging for Corrosion Research
C3	Andrew Cobley	Effect of the use of pulse plating techniques in electrodeposited Sn-Cu Coatings for Pb-free, environmentally-friendly applications
C4	Sikiru Mohammed	Effect of surface roughness on pitting behaviour of X65 carbon steel in saturated CO ₂ environment
C5	Angus Cook	Towards realistic atmospheric aerosol deposits – automated ultrasonic deposition
C6	Petre-Flaviu Gostin	Characterisation of Corrosion Products of a Ti-Based Metallic Glass in Artificial Pits by In Situ Synchrotron X-ray Diffraction
C7	Joshua Owen	Analysis of X65 Carbon Steel Surfaces After Erosion-Corrosion Testing Using a Submerged Impingement Jet
C8	Mohammed Majeed	Potentiodynamic Anodic Polarisation Parameters as Indicators to Erosion-Corrosion of Stainless Steel
C9	Jiejie Wu	Finite Element Modelling of Corrosion Product Deposition in Nuclear Plants
C10	Alex Nielsen	Novel assessment of atmospheric corrosion of brass under sodium chloride-containing water droplets using the scanning Kelvin probe
C11	Nofrizal Nofrizal	Preferential Weld Corrosion of High Strength Pipeline Steels
C12	Amir Shamsa	Influence of Ca ²⁺ ions on CO ₂ corrosion of X65 carbon steel at elevated temperature
C13	Tianyang Lan	Comparison of two electrochemical methods (ENM and EIS) for detection of Corrosion under Insulation (CUI)
C14	Yading Wang	Corrosion control of magnesium alloys with its hydroxide (using a hydrothermal route).
C15	So Aoki	Optical Microscopic In-situ Observation of Crevice Corrosion of a Duplex Stainless Steel
C16	Yong Hua	Comparison of corrosion behaviour of X65 steels in water-containing supercritical CO ₂ environments with NO ₂ /O ₂
C17	Yuxiang Liu	Comparative Studies of corrosion Behaviour of Casting and Laser-treated Mg-1Ca Alloy in Simulated Body Fluid and 0.9 wt% NaCl Solution
C18	Stacy Moore	Investigating Corrosion Using High-Speed AFM
C19	Matthew Kitchen	Using the Scanning Droplet Cell to Accelerate the Formation of Copper Patina Detected in the Marine Environment

Invited Speakers

Abstracts

Faraday Medal: Marc Koper

Proton-coupled electron transfer and electrocatalysis

Marc T.M. Koper

Leiden Institute of Chemistry, Leiden University, 2300 RA Leiden, The Netherlands

Email: m.koper@chem.leidenuniv.nl

This talk will outline a simple but general analysis for multiple proton-electron transfer reactions, based on the microscopic theory of proton-coupled electron transfer reactions, recent developments in the thermodynamic theory of multi-step electron transfer reactions, and the experimental realization that many multiple proton-coupled electron transfer reactions feature decoupled proton-electron steps in their mechanism. It is shown that decoupling of proton and electron transfer leads to a strong pH dependence of the overall catalytic reaction, implying an optimal pH for high catalytic turnover, and an associated optimal catalyst at the optimal pH. When more than one catalytic intermediate is involved, scaling relationships between intermediates may dictate the optimal catalyst and limit the extent of reversibility that may be achievable for a multiple proton-electron-transfer reaction. These scaling relationships follow from a valence-bond-type binding of intermediates to the catalyst surface. The theory is discussed in relation to the oxygen evolution reaction and the electrocatalytic reduction of CO₂, focusing on the importance of charged intermediates, their pH dependence and structure sensitivity.

Evans Medal/Sword:

Dr Hugh Isaacs

Dr Hugh S Isaacs was named as this year's Evans Award winner shortly before his death in December 2016. Hugh's career in electrochemistry and corrosion spanned over 5 decades and he made significant contributions to our understanding of localized corrosion and of oxide film growth and passivity. He was an innovative experimentalist, and an early adopter and developer of new techniques including scanning electrode and synchrotron-based methodologies. He was also a great mentor to many electrochemists and an active member of the corrosion community.

The lecture will be given by Prof Mary Ryan and shall provide an overview of Hugh's career, work and his many contributions to corrosion science.

Fleischmann Lecture:

Stephen Fletcher

Martin Fleischmann's Epochal Contributions to the Kinetics of Phase Change, and Pathways to the Future.

Stephen Fletcher

*The Fletcher Consultancy,
Loughborough
Leicestershire, LE11 3LU (UK)*

Email: ProfSFletcher@Virginmedia.com

Martin Fleischmann FRS (29 March 1927- 03 August 2012) was a central figure in the post-war development of transient techniques in electrochemistry. He used these dynamic methods to study the kinetics of phase changes at electrode surfaces, and, in particular, he established the widespread occurrence of nucleation and growth kinetics in metal deposition reactions and in anodic film formation reactions. He also used his considerable mathematical prowess to model these phenomena. His work forms the bedrock of much present-day research in these important areas, and extends from quantum phenomena through to large scale corrosion.

In this lecture, I will attempt to summarize (briefly) Martin's work on the kinetics of phase change, which forms only a fraction of his total achievement. I will then describe the current status and outstanding problems of nucleation and growth theory in electrochemistry, which must be solved before further progress can be made. Finally, I will indicate some important directions for next-generation research.

Energy & Environmental

Oral Abstracts

Role of the adsorbed oxygen species in the selective electrochemical reduction of CO₂ to alcohols on copper single-crystal electrodes

Cecile S. Le Duff, Paramaconi Rodriguez

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

Email: P.B.Rodriguez@bham.ac.uk

To date, copper and copper oxide-derived surfaces are the only catalysts that could electrochemically convert CO₂ to high-value and energy-dense products such as methane ethylene, formic acid, methanol and ethanol, among others.¹⁻³ However, the efficiency and the selectivity of this process are far from optimal and the parameters controlling these factors are not-fully understood. Until now, such differences in reactivity and selectivity have been attributed to the surface area, surface structure, the oxidation state of the Cu, the oxygen content on the films and roughness as well as to the history of the electrode.^{1,3-7}

We have recently used Cu(100) and Cu(111) electrodes and have pulsed voltammetry to control the surface structure and the oxygen content at the surface. The pulse sequence was programmed to guarantee reproducible initial conditions for the reaction (Figure 1A) at every fraction of time and at any given frequency without compromising the surface structure.

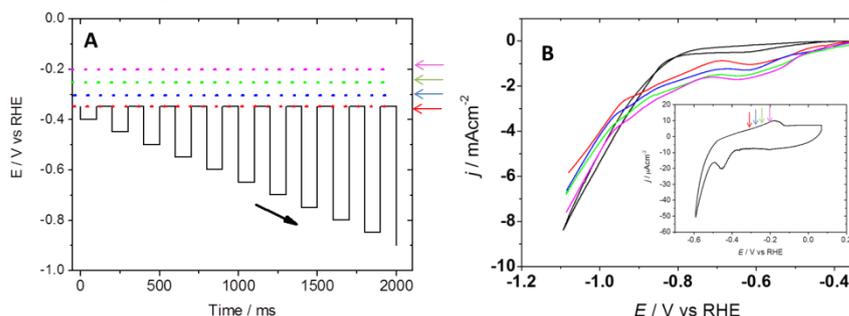


Figure 1: (A) Pulse program for the pulsed voltammetry. (B) Pulse voltammeteries of Cu(111) electrodes in phosphate buffer solution in presence of CO₂. The black curves correspond to the cyclic voltammetry's at ($v=10$ mV/s). Inset: cyclic voltammetry's in absence of CO₂ of the Cu(111) and Cu(100). The arrows indicate the e positive potential steps during the pulse voltammetry's.

We have found that oxygenated hydrocarbon species – formaldehyde, formate, methanol, ethanol, acetone and acetaldehyde – were only observed under pulse potential conditions. This may be associated to the adsorption of OH species to the surface when the potential is stepped up to the upper potential. The product selectivity would be associated to the OH coverage, which is surface structure and potential dependent.

- (1) Hori, Y. *et al.* *The Journal of Physical Chemistry B* **2002**, *106*, 15.
- (2) Montoya, J. H. *et al.* *Chemcatchem* **2013**, *5*, 737.
- (3) Kas, R. *et al.* *Physical Chemistry Chemical Physics* **2014**, *16*, 12194.
- (4) Le, M. *et al.* *Journal of the Electrochemical Society* **2011**, *158*, E45.
- (5) Monzo, J. *et al.* *Journal of Materials Chemistry A* **2015**, *3*, 23690.
- (6) Handoko, A. D. *et al.* *The Journal of Physical Chemistry C* **2016**, *120*, 20058.
- (7) Li, C. W. *et al.* *J. Am. Chem. Soc.* **2012**, *134*, 7231.

Scanning Electrochemical Cell Microscopy (SECCM): A Versatile Tool for Probing the Active Sites and Quantifying the Activity of Electrocatalysts

Cameron L. Bentley^a, Minkyung Kanga, Faduma M. Maddara, Fengwang Lib, Marc Walkerc, Jie Zhangb and Patrick R. Unwina

^aDepartment of Chemistry, University of Warwick, Coventry CV4 7AL, U.K.

^bSchool of Chemistry, Monash University, Clayton, Vic 3800, Australia

^cDepartment of Physics, University of Warwick, Coventry CV4 7AL, U.K.

Email: C.Bentley.1@warwick.ac.uk

The (electro)catalytic performance of (nano)materials is usually evaluated from the “total electrode activity”, measured with macroscopic (“bulk”) electrochemical techniques (*e.g.*, cyclic voltammetry) after immobilization on a supposedly inert, conducting substrate. Taking this approach, the intrinsic activity of each catalytic site can only be inferred from the total electrode activity if the number of active sites is known, which is generally challenging to measure for functional catalysts. In contrast, high resolution electrochemical imaging techniques, such as Scanning Electrochemical Cell Microscopy (SECCM) considered herein¹, are able to investigate and map the electrochemical activity of complex (catalytic) materials at the nanoscale, and target particular characteristic features on a surface (*e.g.*, edge plane vs. basal plane).

In this work², we report the first spatially-resolved measurements of hydrogen evolution reaction (HER) activity on natural crystals of molybdenum disulfide (MoS₂), which has shown promise as an abundant and low-cost alternative electrocatalyst to platinum in this application. This is achieved using voltammetric SECCM, whereby pixel-resolved linear-sweep voltammogram (LSV) measurements have allowed the HER to be visualized at multiple different potentials to construct electrochemical flux movies with nanoscale resolution. Through correlation of the local voltammetric response with information from scanning electron microscopy (SEM) and atomic force microscopy (AFM) in a *multi-microscopy approach*, it is demonstrated unequivocally that the basal plane of MoS₂ is much more active than previously considered, and that the HER is greatly facilitated at surface defects (*e.g.*, steps, edges or crevices), with important implications for the design of MoS₂ electrocatalysts. Semi-quantitative treatment of the voltammetric data reveals that the HER at the basal plane of MoS₂ has a Tafel slope and exchange current density (*J*₀) of ~120 mV/decade and 2.5×10^{-6} A cm⁻² (*i.e.*, comparable to polycrystalline Co, Ni, Cu and Au), respectively, while the edge plane has a comparable Tafel slope and a *J*₀ that is estimated to be more than an order-of-magnitude larger than that of the basal plane ($\sim 1 \times 10^{-4}$ A cm⁻²).

¹Ebejer, N.; Güell, A. G.; Lai, S. C. S.; McKelvey, K.; Snowden, M. E.; Unwin, P. R. In *Annual Review of Analytical Chemistry*, Vol 6; Cooks, R. G., Pemberton, J. E., Eds.; Annual Reviews: Palo Alto, **2013**; Vol. 6, p 329

²Bentley, C. L.; Kang, M.; Maddar, F. M.; Li, F.; Walker, M.; Zhang, J.; Unwin, P. R., Electrochemical Maps and Movies of the Hydrogen Evolution Reaction on Natural Crystals of Molybdenite: Basal vs. Edge Plane Activity. *Submitted*, **2017**

Poly-amine Modified Copper Foam Electrodes for Enhanced Electrochemical Reduction of Carbon Dioxide

Sunyhik Ahn,^{a,b} Konstantin Klykin,^c Russell J. Wakeham,^b Francesco Carla,^d Vitaly Alexandrov^c, and Enrico Andreoli^b

a) Department of Materials Chemistry, Kyoto University, Nishikyo-ku, Kyoto, 615-8520, Japan

b) Energy Safety Research Institute, Swansea University, Bay Campus, Swansea, SA1 8EN, UK

c) Department of Chemical and Biomolecular Engineering, University of Nebraska-Lincoln, Lincoln, USA

d) European Synchrotron Radiation Facility, CS 40220, 38043, Grenoble Cedex 9, France

Email: sunyhik.ahn@gmail.com

Electrochemical reduction of CO₂ into hydrocarbons and alcohols is a particularly attractive prospect given the tremendous infrastructure in place for the storage, transport and utilisation of such fuels and industrial feedstock. In this study, large surface area metallic copper foam electrodes are modified with polyamine groups for electrochemical reduction of CO₂. It is shown that the activity of copper towards CO₂ reduction can be enhanced or completely switched off depending on the chemical nature of the modifying polymer groups, with poly(acrylamide) leading to record levels of (geometric) partial current for hydrocarbons. Well reported effects from oxide derived copper and distribution of crystalline phases are ruled out as the source of enhancement by correlating changes in selectivity with material properties probed with XPS and in-situ XRD. Supporting density functional theory calculations suggest that the poly(acrylamide) stabilise the CO-CO* intermediate which enhances selectivity for ethylene and ethanol as observed in the experimental data. Tethering functional groups on copper that affect catalysis kinetics offers an additional tuneable parameter that can synergize with the conventional approach of modifying catalyst-intermediate binding strength, this demonstrates a new approach to the optimization and design of CO₂ reduction catalysts.

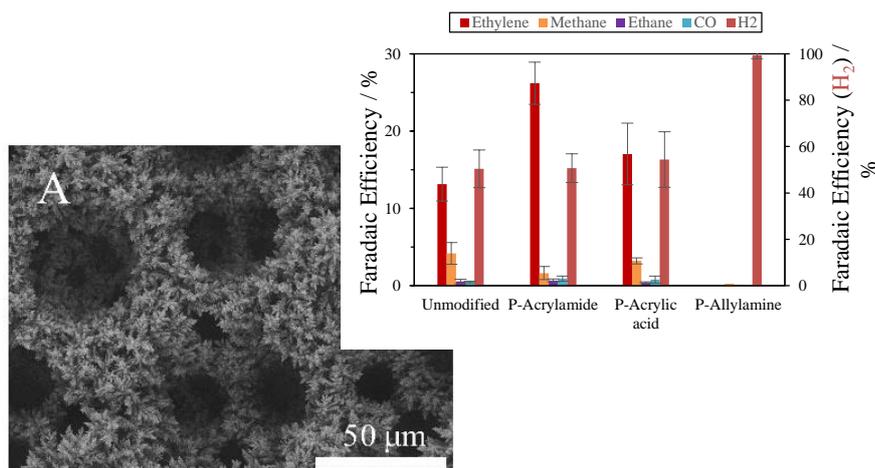


Figure. SEM image of copper foam electrode, with a bar chart of faradaic efficiencies for gaseous CO₂ electrolysis products.

Studying electrocatalytic CO₂ reduction mechanisms with IR-Vis SFG spectroscopy

Gaia Neri,^a Paul Donaldson^b, Alexander Cowan^a

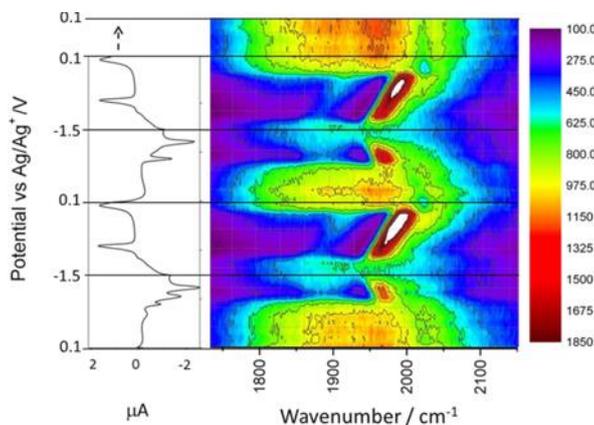
a) Department of Chemistry and Stephenson Institute for Renewable Energy, University of Liverpool, L69 7ZD, Liverpool, UK

b) Central Laser Facility, STFC Rutherford Appleton Laboratory, Harwell, Didcot, Oxfordshire, OX11 0QX, UK

Email: acowan@liverpool.ac.uk

The electrochemical reduction of CO₂ to fuels (CO₂ + 6H⁺ + 6e⁻ → CH₃OH) and feedstock's (CO₂ + 2H⁺ + 2e⁻ → CO + H₂O) is an attractive goal with potentially enormous environmental and economic impacts. However to make such a process economically viable new more efficient electrocatalytic materials and molecules are required. A key issue is that the exact mechanism of many of the state-of-the-art catalysts are unproven experimentally, making rational development difficult.

IR-Vis Sum-Frequency Generation (SFG) spectroscopy specifically probes molecules at interfaces offering a sensitive probe of only the catalytically relevant species at the electrode surface. SFG has been widely used to study heterogeneous electrocatalysis but rarely to explore the mechanisms of molecular electrocatalysts. Here we will present our latest studies exploring the mechanisms of group 6 and 7 transition metal complex mediated CO₂ reduction and demonstrate how this powerful spectroscopic probe can provide unique insights into the factors controlling efficiency.



IR-VIS SFG spectra of Mn(bpy)(CO)₃Br in CH₃CN/Ar recorded at 50 mV s⁻¹ on Au electrode. The full data set recorded in <150 s

Benchmarking the activity, stability and inherent electrochemistry of amorphous MoS_x thin films for the hydrogen evolution reaction

Daniel Escalera-López,^{a,b*} Neil V Rees^a

a) Centre for Hydrogen and Fuel Cell Research, School of Chemical Engineering, University of Birmingham, Birmingham, B15 2TT, UK

b) Nanoscale Physics Research Laboratory, School of Physics and Astronomy, University of Birmingham, Birmingham, B15 2TT, UK

Email: DXE411@bham.ac.uk

Transition metal dichalcogenides (TMDs), and in particular molybdenum disulfide (MoS₂), have been found to be earth-abundant candidates to replace platinum group metal catalysts for the hydrogen evolution reaction (HER) in PEM Electrolyzers. As only the Mo-edge sites are catalytically active,¹ strategies to obtain edge-abundant MoS₂ nanostructures are in high demand.^{2–5} Recent studies reported a one-step, substrate insensitive electrodeposition method to obtain amorphous MoS_x thin films with tunable stoichiometry from a (NH₄)₂MoS₄ aqueous solution.⁶ While initial investigations have focused on the elucidation of the MoS_x electrodeposition mechanism and stoichiometry, critical aspects in catalysts benchmarking such as durability and long-term stability remain unexplored. Several reports not only have confirmed the influence of pH in the inherent electrochemical activity of TMDs⁷ but also its effect in the long-term stability under operating conditions.⁸ Herein we present a comprehensive study of MoS_x thin films deposited on Au substrates for the HER across the 0.6–13 pH range. Plotting of the MoS_x redox peak potentials and peak heights vs. operating pH demonstrates a correlation between the inherent MoS_x redox mechanisms and the final HER activity. Accelerated durability tests on several voltage windows monitored with ex-situ X-ray photoelectron and Raman spectroscopies inform of the electrochemically induced morphology and stoichiometry changes in the MoS_x films. Finally, stability tests (3000 cyclic voltammograms, maximum current density output= 10mA cm⁻²) benchmark the optimum pH operation range for the prepared MoS_x films.

References

- 1 T. F. Jaramillo, K. P. Jørgensen, J. Bonde, J. H. Nielsen, S. Horch and I. Chorkendorff, *Science*, 2007, **317**, 100–103.
- 2 D. Voiry, M. Salehi, R. Silva, T. Fujita and M. Chen, *Nano Lett.*, 2013, **13**, 6222–6227.
- 3 J. Xie, H. Zhang, S. Li, R. Wang, X. Sun, M. Zhou, J. Zhou, X. W. D. Lou and Y. Xie, *Adv. Mater.*, 2013, **25**, 5807–13.
- 4 D. Kong, H. Wang, J. Cha, M. Pasta and K. Koski, *Nano Lett.*, 2013, **13**, 1341–1347.
- 5 A. Ambrosi, Z. Sofer and M. Pumera, *Small*, 2015, **11**, 605–12.
- 6 H. Vrabel and X. Hu, *ACS Catal.*, 2013, **3**, 2002–2011.
- 7 M. Zafir Mohamad Nasir, Z. Sofer and M. Pumera, *ChemElectroChem*, 2015, **2**, 1713–1718.
- 8 J. Shi and J. Hu, *Electrochim. Acta*, 2015, **168**, 256–260.

Keynote: Nuria Garcia-Araez

Using redox mediators for Li-O₂ and Li-S batteries and Li recycling

N. Garcia-Araez, L. Yang, J.T Frith J. W. Dibden, N. Intaranont, and J.R. Owen

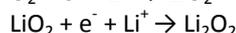
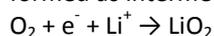
University of Southampton

Highfield Campus, SO17 1BJ, Southampton, United Kingdom

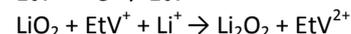
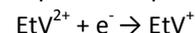
Email: n.garcia-araez@soton.ac.uk

Lithium-oxygen and lithium-sulfur batteries have the potential to revolutionize the energy storage market, since they can in principle store >5 times more energy than the current lithium-ion battery technologies. However, the performance of Li-O₂ and Li-S batteries is currently limited by several fundamental issues.

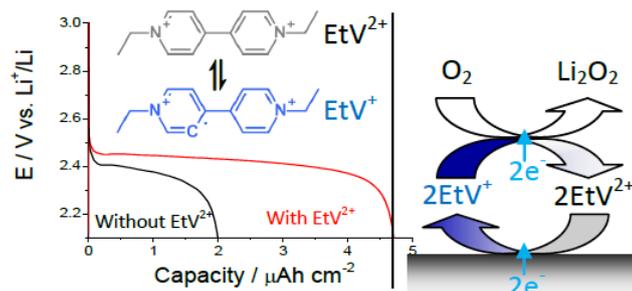
We have recently shown that redox mediators can solve the two more important issues associated to Li-O₂ batteries, i.e. electrode passivation and degradation reactions.¹ Degradation reactions are initiated by superoxide radical species that are formed as intermediates in the pathway of the reduction of oxygen:



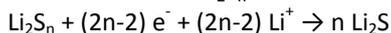
On the example of ethyl viologen, EtV²⁺, we demonstrated that redox mediators can be used to decrease the lifetime of superoxide species by promoting the fast reduction of superoxide to peroxide:



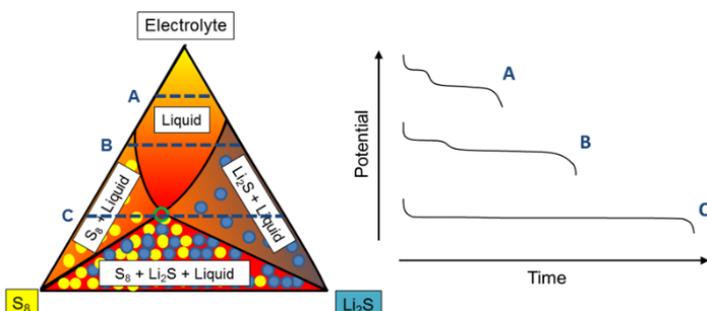
where EtV²⁺ acts as homogeneous catalyst and it is not consumed in the reaction. Furthermore, EtV²⁺ also acts as an electron shuttle, preventing electrode passivation by displacing the location of the reduction of oxygen from the electrode surface to the solution. Indeed, a major increase in capacity is obtained upon addition of EtV²⁺ to a Li-O₂ cell.



In Li-S batteries, a variety of polysulfides, Li₂S_n, are formed in the pathway of the reduction of S to Li₂S:



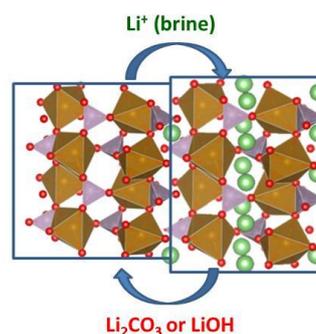
We hypothesize that polysulfides can act as redox mediators and shuttles in Li-S batteries, and their action can be optimized via a selection of suitable electrolytes. We have recently developed a new method that allows predicting the equilibrium concentration of polysulfides in Li-S cells, as well as the theoretical electrochemical response of the cell as a function of the amount of electrolyte.² This new approach, based on the construction of an experimental phase diagram, will be used for the rational screening of electrolytes for Li-S batteries.



Redox mediators are also a promising tool for Li recycling. We have shown that the reaction of battery materials (e.g. LiFePO₄) with redox agents is a fast, selective and efficient new method to extract lithium from natural brines and for recycling spent batteries.³

References:

1. L. Yang, J.T. Frith, N. Garcia-Araez, J.R. Owen. Chem. Commun. 2015, 51,1705-1708.
2. J. W. Dibden, J. W. Smith, N. Zhou, N. Garcia-Araez, J. R. Owen. Chem. Commun. 2016, DOI: 10.1039/C6CC05881G
3. N. Intaranont, N. Garcia-Araez, A. Hector, J.A. Milton, J.R. Owen. J. Mater. Chem. A, 2014, 2, 6374-6377.



Electrochemical Exfoliation and Functionalisation of 2D-materials for Energy Storage Devices

Andinet Ejigu^a, Ian A. Kinloch^b and Robert A.W. Dryfe^a

^aSchool of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, UK

^bSchool of Materials, University of Manchester, Oxford Road, Manchester M13 9PL, UK

Email: andinet.aynalem@manchester.ac.uk and robert.dryfe@manchester.ac.uk

Electrochemical exfoliation of graphite is considered to be a fast, scalable and eco-friendly way to produce graphene.^{1,2} Cathodic exfoliation in organic electrolyte, unlike anodic exfoliation, produces high quality graphene as it avoids the formation of oxygen containing functional groups.² However, development of applications of graphene is currently hampered by its poor dispersion in common, low-boiling point, solvents. In this contribution, we describe the single step simultaneous electrochemical exfoliation and functionalisation of graphene using diazonium compounds.³ Using caesium salt (dissolved in dimethyl sulfoxide) the intercalating ions, functionalisation was achieved in combination with diazonium salt (either 4-nitrobenzenediazoniumtetrafluoroborate, 4 bromobenzenediazonium tetrafluoroborate or anthraquinone-1-diazonium chloride) as functionalisation moieties. We found that the presence of diazonium compounds in solution not only acts to functionalise the graphene but also aids the exfoliation through the generation of N₂ gas which assists the separation of the functionalised graphene layers. The functionalisation also enhanced the dispersibility of graphene in aqueous solution by two orders of magnitude and increased the charge storage capacity of graphene by three times because of the introduction of surface active redox reactions (Figure 1). Finally, we will introduce a simple electrochemical route for the synthesis of metallic phase trilayer MoS₂ nanosheets.

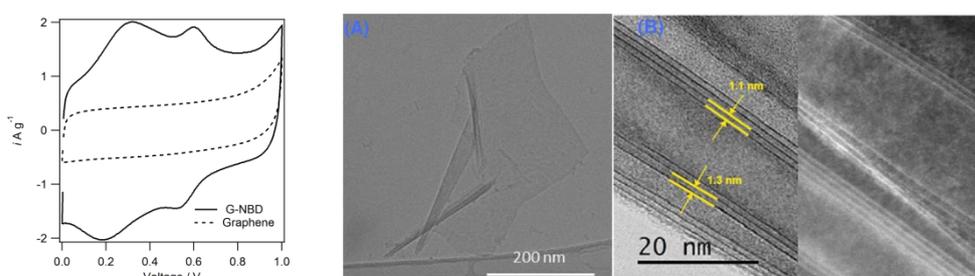


Figure 1: Cyclic voltammograms recorded at 100 mV s⁻¹ in 6.0 M KOH (aq) using symmetrical coin cells constructed from electrochemically exfoliated restacked graphene and graphene functionalised insitu with 4-nitrobenzenediazoniumtetrafluoroborate (G-NBD) and high resolution TEM image of electrochemically exfoliated MoS₂ (A and B)

References (1) K. Parvez, R. J. Li, S. R. Puniredd, Y. Hernandez, F. Hinkel, S. H. Wang, X. L. Feng and K. Mullen, *ACS Nano*, 2013, **7**, 3598-3606. (2) A. J. Cooper, N. R. Wilson, I. A. Kinloch and R. A. W. Dryfe, *Carbon*, 2014, **66**, 340-350 and (3) D. W. Johnson, B. P. Dobson and K. S. Coleman, *Current Opinion in Colloid & Interface Science*, 2015, **20**, 367-382.

Complexes with Tuneable Ligands as Redox Flow Battery Mediators

Kathryn E. Toghill,^a Craig Armstrong^a

Department of Chemistry, Lancaster University, Lancaster, UK, LA1 4YB

Email: k.toghill@lancaster.ac.uk

Redox flow batteries are a fast emerging class of electrochemical energy storage system, aimed primarily at large grid scale storage. They are unique in the electrochemical energy genre, in that their design inherently decouples power and storage capacity, providing a flexible system ideal for an increasingly complex energy network. Commercialised systems comprise electrolytes of vanadium, dissolved to high concentrations in sulphuric acid. Whilst efficient and low maintenance, these systems are not viable for long term scale up and roll out, due to the crippling cost of vanadium. Alternative chemistry is being sought to provide a redox flow battery that retains the attributes of the all vanadium flow battery, whilst offering sustainability, lower costs, and long-term viability.

Metal-organic compounds are a potential source of redox mediators that may be molecularly engineered to deliver properties desirable in a flow battery, whilst comprising earth abundant elements. They also offer the prospect of working in non-aqueous solvents, to attain higher cell voltages, and to engage in multielectron transitions, thus introducing a much higher energy density system than the VRB.

Recently we have explored a new class of cobalt(II) complexes with 'tuneable' tridentate azole-pyridine type ligands. Four structures were synthesised and their electrochemical, physical and battery characteristics were investigated as a function of successive substitution of the ligand terminal pyridyl donors. Modification of the ligand demonstrated tuneable redox potentials in which the cobalt potential difference was increased from 1.07 to 1.91 V via pyridine substitution. The charge-discharge properties of the system were evaluated using static and flow systems, the results of which will be discussed. Modification of the ligands also improved solubility from 0.18 M to 0.50 M via pyridyl substitution with 3,5-dimethylpyrazole, though the low solubility of the complexes limits the overall energy capacity to between 2.58 to 12.80 Wh L⁻¹.

References:

Armstrong, Craig G.; Toghill, Kathryn E., *Journal of Power Sources*, Vol. 349, p. 121-129.

Cyclable All-Iron Membraneless Redox Flow Battery Based on Multiphase Immiscible Liquid Electrolytes

Musbaudeen O. Bamgbopa^a, Ibrahim Mustafa^a, Saif Almheiri^a

a) Institute Center for Energy, Masdar Institute, P.O. Box 54224, Abu Dhabi, United Arab Emirates

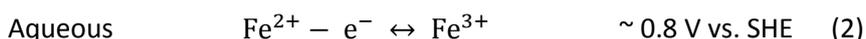
Email: mbamgbopa@masdar.ac.ae

Introduction

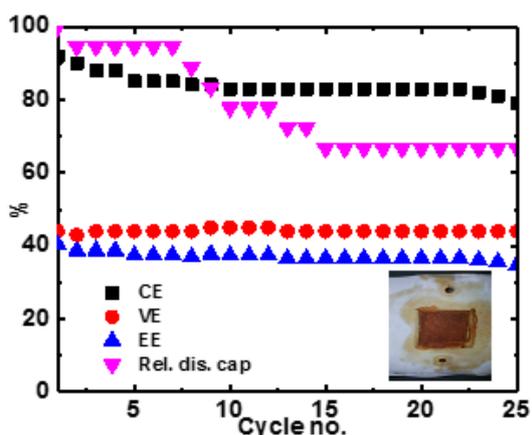
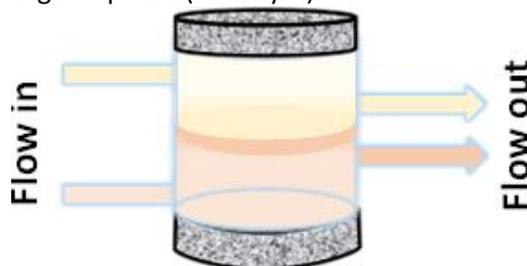
Previous attempts at true membraneless redox flow batteries (RFB) have not been able to demonstrate multiple cycling due to reactant crossover (which limit capacity retention) and difficulty of separation of the mixed electrolyte after charging for a recharging pass¹. Even the notable higher power density hydrogen-bromine² and vanadium species³ based membraneless RFBs did not demonstrate capacity retention from multiple cycling of recirculated electrolyte. In response, we pioneer a membraneless (non-hybrid) RFB capable of recharge/recirculation of the same electrolyte for multiple cycles by applying immiscible aqueous - organic anolyte - catholyte liquid streams respectively.

Preliminary results

Based on environmentally benign materials, an all iron chemistry was setup with; iron(II) sulfate (FeSO_4) as active species on the aqueous side (anolyte), and our recently investigated iron(III) acetylacetonate ($\text{Fe}(\text{acac})_3$)⁴ as active species dissolved in hydrophobic ionic liquid (1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide)



supported ethyl acetate in the immiscible organic phase (catholyte).



At the present work stage, over 65% of first discharge capacity can be retained even after 25 cycles, where columbic and energy efficiencies averaged at 85 and 38% respectively on a test flow cell utilizing 0.1 M FeSO_4 + 0.5 M sodium chloride in the aqueous anolyte and 0.1 M $\text{Fe}(\text{acac})_3$ in

60/40 volume percentage ethyl acetate/ionic liquid catholyte.

References

- 1 M. O. Bamgbopa, S. Almheiri and H. Sun, *Renew. Sustain. Energy Rev.*, 2017, 70, 506–518.
- 2 W. A. Braff, M. Z. Bazant and C. R. Buie, *Nat. Commun.*, 2013, 4, 2346.
- 3 J. W. Lee, M.-A. Goulet and E. Kjeang, *Lab. Chip*, 2013, 13, 2504–2507.
- 4 M. O. Bamgbopa, Y. Shao-Horn and S. Almheiri, *J. Mater. Chem. A*, 2017, DOI:10.1039/C7TA02022H.

Two-step electrochemical intercalation and oxidation for mass production of graphene oxide

Jianyun Cao,^a Pei He,^a Mahdi A. Mohammed,^a Xin Zhao,^a Ian Kinloch,^a Robert Dryfe^b

a) School of Materials, University of Manchester, Manchester, M13 9PL, U.K.

b) School of Chemistry, University of Manchester, Manchester M13 9PL, U.K.

Email: jianyun.cao@manchester.ac.uk

Graphene oxide (GO), a single layer graphene sheet functionalized with oxygen groups, has numerous applications in both functional and structural areas, such as printed electronics, energy storage, polymer composites, etc. Conventional chemical oxidation to produce GO suffers from environmental and safety issues due to the use of hazardous and explosive chemicals. To mitigate such problems, electrochemical oxidation of graphite is a very promising alternative route to GO although it faces challenges associated with low yield (inhomogeneous oxidation) and complicated cell configuration (scalability). Here we report a two-step electrochemical intercalation and oxidation approach to produce GO on a large scale (tens of grams): (1) forming stage 1 graphite intercalation compound (GIC) in concentrated sulfuric acid; (2) oxidizing and exfoliating the stage 1 GIC in aqueous ammonium sulfate solution. This two-step approach leads to GO with high yield (>70 wt.%), good quality (>90% monolayer), and oxygen content that is lower than that typically obtained from chemical routes (17.5 at.%). Moreover, the as-produced GO could be deeply reduced (3.25 at.% oxygen; C/O ratio 29.8) to highly conductive (54600 S m^{-1}) graphene. Use of the resultant reduced material as an electrochemical capacitor shows ultra-high rate capability up to 10 V s^{-1} . The two-step method is expected to advance research in electrochemical production of GO and extend its application to various areas.

Modification of Ti Surface as a Way to Reduce Excessive Surface Passivation During PEM Water Electrolysis Operation

Tomas Bystron,^a Petra Diblikova,^a Martin Paidar,^a Karel Bouzek^a

a) *University of Chemistry and Technology Prague, Technicka 5, 166 28, Prague 6, Czech Republic*

Email: bystront@vscht.cz

PEM water electrolysis represents important technology in hydrogen economy scheme. It is given mainly by the fact that it allows flexible operation even at very high intensity. PEM water electrolysis suffers, however, from several issues. The most critical one is stability of the materials on the anode side of the cell. This is given by a combination of acidic environment and high positive potential. Under these conditions the majority of electron conducting materials undergo dissolution which greatly limits list of materials available for anode catalyst and gas diffusion layer. For this reason the practically only useful anode catalyst material is based on Ir and gas diffusion layer is commonly made of Ti (or Ta). These metals are under such conditions stable only due to the presence of protecting passivation layer on their surface. However, the passivation layer itself is electrically insulating. The passivation layer of excessive thickness is therefore causing substantial surface contact resistance and leads to substantial energy loss, especially when the electrolysis process is operated at high current density. A common way of solving this issue is to cover the Ti surface with protecting layer based on Pt metal. This approach, however, leads to substantial increase in precious metal loading and further raises already very high investment cost of the PEM water electrolyser .

Aim of this work was to test an alternative approach based on appropriate modification of the Ti surface with acid. Results showed that etching of the Ti with hydrochloric acid leads, first of all, to a removal of the existing surface passivation layer, which decreases surface contact resistance. Additionally, a hydrogen generated during Ti metal dissolution in acid penetrates into bulk of Ti metal and forms subsurface layer of Ti hydrides slowing down growth of the newly forming passivation layer. The hydride layer formation was investigated using various electrochemical techniques, focused ionic beam in combination with secondary ion mass spectrometry, X-ray photoelectron spectroscopy and X-ray diffraction. The positive effect of Ti etching was confirmed during PEM water electrolysis operation.

Financial support by the Czech Science Foundation within the framework of the project No. 15-02407J, is gratefully acknowledged.

Platinum Decorated Manganese Oxide – Graphene Oxide sheets for Methanol Oxidation Reaction in Direct Methanol Fuel Cells

Aimee F Jackson^a, Surbhi Sharma^b, Neil V Rees^a

a) Centre for Fuel Cell and Hydrogen Research, University of Birmingham, B15 2TT

b) School of Biosciences, University of Birmingham, B15 2TT

Email: axj472@bham.ac.uk

Manganese Oxide – reduced Graphene Oxide (MnOx-GO) hybrid catalyst supports have promise for improving the performance of direct methanol fuel cells (DMFCs)^[1], by improving the durability and stability of the expensive precious metal catalyst currently used in such devices.

MnOx – GO hybrid materials are highly tuneable, due to the numerous possible oxidation states of manganese, and different morphologies that can be produced.

In this instance, manganese oxide has been grown on graphene oxide via a rapid microwave assisted one pot wet chemical method^[2]. This relatively ‘green’ synthesis route uses low energy microwaves and aqueous solvent and also promises facile scale up as it is fast and relatively simple. These hybrid MnOx-GO materials have subsequently been decorated with platinum nanoparticles via a further one pot microwave assisted polyol process^[2], in order to test them for use in DMFCs.

These Pt/MnOx-GO materials have been thoroughly characterised via: thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM), showing that the MnOx content in the support affects the growth of platinum nanoparticles.

Ex-situ electrochemical testing has been carried out to determine the material’s suitability for use in DMFCs. The Pt/MnOx-GO produced shows promise in improving the tolerance of the platinum catalyst to methanol intermediates.

References:

- [1] H. Huang, Journal of Power Sources, 239 (2013) 189-195
- [2] S. Sharma et.al., J Phys Chem C, 34 (2011) 17009-17019

Low Energy Intensive Electrochemical Reduction of Chromium contaminated wastewater and soil matrices

*Saranya Sriram,^{a,b} Raghuram Chetty,^a Indumathi Nambi,^b
^a Department of Chemical Engineering, ^b Department of Civil Engineering
Indian Institute of Technology Madras, Chennai, India.
*Email: sharan_shree@yahoo.co.in

Hexavalent chromium (Cr^{+6}), a human carcinogen is widely distributed heavy metal in surface, groundwater and soil matrices and is categorized one amongst the national priority pollutant (USEPA). The discharge of Cr^{+6} is prima facie from tannery, textile dyeing or electroplating industries. Though they exist in several oxidation states (from -2 to +6), the most potent forms are +3 (non toxic, insoluble) and +6 (highly toxic, soluble). Various *in-situ* and *ex-situ* treatment technologies such as physical, chemical and biological is well established for remediating Cr^{+6} contaminated wastewater and soil; but several of them have limitations such as generation of secondary wastes, high capital cost, low reliability and efficiency. Electrochemical technologies (ET) on the other hand, offer advantages of clean energy system operable at ambient conditions without the generation of any residual contamination. Though ET is widely accepted, the critical barrier that exists with this technology is the energy expended and the stability of the electrodes at high voltage applications.

Thus our present study investigated the reduction of Cr^{+6} at cathode by assessing the synergistic effect of a suitable electrolyte additive at the anode compartment. Several waste materials were explored to curtail the input energy to our system (from 10V to 5V), and amongst all alkaline urea (a nitrogenous waste) served the best to enhance the reduction of acidic Cr^{+6} . Furthermore, tailoring bare Ti substrate to nanoporous materials, a best performance of 97.7 % reduction of aqueous Cr^{+6} was obtained in 15 mins at 5V. As we were successful with aqueous systems, the study was further extrapolated to clayey soil matrices to mimic a natural environment. Hence, we could simultaneously achieve the dual benefit of remediating Cr contaminated wastewater and soil with oxidation of a nitrogenous waste as an anolyte fuel. The present study aimed in enhancing the energy and treatment efficiency of existing ET, and thus can find its application on field scale on par with several *in-situ* techniques.

Keywords: Chromium removal, electrochemical reduction, low energy intensive system.

Development of a self-cleaning wall-jet flow cell for continuous quality monitoring in drinking water distribution systems

Robert Euan Wilson,^a Ivan Stoianov,^a Danny O'Hare,^b

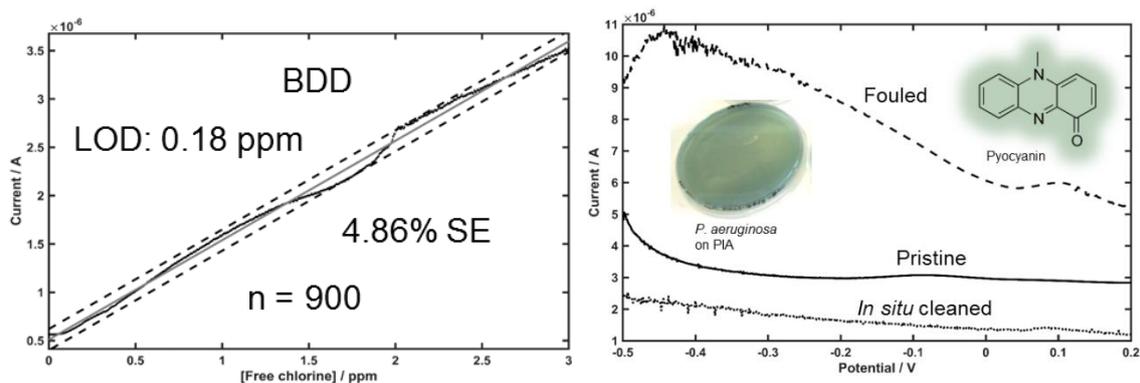
a) Department of Civil and Environmental Engineering, Imperial College London

b) Department of Bioengineering, Imperial College London

Email: r.wilson14@imperial.ac.uk

Long-term, continuous monitoring with electrochemical sensors in complex media is challenging due to the effects of biofouling. Drinking water biofilms reduce the performance of sensors by inhibiting mass transport to the sensor surface. Boron-doped diamond (BDD) electrodes are more resistant to biofouling than conventional electrodes, and remain inert at high potentials. These properties can be exploited to produce a sensor that can resist biofouling, and electrochemically remove biofilm on sensor surfaces, without disassembly or disconnection. Incorporating BDD into a wall-jet flow cell, a geometry that is highly scalable with minimal dead volume, has resulted in the production of prototype self-cleaning sensors which have been tested in both the laboratory and in a drinking water treatment works.

We have demonstrated that a BDD, wall-jet flow cell is both able to detect free chlorine accurately, with a standard error of 4.86%, and with a limit of detection which is less than the accepted minimum required concentration of 0.2 ppm. Additionally, the prototype sensor was capable of detecting the presence of a drinking water biofilm indicator organism, *P. aeruginosa*. The *in situ* cleaning process also compares very favourably to manual sensor surface cleaning methods. The next generation of prototype sensors based on this technology, and the results of laboratory and field trials, is currently under development. These sensors will be installed in drinking water systems to assess long-term performance of free chlorine detection in a challenging environmental medium.



Left: A calibration curve for the amperometric detection of free chlorine in solutions of sodium hypochlorite in deionised water using a prototype BDD sensor. Right: Detection by square wave voltammetry of electroactive Pyocyanin on biofouled sensors, produced by *P. aeruginosa* in drinking water biofilms, before and after both *in situ* cleaning and chemical cleaning.

Robert E. Wilson, Ivan Stoianov, Danny O'Hare, Biofouling and electrochemical cleaning of a boron-doped diamond free chlorine sensor, *Electrochemistry Communications*, Volume 71, 2016, Pages 79-83, ISSN 1388-2481, <http://dx.doi.org/10.1016/j.elecom.2016.08.015>.

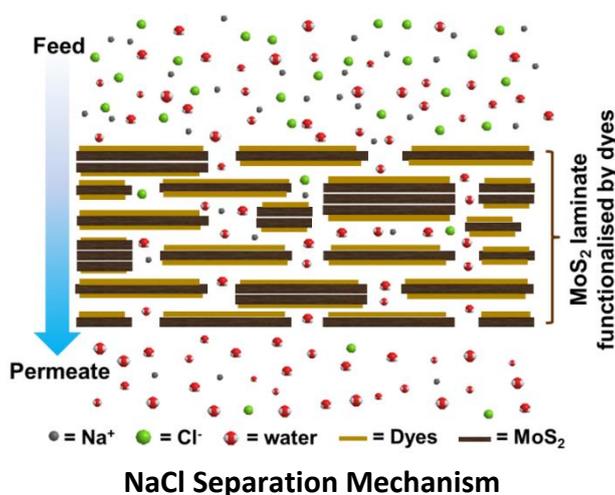
Desalination and Nanofiltration through Functionalised Laminar MoS₂ Membranes

Wisit Hirunpinyopas,^{a,b,c} Eric Prestat,^b Stephen D. Worrall,^c Sarah J. Haigh,^b Robert A. W. Dryfe,^{a,c,*} Mark A. Bissett^{a,b,*}

a) National Graphene Institute, b) School of Materials, and c) School of Chemistry, University of Manchester, Oxford Road, Manchester, UK, M13 9PL

*Email: Wisit.Hirunpinyopas@manchester.ac.uk, *Robert.Dryfe@manchester.ac.uk,
Mark.Bissett@manchester.ac.uk

Laminar membranes consisting of two-dimensional materials are excellent candidates for efficient water filtration applications. The restacking of individual crystal layers leads to the formation of a network of nanocapillaries that can exhibit a molecular and ionic sieving effect, while allowing high water flux. This approach has been exemplified recently with graphene oxide but these membranes suffer from swelling when exposed to liquid water, leading to low salt rejection which is critical for desalination applications. Here we demonstrate that by producing laminar membranes of exfoliated molybdenum disulphide (MoS₂), followed by a simple chemical functionalisation step, we can efficiently filter out the ions commonly found in sea water, while maintaining excellent water flux. These functionalised MoS₂ membranes, which can be produced in a simple and scalable process, are shown to be highly stable in a range of liquid solvents, indicating that they are ideal for a variety of technologically important filtration applications.



The influence of anions on the release of Ag(I) from silver nanoparticles (AgNPs).

A S Nomor and B R Horrocks

School of Chemistry, Bedson building, Newcastle University, NE1 7RU, UK.

Email: a.s.nomor@ncl.ac.uk

Silver nanoparticles (AgNPs) are widely being incorporated into products such as socks [1], sportswear and wound dressings [2] to serve as antibacterials. As these products are washed, the silver nanoparticles are leached and disperse in water where they may release Ag(I) ions. Ag(I) is very toxic to aquatic organisms [3] that make up the base of a series of food chains. In this study, AgNPs were prepared in the presence of various anions and in pure water in order to examine the effect of the medium on the release of Ag(I). The mean hydrodynamic diameters of AgNPs as measured by DLS ranged from 100 nm in the 10 mM chloride before dialysis to 890 nm in the 50 mM sample after dialysis. In general, the increase was due to aggregation. Individual particle sizes as measured by AFM decreased after dialysis; this suggests corrosion of the AgNPs. The release of Ag(I) was monitored by anodic stripping voltammetry at glassy carbon electrodes. We find that: (i) substantial (90 μM) Ag(I) is present in the initial preparation and (ii) the concentration of Ag(I) after 73 h dialysis was about 4 μM irrespective of the concentration of chloride present.

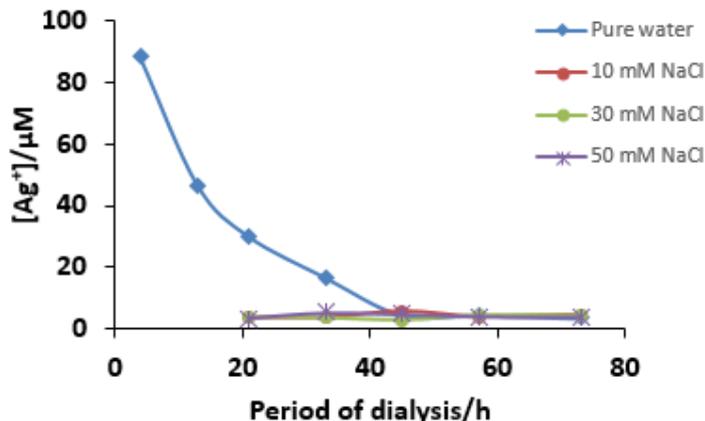


Figure 1. Variation of silver ion concentration in the dialysate with time of dialysis. Four different experiments are shown indicating the composition of the medium against which the sample was dialysed.

References

- [1] T.M. Benn, P.Westerhoff. *Environ. Sci. Technol.* 2008, **42**, 4133-4139.
- [2] A. Hebeish, M.H. El-Rafie, M.A. El-Sheikh, A.A. Saleem, M.E. El-Naggar. *Intnl. Journ. of Macromolecules.* 2014, **65**, 509-515.
- [3] *WHO Guidelines for Drinking-water quality.* 2003. World Health Organisation, Geneva.

Study of model carbon materials with graphitic-N sites for oxygen reduction reaction

Carlota Domínguez^a, Serban N. Stamatina^a, James A. Behan^a, Md. Khairul Hoque^a, Joana M. Vasconcelos^a, Tatiana S. Perova^b and Paula E. Colavita^a

a) School of Chemistry, CRANN and AMBER Research Centres, Trinity College Dublin, Dublin 2, Ireland. b) Department of Electronic and Electrical Engineering, Trinity College Dublin, Dublin 2, Ireland and ITMO University, 49 Kronverskiy pr., Saint Petersburg, 197101, Russia.

Email: dominguc@tcd.ie

Functionalization of carbon materials, especially by nitrogen substitution, can be used to modulate the electronic properties, the morphology and the surface chemistry of carbon materials. Nitrogen-doped carbon materials have showed catalytic activity for the oxygen reduction reaction (ORR), resulting in a potential alternative for the substitution of precious metal catalysts in energy applications, such as metal-air batteries and fuel cells [1, 2]. Nitrogenated carbons typically contain a mix of nitrogen species thus making it difficult to relate an electrochemical response to individual active sites. Pyridinic- and graphitic-N have been attributed as the nitrogen species responsible of the catalytic activity for the ORR [3], however, model electrodes with exclusively pyridinic-N or exclusively graphitic-N remain elusive so far.

Herein, we present the study of amorphous nitrogenated carbon films with only graphitic nitrogen. We report the synthesis, characterization and electrochemical testing of this model nitrogenated carbon materials. Amorphous nitrogenated carbon films were prepared using a combination of physical deposition and thermally-driven reactions yielding nitrogenated carbon materials with smooth topography, excellent electrical contact and homogeneous graphitic-N site presentation. These materials were used to study the effect of these specific sites on the ORR activity. Graphitic-N sites were found to improve the onset potential with respect to the pristine materials. Also, a mixed $2e^-/4e^-$ mechanism was evident from rotating ring disk electrode (RRDE) measurements. Despite the activity observed, graphitic-N sites were found to undergo extremely fast degradation under ORR conditions. We will discuss in-situ electrochemical and ex-situ spectroscopic methods that probe the degradation process.

References

[1] K. Gong, et al., *Science*, 2009, 323, 760. [2] P. Trogadas, et al., *Carbon*, 2014, 75, 5. [3] S. Yasuda, et al. *Chem. Commun.*, 2013, 49, 9627.

N-Doped Carbon Aerogel Supported Cobalt Catalysts by Supercritical Deposition for Oxygen Reduction Reaction

Seçil ÜNSAL^a, Selmi Erim BOZBAĞ^a, Can ERKEY^{a,b}

^a Department of Chemical and Biological Engineering, Koç University, Sarıyer 34450, Istanbul, Turkey

^b Koç University Tüpraş Energy Center (KUTEM), Koç University, Sarıyer, 34450, Istanbul, Turkey
Email: cerkey@ku.edu.tr

Hydrogen fuel cells are promising devices for electricity generation due their higher efficiencies and lower emissions than internal combustion engines. The oxygen reduction reaction (ORR) which occurs at the cathode of a PEM fuel cell has sluggish kinetics and necessitates the usage of expensive catalysts at high loadings for satisfactory fuel cell performance. Although carbon supported Pt catalysts are considered as the best ORR catalysts, high cost of Pt severely hinders the widespread commercialization of fuel cells. To overcome this obstacle, development of low-Pt, Pt-free and even metal free carbon based nanomaterials for ORR has been attracting increased attention. Among these, transition metal containing (usually Co, Fe) N-doped carbon materials are the most promising candidates. N-doped carbon aerogels (CAs) are attractive alternatives to conventional N-doped carbons in preparation of non-noble metal based ORR catalysts due to their unique properties such as high surface area, high porosity, high electrical conductivity and tunable morphological architecture. Conventional techniques to prepare supported metal catalysts are not quite suitable for aerogels because of the high surface tension of the liquids which can cause the collapse of the nano-sized pores of the aerogels. An alternative route for the preparation of aerogel supported metal nanoparticles is supercritical deposition (SCD). The use of scCO₂ for the preparation of aerogel catalysts is advantageous since the low surface tension prevents the collapse of nano-sized pores. SCD consists of the dissolution of a metal complex in a supercritical fluid with subsequent adsorption on the interior surface of porous support followed by the conversion of the metal complex to its metal form. In this study, we prepared highly active N-doped CA supported Co catalysts using SCD combined with ammonia treatment. Firstly, resorcinol formaldehyde aerogels were contacted with a solution of cobalt acetylacetonate (Co(acac)₃) in scCO₂ at 20 MPa and 353 K. The cobalt precursor was found to adsorb and react on the surface of the organic aerogel. Subsequently, the resulting sample was subjected to pyrolysis performed under NH₃ flow resulting in N-doped CA supported Co catalysts. The effects of cobalt loading and pyrolysis temperatures ranging from 700 °C to 900 °C on the properties of the electrocatalysts were investigated. Nitrogen content decreased with increasing pyrolysis temperature and different types of C-N sites, as well as Co-N and metallic Co were detected on the samples by XPS. The electrochemical characterization of the catalysts was performed using cyclic voltammetry (CV) and Rotating Disk Electrode (RDE) measurements. The electrocatalyst pyrolyzed at 800 °C had the highest ORR activity which was 11.03 mA/mg_{catalyst} as determined from the current density at 0.8 V vs RHE in 0.1 M KOH solution. To the best of our knowledge, this is the highest value reported in the literature so far. It also had an onset potential of 1.01 V vs RHE where the cathodic current reached 0.1 mA/cm² compared to 1.04 V for Pt/CA.

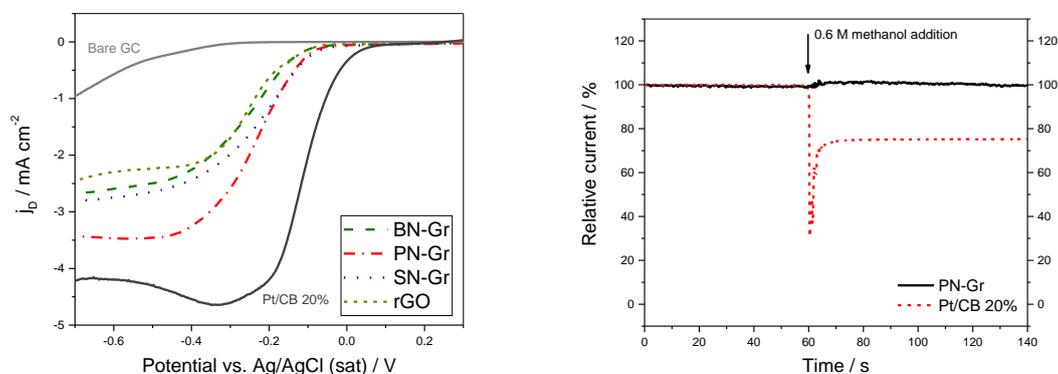
Graphene doped with boron, nitrogen, phosphorus and sulfur as metal-free electrocatalysts for the oxygen reduction

Miguel A. Molina-García*, Neil V. Rees

Doctoral Training Centre in Fuel Cells and their Fuels, School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK. *

E-mail: MAM367@bham.ac.uk

Doping graphene with heteroatoms, such as B, N, P or S, can tailor the properties of the 2D structure of graphene¹ and increase the catalytic activity towards the oxygen reduction reaction (ORR) with respect to pristine graphene.² Here we present a new study in which we compare the performance of single, dual, ternary and quaternary-doped graphene electrocatalysts in terms of physical characterisation and electrochemical performance. The doping-precursor agents are boric acid, melamine, orto-phosphoric acid and benzyl disulfide. These are mixed with a commercial graphene oxide (GO) and subjected to a thermal treatment at 900 °C during 2 hours under a protective N₂ atmosphere. The resulting catalysts are physically characterised using HR-TEM, XRD, Raman and XPS, while the electrochemical ORR performance is evaluated by CV measurements and the number of electrons transferred during the reaction are obtained *via* direct determination of peroxide intermediate by rotating-ring disk electrode measurements. The results demonstrate that the single, ternary and quaternary-doped catalysts do not improve significantly the performance with respect to thermally reduced GO without doping. Nevertheless, dual-doped graphene shows a significant improvement with respect to the other catalysts, especially in the case of PN-Gr (Fig. left). The better performance of the dual-doped graphene catalysts is attributed to a synergistic effect between the two different elements incorporated into the active 2D graphene structure.³ In addition, comparative tests of methanol tolerance conclude that the doped-graphene catalysts are not affected by the presence of methanol, whereas a commercial Pt/C catalyst suffers a 25% of performance decrease in presence of a 0.6 M methanol concentration (Fig. right).



References: [1] X. Wang, G. Sun, P. Routh, D-H. Kim, W. Huang, P. Chen, *Chem. Soc. Rev.*, 43 (2014), 7067. [2] C-H. Choi, S-H. Park, S-I. Woo, *ACS Nano*, 6 (2012), 7084. [3] Z. Wei, R. Li, X. Gou, *ACS Catal.*, 5 (2015), 4133.

Elucidating the Mechanism of High-Rate and High-capacity Lithium-ion Intercalation in Bulk Complex Oxides

Kent Griffith

University of Cambridge

Email: kg376@cam.ac.uk

Energy storage materials with both high capacity and high charge/discharge rate enable applications that require long life, high power, and rapid recharge. Electric double-layer capacitors offer high power and battery electrodes offer relatively high capacity but the combined properties require advanced materials. While nanostructures have dominated this emerging field, there are well-known issues regarding cost, stability, scalability, and safety of nanoparticles for battery applications. Recently, we have demonstrated and characterised complex oxide structures from facile solid-state synthetic methods with promising rate, capacity, and stability for reversible lithium intercalation.¹ Dense particles with high packing density of non-nanostructured T-Nb₂O₅ were shown to intercalate lithium at high rates with capacity performance and retention similar to the best nanostructured analogues; a mechanistic investigation was undertaken to explain this novel behaviour.

References

1. Griffith, Kent J.; Forse, Alexander C.; Griffin, John M.; Grey, Clare P. High-Rate Intercalation without Nanostructuring in Metastable Nb₂O₅ Bronze Phases. *J. Am. Chem. Soc.* **2016**, *138*, 8888–8899.

Effect of different ionomers on the performance of alkaline exchange membrane (AEM) fuel cells

Gaurav Gupta, Mohamed Mamlouk

*School of Chemical Engineering and Advanced Materials,
Newcastle University, UK*

Email: gaurav.gupta2@newcastle.ac.uk

The current AEM fuel cells can be operated only up to 50 °C which limits the performance of the system and requires the use of expensive cooling system and balance of plant. However in order to commercialize the system and operate up to 70 °C at par with proton exchange membrane (PEM) fuel cells, the membranes and ionomers which are stable at higher temperatures needs to be developed. The cost of the systems can be further reduced in comparison to PEM fuel cells by the use of non-noble metal catalyst. This presentation will highlight the results obtained using different ionomers i.e. PVBC-TMA (polyvinyl benzyl chloride - trimethyl amine), SEBS (Styrene-Ethylene Butylene-Styrene) and commercial ionomer with an aim to increase the performance and operating temperature of the fuel cell to 70 °C.

The Relationship Between Synthesis, Formulation and Performance of Low Cost Non Platinum PEM Fuel Cell Catalysts

Laura Allerston,^a Neil V. Rees^a

*a) Centre for Doctoral Training in Fuel Cells and Their Fuels,
School of Chemical Engineering, The University of Birmingham, Birmingham, B15 2TT
Email: lxa482@bham.ac.uk*

A collaborative research project between Amalyst and The University of Birmingham is seeking to evaluate synthesis and formulation alternatives to Amalyst's current process for making platinum replacement fuel cell catalysts.

Although the sluggish cathode catalyst reaction attracts far more research, there is still scope to improve the much faster hydrogen oxidation reaction at the anode. By moving away from pure Pt catalysts in PEM fuel cells, not only can cost savings be made but CO poisoning can be reduced as well as possible augmented activity and stability.

In addition to characterising synthesised catalysts for their polarisation performance, accelerated stress testing is being used as a proxy for in-service transients that are often the cause of significant damage to Pt based materials. Results are presented to show current progress in this collaborative study.

Effects of Sn anode-infiltration on direct-biogas SOFC's electrochemical performance

Lina Troskialina,^{a,b} Aman Dhir^a, Robert Steinberger-Wilckens^a

a) University of Birmingham, Birmingham, B15 2TT, United Kingdom

b) Politeknik Negeri Bandung, Bandung 40559, Indonesia

Email : l.troskialina@bham.ac.uk

This work presents a novel method of Sn-infiltration on SOFC anodes for direct-biogas operation and the effects of Sn-infiltration on the SOFCs' electrochemical performance. Operating an SOFC directly with hydrocarbon fuel poses risks of low efficiency and formation of deleterious carbon. This work shows that Sn infiltration on NiYSZ anode improves the SOFC's efficiency with very low formation of carbon. Sn-infiltrated NiYSZ SOFCs containing varied amounts of Sn were manufactured. Operating in simulated biogas of 1:2 volume ratio of CO₂:CH₄, these SOFCs were tested for their electrochemical performance and quantity of deposited carbon. At 750 °C with H₂ as fuel, non-infiltrated NiYSZ SOFCs were able to generate 350 mA cm⁻² current at 0.7 V; however, when simulated biogas was introduced, current dropped significantly to 90-200 mA cm⁻². On the contrary, a series of Sn-infiltrated cells under the same operating conditions performed well both in H₂ and biogas fuels producing 310 to 450 mA cm⁻² depending on the Sn content. The cells showed stable electrochemical performance over 150 hours of operation both in H₂ and biogas without significant carbon formation. Significant supporting data were generated from mass and electrochemical impedance spectra. Mass spectra of the fuel cell outlet gas show Sn-infiltrated SOFCs produced much more H₂ and CO than the non-infiltrated SOFCs did. Impedance spectra show much lower polarisation resistance observed on Sn-infiltrated cells than those observed on non-infiltrated ones. Several possible mechanisms are proposed to explain the phenomena. These include (i) Sn forms surface Sn-Ni alloy on NiYSZ anode which alters Ni catalytic activity^[1], (ii) Sn breaks Ni atoms ensemble in the surface structure associated with carbon formation^[1,2] (iii) Sn changes the Ni surface electronic structure associated with critical shifts in the Ni d-band electronic centre which in turns change Ni chemical activities and catalytic performance^[2]. More work is required to further evaluate the electrochemical performance in relation to the anode surface and electronic characteristics. So far the results of this work are promising in that Sn-infiltrated NiYSZ-based SOFC can be operated on simulated direct-biogas under dry reforming mode with high electrochemical performance and low carbon deposition.

References:

1. Troskialina, L., A.Dhir, R.Steinberger-Wilckens, *Improved Performance and Durability of Anode Supported SOFC Operating on Biogas*, ECS Transactions, **68** (1) 2503-2513 (2015)
2. Nikolla, E., J. Schwank, and S. Linic, *Measuring and Relating the Electronic Structures of Nonmodel Supported Catalytic Materials to Their Performance*. Journal of the American Chemical Society, 2009. **131**(7): p. 2747-275.

Keynote: Kylie Vincent

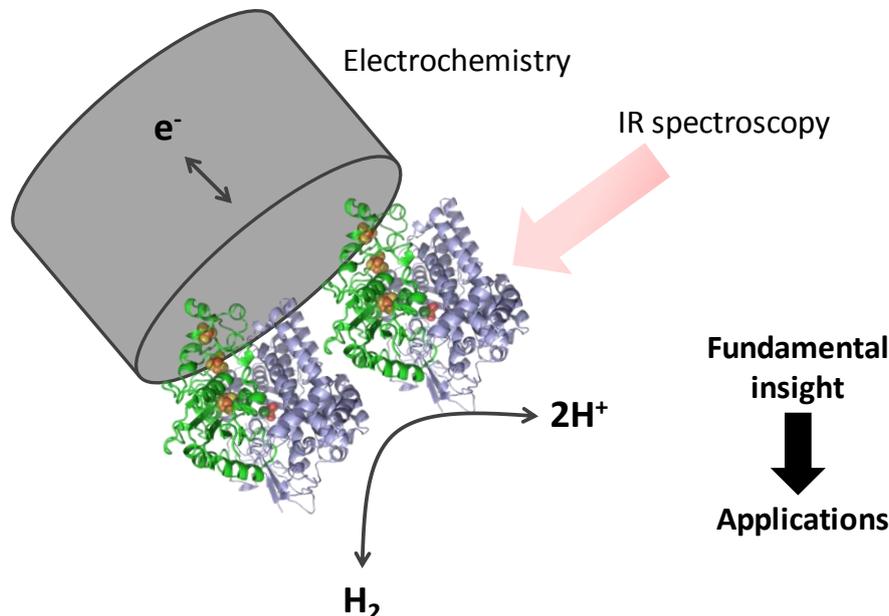
Hydrogen energy in biology: learning from nature's electrocatalysts

Philip A. Ash, Holly A. Reeve, Kylie A. Vincent

University of Oxford, Department of Chemistry, Inorganic Chemistry Laboratory, South Parks Road, Oxford, OX1 3QR, UK.

Email: kylie.vincent@chem.ox.ac.uk

Hydrogen is widely used in the microbial world as an energy source or sink, and nature has a specially tailored array of catalysts (enzymes) for redox reactions to manage hydrogen utilisation, storage and production. In our research, we are interested in studying the mechanisms of these enzymes to see how we might learn from nature's finely tuned catalysts. To do this, we separate individual enzymes from their biological redox circuits and interface them with electrodes. In this way, we interpret the current response as the enzyme engages in electrocatalysis on an electrode, alongside spectral information from in situ infrared spectroscopy probing the enzyme at the electrode interface.¹ What we have learnt about hydrogen in biology has inspired development of a technology for hydrogen-driven synthesis of fine chemicals, relying on cascades of redox enzymes 'plugged in' to conductive carbon beads.² This talk will cover some of our fundamental studies of hydrogenases as electrocatalysts, through to development of applications in clean chemical synthesis.



1. Hidalgo, R., Ash, P.A., Healy, A.J., Vincent, K.A. 'Infrared Spectroscopy During Electrocatalytic Turnover Reveals the Ni-L Active Site State During H_2 Oxidation by a NiFe Hydrogenase' *Angew. Chemie. Int. Ed.* 2015, 54, 7110-7113.

2. Reeve, H.A., Ash, P.A., Park, H., Huang, A., Posidias, M., Tomlinson, C., Lenz, O., Vincent, K.A., 'Enzymes as modular catalysts for redox half reactions in H_2 -powered chemical synthesis: from biology to technology', *Biochemical Journal*, 2017, 474, 215-230.

Living electrodes: using microbes as electrocatalysts for a sustainable future.

Paul Kavanagh,^a Krishna Katuri,^b Partha Jana,^b Donal Leech,^b Florence Abram^c

a) School of Chemistry and Chemical Engineering, Queens University Belfast, David Keir Building, Stranmillis Road, BT9 5AG Belfast, UK

b) School of Chemistry, National University of Ireland Galway, University Road, Galway, Ireland

c) School of Natural Sciences, National University of Ireland Galway, University Road, Galway, Ireland

Email: p.kavanagh@qub.ac.uk

A class of microbes, known as 'electrogens', are capable of directly exchanging electrons with an adequately polarised solid electrode (1). Naturally, such microbes, which are mainly anaerobic, use electron acceptors / donators, such as iron oxide, present in their environment as oxidising / reducing equivalents for respiration. Bio-corrosion is a common example of this process. In the last twenty years intensive research has focused on using this class of microbes as catalysts for electrochemical reactions. *Geobacter* and *Shewanella* species are two of the most widely studied 'electrogenic' bacteria which form thick electron conducting biofilms on electrodes. Such biofilms oxidise complex organic molecules down to CO₂ and transfer liberated electrons to the electrode leading to applications in wastewater treatment and bioremediation (2). Although the ability of these biofilms to conduct electrons is well established, the mechanism by which electrons are transferred from within the cell cytoplasm, across a double membrane, through the biofilm, and to the solid electrode is still unclear. In this presentation, we present insights into this mechanism using a combination of voltammetric and proteomic analysis of biofilms (3,4). We also present how 'electrogenic' biofilms immobilised at electrodes may be utilised in emerging electrochemical carbon capture and utilisation technologies.

References

3. A. Kumar, L. Huan-Hsuan Hsu, P. Kavanagh, F. Barrière, P.N.L. Lens, L. Lapinsonniere, V. Lienhard, U. Schröder, X. Jiang, D. Leech, *Nat. Rev. Chem.* 2017, 1, 0024.
4. D. R. Lovely, *Curr. Opin. Biotechnol.* 2008, 19, 564–571
5. P.S. Jana, K. Katuri, P. Kavanagh, A. Kumar, D. Leech, *Phys. Chem. Chem. Phys.* 2014, 16, 9039-9046.
6. P. Kavanagh, C.H. Botting, P.S. Jana, D. Leech, F. Abram, *J. Proteome Res.* 2016, 15, 4135-4145.

Biopower and biosensors: aspects of enzymatic electrodes

Richard Bennett^a, Peter Ó Conghaile^b, Dónal Leech^a

^aBiomolecular Electronics Research Laboratory, School of Chemistry & Ryan Institute, National University of Ireland Galway, Ireland.

^bNational Centre for Sensor research, Dublin City University, Dublin
Email: r.bennett1@nuigalway.ie

Applications of biomedical devices as implantable and semi-implantable systems such as sensors, valves and pumps is of increased importance. These devices rely heavily on battery power which are reliant on re-charging or sufficient reagents contained within. An alternative strategy is fuel cell technology, using readily available in-vivo substrates (glucose and oxygen) as fuel and oxidant. This is difficult to achieve using chemical catalysts as they are non-selective and operate under harsh conditions (pH and temperature). Enzymes as catalysts offer an alternative route towards powering of such devices. Enzymatic active sites are selective and operate under mild conditions thus offering a potential solution for semi-implantable devices.

Here we report on co-immobilisation of osmium based redox complexes and support polymers with specific enzymes on electrode surfaces. These enzymes are capable of substrate catalysis (glucose oxidation and oxygen reduction) [1]. Tailoring of the osmium redox potential to the enzyme active site improves electron transfer to electrode surface. Combining enzyme and redox centre with nano supports such as carbon nanotubes achieves higher current densities and greater power outputs. This is achieved through refinement of the immobilisation procedures as well as optimisation of the enzyme electrode components.

Our research compares the electropolymerisation of L-dopa with the dropcoating of polymer supports as a route towards immobilisation. Current densities of 0.25 mA cm⁻² have been achieved to date. A design of experiment approach to component optimisation has been used to improve anodic current density using glucose dehydrogenase. Previous work improved current density by 32% over traditional approaches [2].

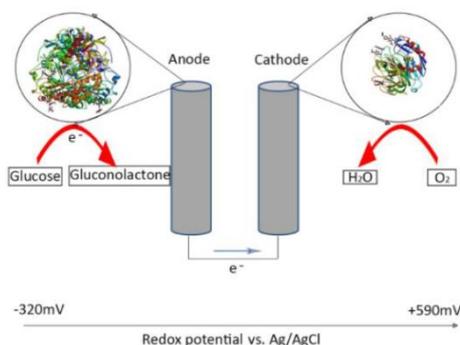


Figure 1: Schematic representation showing the principle of an enzymatic fuel cell with the immobilisation of a glucose oxidising enzyme on the anode and an oxygen reducing enzyme on the cathode.

1. Ó Conghaile, Peter, et al. *Analytical chemistry* 88.4 (2016): 2156-2163.
2. Kumar, R.; Leech, D. *Bioelectrochemistry* 106 (2015): 41–46.

Solution-Processed Cascaded-Junction Quantum Dot Solar Cells

Dr. Bo Hou^a, Prof. SeungNam Cha^a and Prof. Jongmin Kim^b

a) Department of Engineering Science, University of Oxford, Parks Road, Oxford OX1 3PJ, U.K.

b) Department of Engineering, University of Cambridge, 9 JJ Thomson Avenue, Cambridge CB3 0FA U.K.

*Email: *Bo.Hou@eng.ox.ac.uk*

The infinitesimal semiconducting nanocrystals, which are called ‘quantum dot’ (QD) have been shining the light to the next generation solar cells. The advantage of employing the photoactive semiconductor in the state of QD is due to the band gap (ϵ_{gap}) tuning accessibility and solution-processed reproducibility. Due to the size-dependent quantum confinement effect, the QD ϵ_{gap} can be easily adjusted by tuning the size. Lead sulphide (PbS) QDs is considered as one of the most promising candidates for QDs solar cell due to wide ϵ_{gap} adjustability from NIR to visible emission spectrum.¹ PbS QDs have been deployed into different types of solar cell system, such as DSSC type solar cell, Schottky junction solar cells, p-n junction solar cells and organic dye hybrids solar cells. PbS QDs solar cell (QDSC) has been improved their light harvest efficiency dramatically in recently years. Up to now, the lab scale cell efficiency has been achieved by around 10%. Recently, we elucidate an efficient and reliable synthesis protocol for fabricating high-quality PbS QDs. Through adjusting the precursor concentration systematically, in a fixed reaction time, a wide range of different sizes of colloidal PbS QDs is produced with a narrow size distribution and high reproducibility.² Typically, in QDSC, the PbS QD films are ligand exchanged from pristine oleic acid to tetrabutylammonium iodide or 1, 2-ethanedithiol for efficient charge depletions. ZnO nanoparticles which spin coated on top of ITO play a role as electron depletion layer and also forming a quasi ‘p-n’ junction with the QDs. In the end, gold films are deposited by thermal evaporator on the QD films as an anode electrode. Based this structure, we have achieved a lab-scale device power conversion efficiency (PCE) above 8%. In the end, based on the understanding of optical-electrical properties of as-prepared PbS QDs and QDSCs, three distinct sizes PbS QDs are selected and tentatively fabricated into Cascaded-Junction solar cells. The elaborately designed devices show impressive high PCE (9.05%) and short circuit current density (32.51mAcm^{-2}) compared with previously reported devices.²

1. Hou, B.; Cho, Y.; Kim, B. S.; Ahn, D.; Lee, S.; Park, J.B.; Lee, Y.-W.; Hong, J.; Im, H.; Morris, S. M.; Sohn, J. I.; Cha, S.; Kim, J. M. *J. Mater. Chem. C* **2017**, 5, 3692-3698.

2. Hou, B.; Cho, Y.; Kim, B. S.; Hong, J.; Park, J. B.; Ahn, S. J.; Sohn, J. I.; Cha, S.; Kim, J. M. *ACS Energy Lett.* **2016**, 834-839.

Photo-Induced Electron Transfer at Porphyrin Sensitised Water-Oil Interfaces for Solar Energy Conversion

Micheál D. Scanlon,^a Andrés F. Molina Osorio^a

*a) Department of Chemical Sciences & The Bernal Institute,
University of Limerick (UL), Republic of Ireland.
Email: micheal.scanlon@ul.ie*

A photoactive assembly of photosensitizer aggregates at an electrified immiscible water-oil interface, often termed the *interface between two immiscible electrolyte solutions* (ITIES), may achieve **incident-photon-to-current conversion without using solid electrodes to effect charge separation** by a process known as photo-induced heterogeneous electron transfer [1], as detailed in **Fig. 1**.

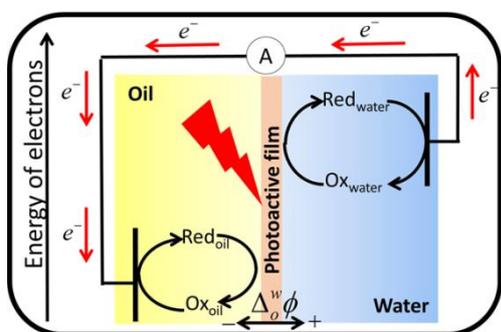


Fig. 1: Scheme illustrating the concept that photoactive films trap solar energy, generating high-energy electrons. In theory this allows electron transfer across the interface between redox couples that thermodynamically are incapable of heterogeneous electron transfer in the dark due to their respective redox potentials in each phase.

The basic design of all solar energy conversion devices necessitates **the efficient harvesting of light energy combined with an embedded asymmetry in the charge separation process**. The ITIES possess attributes to fulfil this remit including: (i) their ease of functionalisation with light harvesting photosensitizer molecules; and (ii) the separation of photoproducts on either side of the interface by local hydrophobicity gradients beneficially limiting unwanted recombination pathways to improve charge separation.

In this presentation, the dynamics of the different charge transfer reactions (rates of electron transfer, photoproduct separation; *etc.*) during the photo-induced heterogeneous electron transfer process at an ITIES functionalized with interfacial supramolecular assemblies of zinc tetrakis(4-carboxyphenyl) porphyrin (ZnTPPC) were studied by **photocurrent transient** and **intensity modulated photoelectron spectroscopy (IMPS)** measurements [2-3], commonly applied to DSSCs. These photoelectrochemical experiments allow us to identify the precise experimental conditions required (in terms of interfacial aggregate surface coverage, aqueous phase pH, magnitude of the interfacial electrical polarization, *etc.*) to **maximise the photoconversion efficiencies possible at the ITIES** (currently unsatisfactorily < 1 %).

- References:** [1] Fermin, D.J. *et al.*, *Phys. Chem. Chem. Phys.*, (1999), **1**, 1461.
[2] Eugster, N. *et al.*, *J. Phys. Chem. B.*, (2002), **106**, 3428.
[3] Eugster, N. *et al.*, *J. Am. Chem. Soc.*, (2003), **125**, 4862.

Tuning the size and shape of novel nanoscale metal oxide photocatalysts using the cathodic corrosion method

Matthew Lawrence[‡], Matthew L. Kromer[§], Alex Yanson[&], Joaquin Rodríguez-López^{§*},
Paramaconi Rodríguez^{‡*}

[‡]*School of Chemistry, University of Birmingham, Edgbaston, B15 2TT, UK*

[§]*Department of Chemistry, Beckman Institute, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA.*

[&]*Cosine Measurement Systems, Oosteinde 36, 2361 HE, Leiden, The Netherlands*

*Email: joaquinr@illinois.edu ; P.B.Rodriguez@bham.ac.uk

Growing energetic demands, in conjunction with the ever-growing consensus surrounding the increasing adverse effects of climate change and global warming, have led to much research dedication to the development of renewable energy technologies. A hydrogen economy has long been sought after, but with most the earth's hydrogen stored in water and the main source of hydrogen production involving the burning of fossil fuels, a widely applicable alternative is required.

Transition metal oxide semiconductors were first shown to be active towards hydrogen evolution from water under UV-irradiation by Fujishima and Honda.¹ Nanoscale photocatalysts are desired to overcome the limitations surrounding the low natural abundance of solar UV light by modifying the semiconductor band gaps to harness more of the visible spectrum and minimize ion carrier migration distances. Current state-of-the-art photocatalysts include TiO₂, FeTiO₃, H₂WO₄, BiVO₄ and their metal-doped analogues.

Cathodic corrosion^{2–4} is a powerful tool for the electrochemical synthesis of nanomaterials with enhanced electrochemical properties. Here we demonstrate that the particle size and shape of mixed transition metal oxide semiconductor nanoparticles can be tuned by changing the synthesis conditions. This has resulted in an effective way to change the photocatalytic properties of the nanomaterials. The structure-reactivity relationship for the photocatalytic water oxidation will be presented.

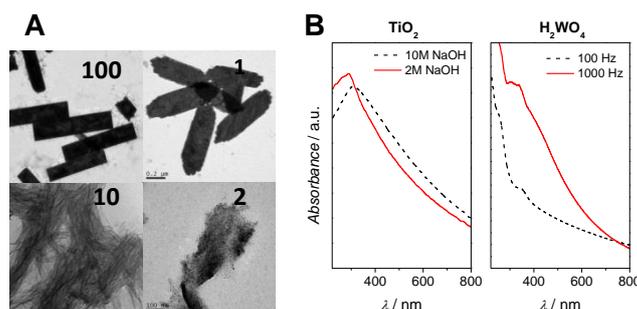


Figure 1. (A) TEM images of H₂WO₄ (top) and TiO₂ (bottom) nanoparticles synthesized by cathodic corrosion using varying conditions as indicated in the figure; frequency of the square wave form and concentrations of NaOH (B) UV-vis absorption spectrum of the H₂WO₄ and TiO₂ nanoparticles.

References

- 1 A. Fujishima and K. Honda, *Nature*, 1972, **238**, 37–38.
- 2 A. I. Yanson, P. Rodriguez, N. Garcia-Araez, R. V. Mom, F. D. Tichelaar and M. T. M. Koper, *Angew. Chemie - Int. Ed.*, 2011, **50**, 6346–6350.
- 3 P. Rodriguez, F. D. Tichelaar, M. T. M. Koper and A. I. Yanson, *J. Am. Chem. Soc.*, 2011, **133**, 17626–17629.
- 4 A. I. Yanson, P. V. Antonov, Y. I. Yanson and M. T. M. Koper, *Electrochim. Acta*, 2013, **110**, 796–800.

Effect of water on Cu electrodeposition from a water-containing deep eutectic solvent

Priscila Valverde,^a Sudipta Roy^b, Todd Green^c

a,b) Department of Chemical and Process Engineering, University of Strathclyde, Glasgow

Email: priscila.valverde-armas@strath.ac.uk^a, sudipta.roy@strath.ac.uk^b, todd.green@strath.ac.uk^c

Ionic Liquids (ILs) have been proposed as alternative electrolytes for metal electrodeposition. Deep Eutectic Solvents (DESs) are a novel type of ILs tolerant to water. Moreover, DESs formulated from quaternary ammonium salts and hydrogen bond donors are promising electrolytes since they are water tolerant and they are available at a reasonable cost. Although DESs are hygroscopic and absorb water from the atmosphere, earlier studies to plate Cu have concentrated on low-water containing DESs (<0.5 wt% H₂O). However, for DESs to become exploitable, metal deposition from water-containing electrolytes requires to be investigated.

In this work, we have endeavoured to establish a quantitative correlation that might explain the effect of water content on the electrolyte and on Cu deposition process. The intrinsic concentration of water in the electrolyte was measured using Karl Fischer titration. Thereafter, to quantify the electrolyte uptake of water a time-dependant test was conducted. After adding various concentration of water to the electrolyte determined from the time-dependant experiment (3 to 15 wt%), the influence of water content was examined with polarisation experiments collected using a rotating disc electrode. Finally, Cu deposition was carried on steel substrata from electrolytes containing different weight percentages of water. Cu deposits were characterised with Scanning Electron Microscopy (SEM) (Figure 1) and Energy Dispersive X-ray Spectroscopy (EDS).

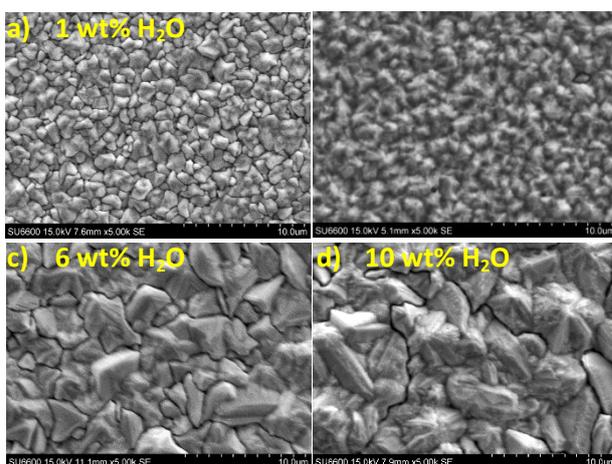


Figure 1. Micrographs of Cu deposits electroplated using an inert anode at 25 °C, rotation speed of 700 rpm from water-containing electrolytes (a) 1 wt%, (b) 3wt%, (c) 6wt% and (d) 10 wt% total H₂O.

Different water contents in the electrolyte reduced the viscosity of the liquid which promotes the diffusivity of Cu²⁺ ions in the liquid. As a result, the limiting currents of the process increased. Higher water content changed the morphology of Cu films. Even at low water content (~3 wt%), the current distribution on the deposits is non-uniform. Furthermore, adding H₂O worsens the already uneven current distribution leading to less uniform Cu deposits.

A New Procedure for the Template Synthesis of Metal Nanowires

J.E. Graves^a, M.E.A. Bowker^a, A. Greenwood^b

C. Ponce de León^c, F.C. Walsh^c

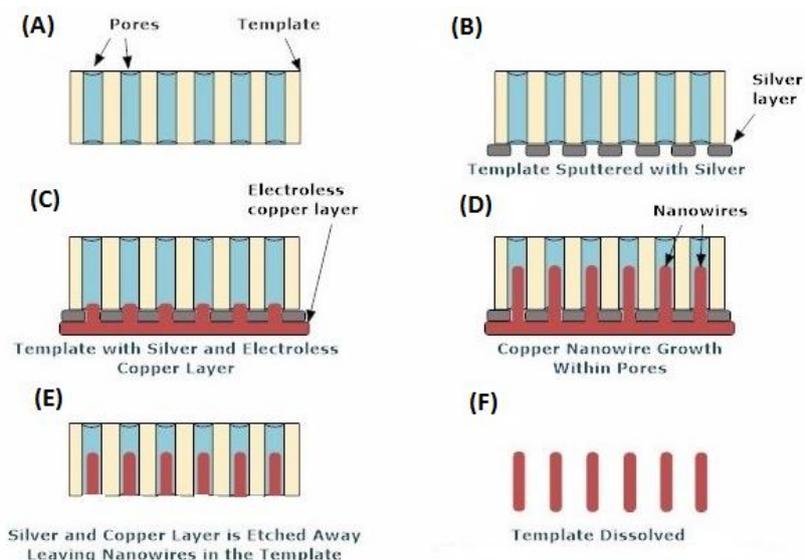
a) Centre for Manufacturing and Materials Engineering, Coventry University, CV1 5FB

b) Faculty of Health and Life Sciences, Coventry University, CV1 5FB, UK

c) Electrochemical Engineering Laboratory, Energy Technology Research Group, Engineering Sciences and the Environment, University of Southampton SO17 1BJ, Southampton University

Email: j.graves@coventry.ac.uk

Metal nanowires fabricated by electrochemical template deposition have been investigated in a wide variety of applications for energy generation^{1,2}. This work describes a new procedure for the fabrication of metal nanowires by template assisted electrodeposition. Porous polycarbonate membranes were chosen as templates, (A). A thin silver sputtered film, typically < 15 nm in thickness, was deposited on one side of the template (B). The layer was used to catalyse electroless copper deposition and a copper layer was grown to a thickness of 500 nm in less than 10 mins (C). The deposited layer ensured the pores on one side were completely covered and the electrode layer had a high electrical conductivity for good uniform growth of the nanowires by electroplating (D). Furthermore, the copper layer could be easily removed, using a chemical etchant (E), to aid the release of the nanowires from the template (F). To demonstrate the process, copper nanowires were prepared by controlled potential deposition and characterised by SEM and TEM. This new procedure has the potential to be applied to the preparation of a wide range of metallic nanostructures over a wide range of scale; it avoids the need for an extended vacuum deposition step and has the advantage of using inexpensive metals in a combined vacuum / wet chemical process to form the important electrode layer for nanowire growth.



References

1. T. Chang et al., *Electrochimica Acta* 161 (2015) 403–407.
2. W. Yan et al., *Electrochimica Acta* 134, (2014) 266-271.

Copper turmeric electrochemically deposited composite coatings

R. J. Merrill^a, Dr A. Cobley^b Dr J. E. Graves, and Dr J. Beddow

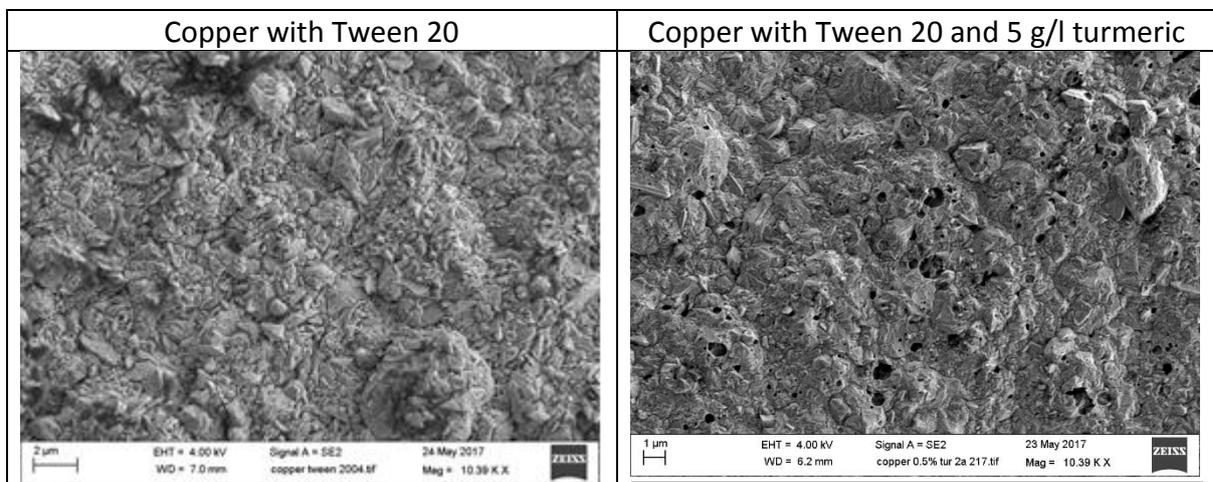
*The Functional Materials Research Group, Centre for Manufacturing and Materials Engineering,
Coventry University, Coventry, United Kingdom*

Email: merrillr@uni.coventry.ac.uk

Composite coatings can be used to change the surface properties of a material whilst leaving the underlying material unchanged. As such they have been used in corrosion resistance, wear resistance, thermal resistance and even antibacterial applications. Composite coatings can be produced by several methods including electrochemical deposition [1-8]. Electrochemical deposition factors such as current density, type of particle (also concentration), and bath composition can all effect the morphology and characteristics of the coating, making it of great academic interest [8]. Unfortunately, composite materials are notoriously difficult to recycle and particles that are used in them are often expensive requiring energy intensive production, making them unsustainable in the long term [9]. The Aim of this research was to produce composite coatings by electrochemical deposition, using a more sustainable source of particles that had not previously been electrochemically deposited.

Turmeric is a common kitchen spice which is often used in Indian cuisine; it has been shown to have strong antibacterial activity [10]. A known amount of turmeric was placed in an acid copper electrolyte with 10 ml/l of Tween 20, and deposited onto a substrate. The concentration of turmeric and the current density used to deposit it were varied. The morphology of the coatings was then examined and the coatings further characterised in terms of hardness, contact angle and antibacterial activity.

Results have shown that the addition of just a small amount of turmeric to the plating bath had a significant effect on the morphology of the deposit and increased both the hardness and the contact angle of the composite coating. Although the composite coating did show strong antibacterial activity, pure copper showed stronger antibacterial activity.



- [1] P. Baumli, A. Al-Azzawi, METHODS OF COMPOSITE COATING: A REVIEW, *Materials Science and Engineering*. 40 (2015) 26-32.
- [2] Y.T. Pei, J.H. Ouyang, T.C. Lei, Y. Zhou, Microstructure of laser- clad SiC-(Ni alloy) composite coating, *Materials Science & Engineering A*. 194 (1995) 219-224.
- [3] Y.T. Pei, T.C. Zuo, Gradient microstructure in laser clad TiC- reinforced Ni- alloy composite coating, *Materials Science & Engineering A*. 241 (1998) 259-263.
- [4] F. Liu, Y. Deng, X. Han, W. Hu, C. Zhong, Electrodeposition of metals and alloys from ionic liquids, *J. Alloys Compounds*. 654 (2016) 163-170.
- [5] Q. Ming, L.C. Lim, Z.D. Chen, Laser cladding of nickel- based hardfacing alloys, *Surf. Coat. Technol.* 106 (1998) 174-182.
- [6] G. Kaptay, Interfacial Phenomena during Melt Processing of Ceramic Particle-Reinforced Metal Matrix Composites. Part I. Introduction (incorporation) of solid particles into melts, *Materials Science Forum*. 215-216 (1996) 459-466.
- [7] O. Verezub, Z. Kálazi, G. Buza, N.V. Verezub, G. Kaptay, In- situ synthesis of a carbide reinforced steel matrix surface nanocomposite by laser melt injection technology and subsequent heat treatment, *Surf. Coat. Technol.* 203 (2009) 3049-3057.
- [8] F. C. Walsh* C. Ponce de Leon., A review of the electrodeposition of metal matrix composite coatings by inclusion of particles in a metal layer: an established and diversifying technology, *Transactions of the IMF*. 92 (2014) 83-98.
- [9] The SEAC special interest group, Time for strategic change: UK Surface engineering and advanced coatings industry, June 2014 (2014).
- [10] S. Singh, B. Sankar, S. Rajesh, K. Sahoo, E. Subudhi, S. Nayak, Chemical composition of turmeric oil (*Curcuma longa* L. cv. Roma) and its antimicrobial activity against eye infecting pathogens, *J. Essent. Oil Res.* 23 (2011) 11-18.

Sensors & Analytical

Oral Abstracts

Sensor using Molecular Dynamics of Drugs in Carbon Nanotubes Under External Uniform Electric Field

Júlio C. N. Aires^{a,b}, Rafael P. Pantoja^a, Tais S.S. Pereira^a, Adriana T. Amador^a and Antonio M. J. C. Neto^{a,b,c}

a) *Laboratory of Preparation and Computation of Nanomaterials (LPCN), Federal University of Pará, C. P. 479, 66075-110 Belém, PA, Brazil.*

b) *Graduate Program in Engineering of Natural Resources of the Amazon, ITEC, Federal University of Pará, C. P. 2626, 66.050-540, Belém, PA, Brazil*

c) *c)Graduate Program in Chemical Engineering, ITEC, Federal University of Pará, C. P. 479, 66075-900 Belém, PA, Brazil*

Email: amchaves@ufpa.br

We present an analysis on molecular dynamics between hallucinogenic drugs molecules (cocaine, heroin, morphine, etc) interacting with one carbon nanotube section at low initial-temperature of simulation, corresponding to 10–3 K, and under uniform electric field, in order to verify the performance of this system like as drugs sensor. During simulations, each drug was relaxed for 50 *ps* inside and outside of carbon nanotube, describing each possible arrangement for the capture of each drug, and an constant electric field was applied over the system, longitudinally to the carbon nanotube length, promoting an evanescent effect, able to trap each drug orbiting the carbon nanotube. Simulations for electric fields intensities in a range of 10^{-6} au up to 10^{-1} a.u. were performed, and mean orbit radius are estimated, as well as, some physical quantities of the system. The quantities calculated were: kinetic energy, potential energy, total energy and temperature *in situ*, among molar entropy variation. Our results indicates that a combination of uniform electric field and van der Waals interactions derivatives of carbon nanotube is enough to create an evanescent field with attractive potential, showing it system as a good drugs sensor.

Keywords: Drugs, Carbon Nanotube, Electric Field, Evanescence Effect, Molecular Dynamics.

Electrochemical stability of thiols and disulfides assembled on gold in physiological medium

Adam Kolodziej, Carlos Guillen Posteguillo, Roshni Mistry, Francisco Fernandez-Trillo, Paramaconi Rodriguez

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

Email: axk595@bham.ac.uk

The importance of thiol-modified gold surfaces has been continuously investigated by the development of sensors¹, immobilised catalysts² and drug delivery strategies³, with a substantial effort being focused on biomedical applications.

Electrochemistry has been widely applied in the field of sensors because its high sensitivity⁴ and recently the electrochemically-controlled delivery of drugs have also attracted the attention of researchers around the globe.⁵ Therefore, electrochemical desorption of thiols is of interest since it determines the operational limits for the reliable sensor performance. On the other hand, it provides the conditions of a platform for a systematic drug delivery. While the electrochemical desorption of thiols from gold surfaces has been mainly studied in alkaline media using a range of techniques, only a few attempts have been conducted in neutral medium; and none of them in an electrolyte that mimics physiological conditions.⁶

In this work, we explore the electrochemical stability of thiol-modified electrodes in physiological medium. First, we investigate the stability of 4 different thiols: 3-mercaptopropionic acid, 2-mercaptoethanol, 1,4-dithiothreitol and thioctic acid on polycrystalline bead-electrodes using cyclic voltammetry (CV) and newly introduced progressive potential-step chronoamperometry. Subsequently, we study the impact of the crystalline structure of gold on the electrochemical desorption of thiols.

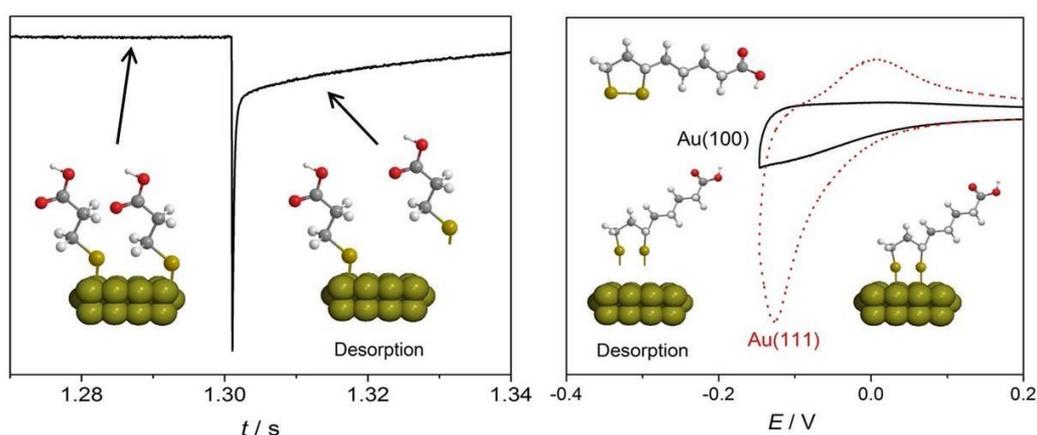


Figure 1: Chronoamperometric profile showing desorption of 2-mercaptoethanol from polycrystalline gold electrode (left panel). Voltammetric profiles showing desorption of thioctic acid from Au (111) (dotted line) and Au (100) (solid line) (right panel).

Our results indicate that SAMs of disulfides on gold electrodes are more stable than SAMs formed by thiols. We also report on the superior stability of the SAM on the Au(100) in comparison with the monolayers adsorbed on the Au(111) electrode.

References:

1. D. Mandler and I. Turyan, *Electroanalysis*, 1996, **8**, 207-213.
2. D. P. Wernette, C. Mead, P. W. Bohn and Y. Lu, *Langmuir*, 2007, **23**, 9513-9521.
3. P. Mali, N. Bhattacharjee and P. C. Searson, *Nano letters*, 2006, **6**, 1250-1253.
4. J. Monzo, I. Insua, F. Fernandez-Trillo and P. Rodriguez, *Analyst*, 2015, **140**, 7116-7128.
5. J. Wang, G. Rivas, M. Jiang and X. Zhang, *Langmuir*, 1999, **15**, 6541-6545.
6. E. Boubour and R. B. Lennox, *Langmuir*, 2000, **16**, 7464-7470.

Electrochemical Detection of DNA Methylation: A possible method for detecting changes to health

Amy E. Morgan,^a Garrett Thompson,^b Katie D. Acutt,^a Jeffrey M. Halpern,^b Mark T. McAuley,^a and Trevor J. Davies^a

a) Faculty of Science and Engineering, University of Chester, UK

b) Department of Chemical Engineering, University of New Hampshire, USA

Email: t.davies@chester.ac.uk

An increase in DNA methylation has been shown to correlate with around 80% of all cancers, where a large proportion of carcinogenic gene silencing is the result of altered levels of methylation at cytosine residues [1]. In addition to cancer, aberrant DNA methylation has an emerging role to play in many age-related diseases, including cardiovascular disease (CVD), Alzheimer's disease, osteoporosis/osteoarthritis and ageing [2]. A number of electrochemical methods have been developed to detect the relative amounts of methylation in real and synthetic DNA/genes. Of particular interest is the elegant and low cost eMethylsorb technique, which exploits the strong affinity of adenine groups to gold [3]. In this technique, a gene of specific interest is selectively extracted from a patient's DNA, multiplied and then treated via a process that produces adenine enriched samples. The higher the methylation level of the gene, the lower the amount of adenine in the test sample. A gold electrode is then exposed to the sample and the relative amount of DNA/gene adsorption, which is indicative of the relative amount of methylation, is determined via a voltammetric method that monitors the deactivation of the electrode surface.

This work reports a thorough investigation of the key parameters in the eMethylsorb technique. Using a methylated and the analogous unmethylated synthetic gene sequence, differential pulse voltammetry, cyclic voltammetry and electrochemical impedance spectroscopy are compared to find the optimum electrochemical technique to assess the different levels of electrode deactivation. The effect of solution flow during the adsorption stage is shown to be of critical importance in producing repeatable results with significant differences between methylated and unmethylated DNA samples. Once optimised, the improved method is used to measure methylation levels in real DNA samples. The results offer a considerable improvement on the repeatability of the eMethylsorb technique and demonstrate the potential value of this approach as a complimentary tool for the early diagnosis of cancer and age-related diseases.

[1] M.R. Stratton, P.J. Campbell, P.A. Futreal, The cancer genome, *Nature*, 458 (2009) 719.

[2] D.A. Rowbotham, E.A. Marshall, E.A. Vucic, J.Y. Kennett, W.L. Lam and V.D. Martinez, Epigenetic changes in aging and Age-related disease, *Journal of Aging Science*, 3 (2014) 1.

[3] K.M. Koo, A.A.I. Sina, L.G. Carrascosa, M.J.A. Shiddihy, M. Trau, eMethylsorb: rapid quantification of DNA methylation in cancer cells on screen-printed gold electrodes, *Analyst*, 139 (2014) 6178.

Fabricating Cellular Bioelectronic Systems by Combining Inkjet Printing with Bipolar Electrochemistry

Frankie J Rawson^a, Paola Sanjuan-Alberte^a, Ehab Saleh^b Morgan R Alexander^a, Richard Hague^b

a) School of Pharmacy, University of Nottingham, NG7 2QL, UK

b) Additive Manufacturing and 3D Printing, School of Engineering, University of Nottingham, Nottingham, NG7 2QL, UK

Email: frankie.rawson@nottingham.ac.uk

In order to seamlessly integrate electronics with cells there is a pressing need to develop new methods that advance our ability to construct 3D multi-material conductive systems. Moreover, to ease the transition of building cellular electronic systems an in-situ remote approach to merging electrical components with cells is desirable. We present a method that combines inkjet printing with bipolar electrochemistry to fabricate conductive wires of silver with key diameters of up to 200 nm. Wires were formed by self-assembly of silver nanoparticles, generated by applying a potential difference to inkjet printed electrodes. Conductive wires were grown via bipolar electrochemistry in a 3D coordinated manner to connect electrical components and importantly, forming such connections between elements in different z-planes. We then use the same approach to grow and interface conductive conduits in-situ with mammalian cells. This subsequently allowed for sensing of cell redox events. This technological approach provides a platform to fabricate and advance the development of 3D multifunctional bioelectronic systems.²

1. Kong, Y. L.; Gupta, M. K.; Johnson, B. N.; McAlpine, M. C. 3D printed bionic nanodevices. *Nano Today* 2016.
2. Paola Sanjuan-Alberte, Ehab Saleh, Lee L. Lin, Morgan R. Alexander, Richard J. M. Hague, Frankie J. Rawson, A New Paradigm in Merging Biology with Electronics by Printing Electrochemical 3D Nano-Wireless Systems, Submitted for publication

Electrochemical characterisation and regeneration of sulfur poisoned Pt catalysts

Chang-Hui Chen^a, Adam Halford^b, David Fermin^c, Colin Brennan^d, Paramaconi Rodriguez^b and Patrick R. Unwin^a

a) Department of Chemistry, University of Warwick, Gibbet Hill Rd, Coventry, CV4 7AL, U.K.

b) School of Chemistry, University of Birmingham, Edgbaston, Birmingham, B15 2TT, U.K.

c) School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, U.K.

d) Syngenta, Jealott's Hill International Research Centre, Bracknell, Berkshire, RG42 6EY, U.K.

Email: c.chen.26@warwick.ac.uk

Catalytic hydrogenation processes are widely employed in chemical industry for the synthesis of organic compounds. Typically, the catalysts in these processes consist of Pt and Pt-group nanoparticles supported on carbon.^{1,2} Additionally, sulfuric acid is frequently added, for operational reasons, to protonate the products and prevent product binding or over-reactions. However, it is found that the presence of sulfuric acid may lead to a poisoning of Pt catalysts,^{1,3} and it is unclear what species causes this effect, *i.e.* is it due to the presence of bisulfate, or due to sulfide owing to sulfuric acid reduction? Little is known about the sulfate/sulfide redox chemistry at Pt surfaces, nor is there a diagnostic measurement to identify and quantify the process.

In this work, we have studied the electro-oxidation of sulfur-containing species adsorbed at various types of Pt electrodes, namely polycrystalline, single-crystal and Pt nanoparticles on a glassy carbon support. A number of sulfur compounds were considered, with the oxidation states of sulfur ranging from 2- to 6+. We demonstrate that almost all sulfur-containing compounds investigated lead to poisoning of the Pt surfaces. Furthermore, we show that the poisoned Pt electrodes can be regenerated by repeated CV cycling, in the range of 0.05 – 1.2 V (versus palladium-hydrogen electrode). Importantly, the recovery kinetics are strongly related to the initial sulfur sources. Additionally, single-crystal studies allow decoupling the effect of steps and terraces. Finally, XPS analysis is also employed, to elucidate the chemical state of sulfur species during recovery process.

This approach introduces electrochemical processing for the regeneration of catalysts, and we believe it will offer new ways for understanding and discover new catalysts in hydrogenation reactions.

References

- (1) Rylander, P. *Catalytic hydrogenation over platinum metals*; Elsevier, 2012.
- (2) Serna, P.; Corma, A. *ACS Catalysis* **2015**, 5, 7114.
- (3) Barbier, J.; Lamy-Pitara, E.; Marecot, P.; Boitiaux, J. P.; Cosyns, J.; Verna, F. *Advances in Catalysis* **1990**, 37, 279.

Keynote: Darren Walsh

How Ionic are Ionic Liquids? Measuring the Ionicity of Protic Ionic Liquids using Electroanalytical Chemistry

Darren A. Walsh

GSK Carbon Neutral Laboratory for Sustainable Chemistry, The University of Nottingham

Email: darren.walsh@nottingham.ac.uk

Due to their wide electrochemical windows, thermal stabilities, and inherent conductivities, room temperature ionic liquids (RTILs, salts that are liquid at room temperature) are being proposed for use in devices such as electrochemical sensors, batteries, fuel cells, and supercapacitors. Of particular importance when designing and synthesising RTILs for such applications is determining their degree of “ionicity.” Some RTILs exhibit relatively high vapour pressures, poor thermal stabilities, and low conductivities, due to the presence of neutral molecules and stable ion pairs and clusters in the liquids. These effects are particularly acute for protic ionic liquids (PILs), which can comprise a mixture of the salt and parent neutral acid and base, depending on the extent of proton transfer during synthesis. The formation of non-stoichiometric mixtures of acids and bases in PILs also yields neutral parent molecules. The only methods available for determining the degree of ionicity of PILs are indirect methods, such as conductimetry. However, conductimetry cannot differentiate between the presence of neutral molecules, and neutral ion pairs or clusters, none of which contribute to a PIL’s conductivity.

In this presentation, I will show that residual parent species can be quantified in PILs *in situ* using ultramicroelectrode voltammetry and scanning electrochemical microscopy. Electroanalysis shows that PILs based on acids such as triflic acid and trifluoroacetic acid, when synthesised using common literature methods, can contain significant concentrations of acids (up to 100s of mM), due to loss of thermally-unstable bases from the liquids during synthesis. The excess acids are extremely stable in PILs, even at 10^{-7} mbar. I will also describe a method for analysing the concentration of bases in PILs, which is based on the electrochemical behaviour of H_2 in PILs. Finally, I will discuss some of the electrochemical effects of residual precursors on the electrochemical reactivity of PILs. For example, Figure 1 shows that the onset potential, E_{onset} , for O_2 electroreduction ($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$) in diethylmethylammonium triflate shifts positive by almost 1 V when the PIL contains 0.1 M of the parent acid, demonstrating that the acid plays a key role during O_2 electroreduction in the liquid.

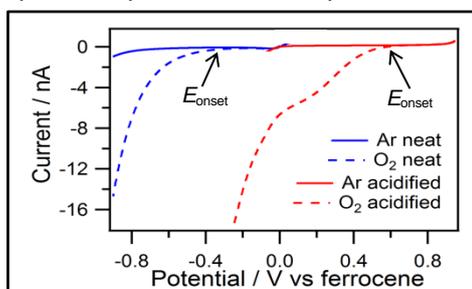


Figure 1. Voltammograms recorded in diethylmethylammonium triflate in the presence (dashed) and absence (solid) of O_2 . The blue curves were recorded using PILs containing no detectable acid and the red curves were recorded in the presence of 0.1 M triflic acid.

Investigating Bacterial ROS with Tailored Carbon Nanotube Sensors

Jacqueline M. Hicks,^a Zhi Yi Wong,^a David J. Scurr,^a Nigel Silman,^b Simon K. Jackson,^c
Paula M. Mendes,^d Jonathan W. Aylott,^a Frankie J. Rawson^a

a) University of Nottingham

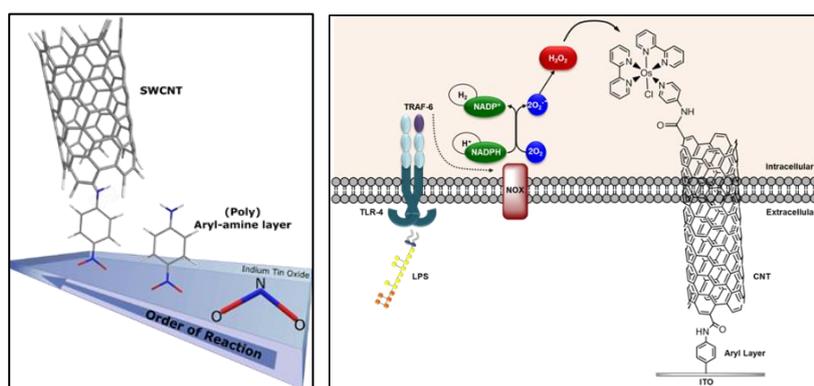
b) Public Health England

c) University of Plymouth

d) University of Birmingham

Email: Jacqueline.hicks@nottingham.ac.uk

Nano sensors are emerging as a key technology for intracellular sensing. With their small size, they can penetrate cell membranes and have proven to be highly sensitive to minor changes in analyte. In this work, we present our ability to tailor the properties of single walled carbon nanotube (SWCNT) based sensors for superior sensing of reactive oxygen species (ROS). The sensors are based on the immobilisation of SWCNTs onto an indium tin oxide (ITO) surface via in situ grafting of aryl diazonium which results in an aryl-amine tether layer between the ITO and the CNTs. By restricting the aryl-amine layer to ~3nm instead of the regular 20nm electron transfer kinetics of the sensors were improved by more than a factor of ten¹. These sensors were then modified as described previously by Rawson et al² with an osmium complex for hydrogen peroxide selectivity. Various surface analysis techniques were used including AFM, ToF-SIMS and ellipsometry in conjugation with electrochemical techniques to analyse the surfaces. A murine macrophage line (RAW264.7) was used in conjugation with the sensors to examine ROS production in response to bacterial infection. With these improved sensors, we have been able to reduce the lower limit of detection of hydrogen peroxide and apply them to numerous bacterial strains of lipopolysaccharides for investigation.



1. Hicks, J. M.; Wong, Z. Y.; Scurr, D. J.; Silman, N.; Jackson, S. K.; Mendes, P. M.; Aylott, J. W.; Rawson, F. J., *Langmuir* **2017**, 33 (20), 4924-4933.
2. Rawson, F. J.; Hicks, J.; Dodd, N.; Abate, W.; Garrett, D. J.; Yip, N.; Fejer, G.; Downard, A. J.; Baronian, K. H.; Jackson, S. K.; Mendes, P. M., *ACS Appl Mater Interfaces* **2015**, 7 (42), 23527-37.

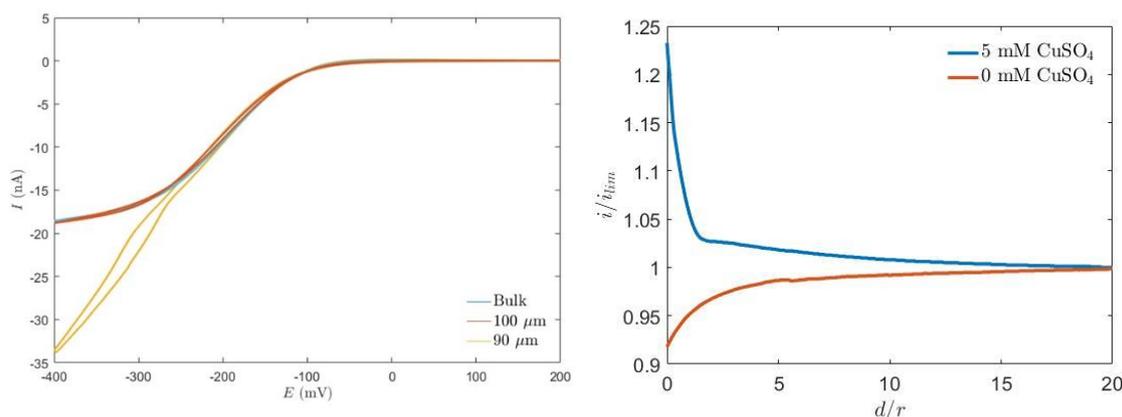
SECM Study of Metals Extraction at the ITIES

Eemi Nieminen, Ella Aikio, Lasse Murtomäki

Aalto University, Department of Chemistry and Materials Science
PO Box 16100, 00076 Aalto, Finland

Email: eemi.nieminen@aalto.fi

Solvent extraction is the elementary process in hydrometallurgy but the solvents used in industry (e.g. kerosene) do not allow conventional electrochemical study because of their very low relative permittivity that impedes dissolution or dissociation of electrolytes. Immiscible liquid-liquid interfaces (ITIES) have now been studied for ca. 40 years but have mainly remained as an analytical tool. Here, we study the transfer of metals across the ITIES, driven by the Galvani potential difference created by a common ion TB^- in the aqueous and organic phases. In addition to shake-flask experiments, SECM measurements are done to elucidate the effect of the Galvani potential difference on the transfer process. An industrially relevant solvent, methyl isobutyl ketone (MIBK) is used as the organic solvent. The target is to find novel means to separate precious and rare earth metals in recycling processes.



Cyclic voltammograms (SECM tip currents) at varying distance from the liquid-liquid interface. $[\text{Cu}^{2+}]^w = 5.0 \text{ mM}$; $[\text{BATB}]^o = [\text{LiTB}]^w = 0.1 \text{ mM}$. Without the potential determining ion TB^- , current does not increase in the linear fashion. Redox mediator TCNQ is reduced on the tip.^{1*}

Approach curves in absence and presence of Cu^{2+} in the aqueous phase. $[\text{BATB}]^o = [\text{LiTB}]^w = 0.1 \text{ mM}$. d is the tip-interface distance and $r = 12.5 \mu\text{m}$, the tip radius. The positive feedback comes from the reduction of Cu^{2+} by TCNQ^- that is oxidised back to TCNQ .

* BA^+ = Bis(triphenylphosphoranylidene), TB^- = Ammonium tetrakis(pentafluorophenyl) borate; TCNQ = Tetracyanoquinodimethane

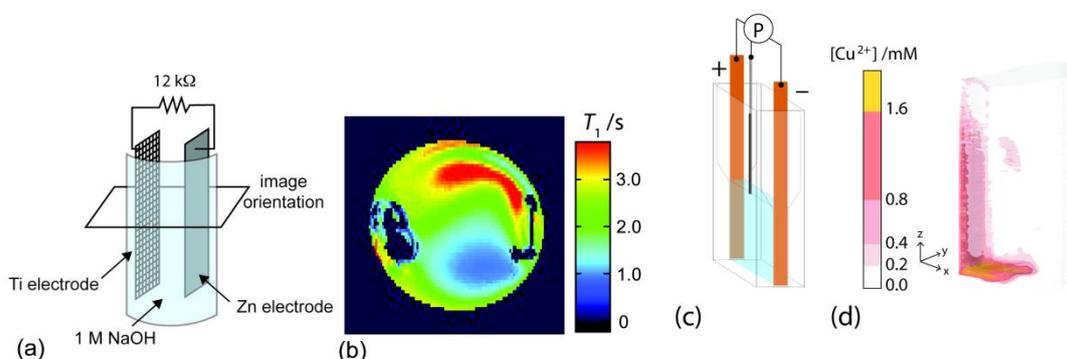
MRI of electrochemical systems: batteries, corrosion and electroplating

Melanie M. Britton

School of Chemistry, University of Birmingham, Birmingham, UK.

Email: m.m.britton@bham.ac.uk

The design and development of improved energy storage devices, and other electrochemical technologies, requires detailed understanding of the electrochemical reactions, ion transport and concentration gradients within these systems. However, there are few methods that are able to visualise and quantify these non-invasively, spatially, in situ and in real time. Magnetic resonance imaging (MRI) has proved to be an excellent tool for non-invasively studying complex, spatially heterogeneous chemical systems in materials, engineering and chemical research¹. While, MRI has enormous potential for in situ investigation of the spatial distribution, speciation, and mobility of molecules and ions in electrochemical devices, there are currently very few examples of MRI being used to probe such systems. This is largely due to the experimental challenges associated with setting up an electrochemical cell inside a strong magnetic field and the imaging artefacts caused by the presence of metals that lead to undesirable variations in the radiofrequency (RF) and magnetic fields across the sample². However, it has been found recently that such technical issues can be overcome and that it is possible to collect viable, quantitative, in situ data³⁻⁶. This paper will discuss the challenges of studying electrochemical systems by MRI and demonstrate how they can be overcome to enable the collection of unique, viable, quantitative, in situ data during the operation of batteries, as well as other electrochemical systems, including corrosion^{3,7} and metal electroplating in ionic liquids.



(a) Model Zn-air cell (b) MRI of Zn dissolution in Zn-air cell⁶ (c) Cu corrosion cell (d) Cu^{2+} concentration map⁷ during electrodisolution of Cu^{2+} .

- (1) Britton, M. M. *Chem. Soc. Rev.* **2010**, *39*, 4036.
- (2) Bennett, L. H. et al. *J. App. Phys.* **1996**, *79*, 4712.
- (3) Davenport, A. J. et al. *Electrochem. Comm.* **2010**, *12*, 44.
- (4) Chandrashekar, S. et al. *Nature Materials* **2012**, *11*, 311.
- (5) Klett, M. et al. *J. Amer. Chem. Soc.* **2012**, *134*, 14654.
- (6) Britton, M. M. et al. *J. Phys. Chem. Lett.* **2013**, *4*, 3019.
- (7) Bray, J. M. et al. *Angew. Chem. Int. Ed.* **2016**, *55*, 9394.

The development of electrochemical online monitoring in nuclear pyroprocessing using in-house microelectrodes.

Simon J. Reeves,^a Damion K. Corrigan,^{a&d} Justin P. Elliott,^a Hannah J. Levene,^a Ewen O. Blair,^b Ilka Schmüser,^b Mike T. Harrison,^c Anthony J. Walton^b and Andrew R. Mount^a

a) EaSTCHEM, School of Chemistry, The University of Edinburgh, Joseph Black Building, The King's Buildings, David Brewster Road, Edinburgh, EH9 3FJ, UK

b) Institute for Integrated Micro and Nano Systems, School of Engineering, The University of Edinburgh, The King's Buildings, Alexander Crum Brown Road, Edinburgh EH9 3FF, UK

c) National Nuclear Laboratory Limited, Sellafield, Seascale, Cumbria, CA20 1PG, UK

d) Department of Biomedical Engineering, Wolfson Centre, University of Strathclyde, 106 Rottenrow East, Glasgow, G4 0NS, UK

Email: s.reeves@sms.ed.ac.uk

Electrochemical techniques are being extensively developed for molten salt pyroprocessing of spent nuclear fuel. For online monitoring, data obtained from macroelectrodes often requires involved analysis to gain key information, particularly due to the contribution and complexity of convection. Microelectrodes have significant advantages that change the measured signal, which improves the quality of collected data and simplifies the analysis required to extract key information. Photolithographically defined and patterned in-house microelectrodes have been developed that we have shown to be capable of withstanding the harsh environment in LiCl-KCl eutectic (LKE) molten salt[1-3] at temperatures up to 500 °C, which is often highly corrosive. This talk will detail our work studying nuclear relevant redox species with macro and microelectrodes (Figure 1), highlighting the significant advantages of the microelectrodes due to the differences in data collected and analysis required.

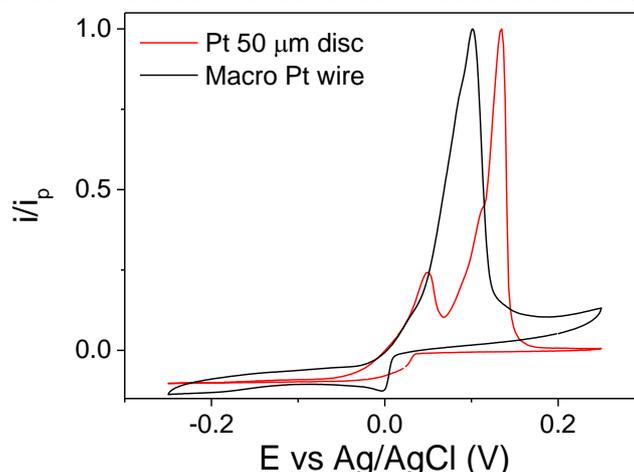


Figure 1: Comparison of CVs of BiCl_3 in LKE on a Pt macroelectrode and microelectrode.

[1] D. K. Corrigan, J. P. Elliott, E. O. Blair, S. J. Reeves, I. Schmüser, A. J. Walton and A. R. Mount, *Faraday Discuss.* **2016**, 190, 351-366

[2] E. O. Blair, D. K. Corrigan, J. G. Terry, A. R. Mount and A. J. Walton, *JMEMS* **2015**, 24 (5), 1346-1354

[3] D. K. Corrigan, E. O. Blair, J. G. Terry, A. J. Walton and A. R. Mount, *Anal. Chem.* **2014**, 86 (22), 11342-11348

Keynote: Tim Albrecht

Nanopore sensing for DNA fingerprinting and profiling applications

T. Albrecht

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

Email: t.albrecht@bham.ac.uk

Nanopore devices are still a relatively new class of stochastic single-molecule sensors, which nevertheless have reached a certain degree of maturity. The fundamental concept is based on small biological channels on one hand and their micrometer-scale, solid-state analogue, the famous Coulter counter on the other. Initially driven by prospects of fast and label-free DNA sequencing, a feat that has now been achieved,[1] new applications are now coming into focus, especially for chip-based nanopore sensors and nanopipettes. In comparison to biological channels, those pores tend to be somewhat larger and less reproducible (at the low-nm scale), but they offer more design flexibility and are more readily be adapted to different and larger analytes, such as protein/DNA complexes.[2-4] To this end, mapping of structural features along a double-stranded DNA (dsDNA) carrier strand has emerged as an area of particular interest and the detection of DNA knots, bound PNA and proteins been demonstrated.[2,4-6] Using electric detection, it is now possible to resolve those features individually in a label-free manner and locate them along the DNA strand.

Building on our recent work on high-speed sensing in nanopipettes with time resolutions in the low microsecond range (and 10s of pA amplitude) and in particular the direct detection of dsDNA fragments as short as 100 bp,[7,8] we have now developed a new sensor concept akin to a DNA assay 'on a string'. Here, we first build a DNA architecture based on molecular self-assembly ('DNA Origami'): it consists of a 7.2 kbp dsDNA carrier with ~100 nt single-stranded (ss) DNA overhangs in known locations along the carrier (currently up to 3). Those can be detected by electric readout in a nanopipette, as spikes superimposed on the translocation event itself ('sub-events'). However, just as in a DNA assay, the ssDNA overhangs can also hybridize with a specific target sequence, e.g. a disease marker, to form dsDNA overhangs. Since the latter are bulkier and presumably more rigid, the sub-events change in comparison to their ssDNA analogues, which can in turn be used to differentiate between hybridized and non-hybridized 'arms'. At present, the effect is not large, but we are confident that optimisation of the carrier and the sensor design can further improve the performance.

[1] D Deamer, M Akeson, D Branton, *Nat. Biotechnol.* 2016, 34, 518-524.

[2] RMM Smeets, SW Kowalczyk, AR Hall, NH Dekker, C Dekker, *Nano Lett.* 2009, 9, 3089-3096.

[3] D Japrun, A Bahrami, A Nadzeyka, L Peto, S Bauerdick, JB Edel, T Albrecht, *J. Phys. Chem. B* 2014, 118, 11605-11612.

[4] P Nuttall, K Lee, P Ciccarella, M Carminati, G Ferrari, K-B Kim, T Albrecht, *J. Phys. Chem. B* 2016, 120, 2106-2114.

[5] A Singer, S Rapireddy, DH Ly, A Meller, *Nano Lett.* 2012, 12, 1722-1728.

[6] C Plesa et al., *Nat. Nanotechnol.* 2016, 11, 1093-1098.

[7] RL Fraccari, P Ciccarella, A Bahrami, M Carminati, G Ferrari, T Albrecht, *Nanoscale* 2016, 8, 7604-7611.

[8] RL Fraccari, M Carminati, G Piantanida, T Leontidou, G Ferrari, T Albrecht, *Faraday Discuss.* 2016, 193, 459-470.

Performance characteristics of New NO₂ and O₃ Low Cost Air Quality Gas Sensors.

Ronan Baron, Wah On Ho, John Saffell

Alphasense Ltd, Sensor Technology House, 300 Avenue West, Great Notley, CM77 7AA, UK.

Email: rpb@alphasense.com

A new generation of air quality NO₂ and O₃ gas sensors have recently been developed at Alphasense. The use of electrochemical sensors for monitoring air quality provides a low cost alternative to the existing methods [1]. These sensors show improvements over standard sensors, especially in air quality monitoring applications. Main criteria include stabilisation time, signal noise, zero temperature dependence, transient humidity performance, linearity at low concentrations, limit of detection, long term sensitivity stability and gas specificity [2]. In particular, these sensors are less sensitive to environmental conditions such as temperature and humidity transients. Limits of detection as low as a few ppbs were obtained in a laboratory environment. The new sensors are now being deployed commercially and corresponding field data will be shown.

[1] Mead, M. I.; Popoola, O. A. M.; Stewart, G. B.; Landshoff, P.; Calleja, M.; Hayes, M.; Baldovi, J. J.; McLeod, M. W.; Hodgson, T. F.; Dicks, J.; Lewis, A.; Cohen, J.; Baron, R.; Saffell, J. R.; Jones, R. L. The use of electrochemical sensors for monitoring urban air quality in low cost, high-density networks. *Atmos. Environ.*, **2013**, *70*, 186-203.

[2] Hossain, M.; Saffell, J.; Baron, R. Differentiating NO₂ and O₃ at low cost air quality amperometric gas sensors. *ACS Sens.*, **2016**, *1*, 1291-1294; **2016**.

Electrodeposition of Tin Nanowires into an Anodic Alumina Template from a dichloromethane electrolyte.

Andrew W.Lodge,^a Mahboba. M. Hasan,^a Andrew L. Hector^a

a) Chemistry, University of Southampton, Highfield, Southampton, SO17 1BJ, UK
Email: A.W.Lodge@soton.ac.uk

Nanowires of various materials have a myriad of potential uses in electrical devices such as transistors¹, thermoelectric materials¹ and solar energy devices² due to their semiconducting properties that occur at smaller nanowire diameters². One method of forming nanowires is to electrodeposit the material inside a porous template such as an anodic alumina membrane³, for control of the nanowire diameter.

Tin was electrodeposited from a dichloromethane solution onto flat substrates at various temperatures. Tin was also electrodeposited into anodic alumina membranes of various pore sizes. The effect of grafting the alumina pore wall with various functional groups was also studied. It was found that decreasing the electrodeposition temperature decreased the crystallite size of the deposited tin and causes the onset of the reduction potential to become more positive. Nanowires of tin were successfully deposited into anodic alumina membranes with 55 and 13 nm pore diameters. It was found that the tin preferentially deposited into the anodic alumina membrane is <200> aligned. Grafting the anodic alumina pore walls with tin had little effect on the tin alignment and deposition.

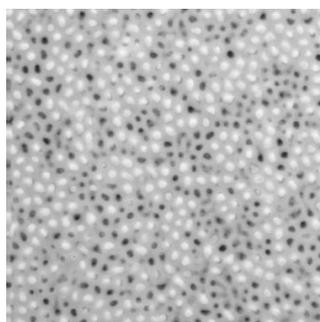


Figure 2: A TEM image showing tin (white spots) deposited in an anodic alumina membrane with 55 nm diameter pores.

References

- 1) P. N. Bartlett, D. A. Cook, M. W. George, A. L. Hector, J. Ke, W. Levason, G. Reid, D. C. Smith and W. Zhang, *Phys. Chem. Chem. Phys.*, 2014, **16**, 9202
- 2) M. Law, J. Goldberger and P. Yang, *Annu. Rev. Mater. Res.*, 2004, **34**, 83–122
- 3) S. Thongmee, H. L. Pang, J. Ding and J. Y. Lin, *J. Magn. Magn. Mater.*, 2009, **321**, 2712–2716.

Development of a Boron doped diamond pH sensor for unbuffered media: The effect of Quinone surface coverage on pH response.

Sam J. Cobb^{a,c}, Zoë J. Ayres^{a,b}, Mark E. Newton^b and Julie V. Macpherson^a

a) Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK

b) Department of Physics, University of Warwick, Coventry CV4 7AL, UK

c) EPSRC Centre for Doctoral Training in Diamond Science and Technology, UK

Email: samuel.cobb@warwick.ac.uk

High power laser micromachining systems are used to cut diamond and have previously been used to manufacture all diamond electrochemical devices, including disk electrodes, band electrodes and ring disk electrodes¹. The machining process also leaves non-diamond (sp^2) carbon behind which has been found to have a significant effect on the electrochemistry observed. Recently, we have shown how we can use this approach to functionalise the BDD surface with sp^2 sites, which are more catalytically active than the surrounding sp^3 BDD surface. The nature of this sp^2 carbon is still not completely understood, but has been shown to contain quinone-like moieties (QLM's) which demonstrate a quantitative pH response² and can be used as a measure of the surface sp^2 content³.

Previous carbon pH sensors based on the electrochemical reduction/oxidation of surface bound quinone groups have been shown to have significant limitations, often struggling at high pH⁴ and in unbuffered solutions. The latter is due to the fact that by making the measurement protons are removed from solution resulting in a changing proton concentration at the surface of the electrode. The surface attachment of these molecules has also been shown to fail in extreme environments^{4,5}.

QLM's produced on the surface of BDD by laser micromachining (figure 1.) have a significant advantage over previous approaches. The QLM's are incredibly stable, being resistant to mechanical abrasion, extremely high temperatures and extreme environments. In this talk we will discuss methods for optimizing the sensor design to provide a linear pH response in unbuffered solutions.

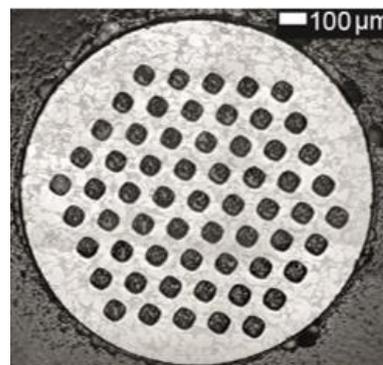


Figure 3: Laser micromachined pH array in a BDD electrode

References

- (1) Joseph, M. B.; Bitziou, E.; Read, T. L.; Meng, L.; Palmer, N. L.; Mollart, T. P.; Newton, M. E.; Macpherson, J. V. *Anal. Chem.* **2014**, *86* (11), 5238–5244.
- (2) Ayres, Z. J.; Borrill, A. J.; Newland, J. C.; Newton, M. E.; Macpherson, J. V. *Anal. Chem.* **2015**, *88* (1), 974–980
- (3) Ayres, Z. J.; Cobb, S. J.; Newton, M. E.; Macpherson, J. V. *Electrochem. commun.* **2016**, *72*, 59–63.
- (4) Dai, C.; Song, P.; Wadhawan, J. D.; Fisher, A. C.; Lawrence, N. S. *Electroanalysis* **2015**, *27* (4), 917–923.
- (5) Kahlert, H. J. *Solid State Electrochem.* **2008**, *12* (10), 1255–1266.

Physical & Fundamental

Oral Abstracts

Electrochemical Processes Leading to Ionic Diode Phenomena

Frank Marken,^a Elena Madrid,^a Barak D.B. Aaronson,^a
Neil B. McKeown,^b and Klaus Mathwig^c

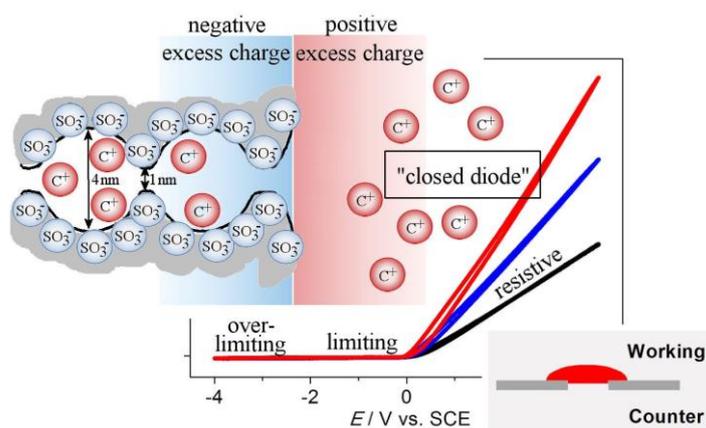
a) Department of Chemistry, University of Bath, Bath BA2 7AY, UK

b) School of Chemistry, University of Edinburgh, Joseph Black Building, West Mains Road, Edinburgh, Scotland EH9 3JJ, UK

c) Groningen Institute of Pharmacy, The University of Groningen, P.O. Box 196, 9700 AD Groningen, The Netherlands

Email: f.marken@bath.ac.uk

Ionic rectifiers (or ionic diodes) work like electronic diodes, but allow ion flow to be controlled. We have developed [1-4] novel ionic diode devices based on ionomer and polymer materials coated onto microholes to typically 5 μm to 40 μm diameter. When a potential is applied across the membrane an open (or “resistive”) state is observed and at the opposite potential a closed (or “limiting”) state occurs. Ionic diodes can respond to pH and external parameters or “invert” polarity, but the underlying mechanisms can be diverse.



[1] E. Madrid, Y.Y. Rong, M. Carta, N.B. McKeown, R. Malpass-Evans, G.A. Attard, T.J. Clarke, S.H. Taylor, Y.T. Long, F. Marken, Metastable Ionic Diodes Derived from an Amine-Based Polymer of Intrinsic Microporosity. *Angew. Chem. Int. Ed.* 2014, 53, 10751-10754.

[2] E. Madrid, P. Cottis, Y.Y. Rong, A.T. Rogers, J.M. Stone, R. Malpass-Evans, M. Carta, N.B. McKeown, F. Marken, Water Desalination Concept Using an Ionic Rectifier Based on a Polymer of Intrinsic Microporosity (PIM). *J. Mater. Chem. A* 2015, 3, 15849-15853

[3] E. Madrid, M.A. Buckingham, J.M. Stone, A.T. Rogers, W.J. Gee, A.D. Burrows, AP.R. Raithby, V. Celorrio, D.J. Fermin, F. Marken, Ion Flow in a Zeolitic Imidazolate Framework Results in Ionic Diode Phenomena. *Chem. Commun.* 2016, 52, 2792-2794

[4] Y.Y. Rong, Q.L. Song, K. Mathwig, E. Madrid, D.P. He, R.G. Niemann, P.J. Cameron, S.E.C. Dale, S. Bending, M. Carta, R. Malpass-Evans, N.B. McKeown, F. Marken, PH-Induced Reversal of Ionic Diode Polarity in 300 nm Thin Membranes Based on a Polymer of Intrinsic Microporosity. *Electrochem. Commun.* 2016, 69, 41-45

The Influence of Acetonitrile on Cu Under-Potential Deposition in presence of adsorbing anions

Nikolas Antonatos,^{a,b} Chris Lucas,^b Yvonne Gründer^{a,b}

a) Stephenson Institute for Renewable Energy, University of Liverpool

b) Department of Physics, University of Liverpool

Email: N.Antonatos@liverpool.ac.uk

The presence of specifically adsorbed anions and/or small organic molecules can significantly affect the electrochemical reactivity of a metal electrode and the formation of metal adlayer on a foreign metal substrate at potentials more positive than the Nernst potential, the under-potential deposition (UPD).^[1] Furthermore, a prominent effect of the interaction between metal ions and anion is the influence on the kinetics of the metal layer formation.^[2]

Acetonitrile (AcN) is an organic molecule which solvates noble metal ions by receiving electrons into the cyanide group of the molecule, an important process in the organometallic complex formation of transition metals. Moreover, it has been presented that AcN molecules compete for adsorption sites on metal electrodes.^[3] For the investigation of the influence of organic molecules on the process of metal deposition it is vital to comprehend their mechanism.

The presentation will demonstrate that different Acetonitrile concentrations show a systematic change in the Cu UPD formation in the presence of sulphate (Figure 1) and perchlorate anions through initial characterisation by cyclic voltammetry, the alteration of the kinetics of the systems by modelling chronoamperometry transients and structural changes between potentials by the use of Surface X-Ray Diffraction.

The increase of Acetonitrile concentration from 10 mM up to 4 M enhanced Cu deposition (positive shift of the cathodic peak) and moreover, chronoamperometry analysis showed that the final Cu coverage in sulphuric increased in the presence of Acetonitrile.

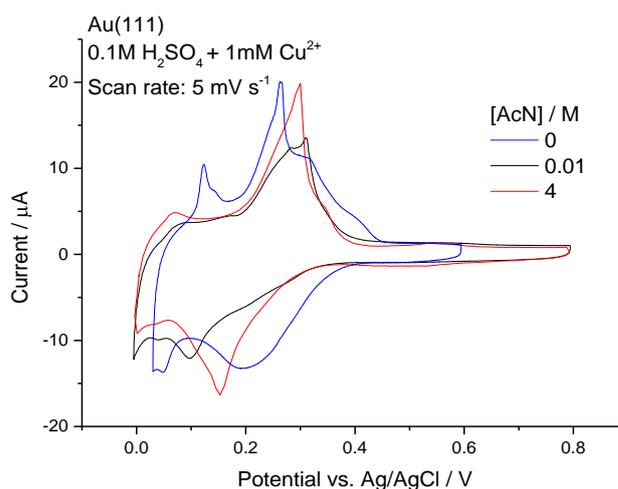


Figure 1. Cyclic voltammogram of Au(111) in 1 mM CuSO₄ / 0.1 M H₂SO₄ in different concentrations of Acetonitrile
Scan rate: 5 mV s⁻¹

References

1. Herrero, E., Buller, L.J., Abruna, H.D., *Chemical Reviews*, 2001, **101**, 1897-1930
2. Rudnev, A.V., Molodkina, E.B., Danilov, A.I., Polukarov, Y.M., Feliu, J.M., *Electrochem. Communications*, 2008, **10**, 502-505
3. Rudnev, A.V., Molodkina, E.B., Danilov, A.I., Polukarov, Y.M., Berna, A., Feliu, J.M., *Electrochimica Acta*, 2009, **54**, 3692-3699

Spectroscopic Evidence of Size-Dependent Buffering of Interfacial pH by Cation Hydrolysis during CO₂ Electroreduction

Onagie Ayemoba and Angel Cuesta Ciscar

University Of Aberdeen, Department of Chemistry, School of Natural and Computing Sciences, University of Aberdeen, AB24 3UE Aberdeen, Scot-land, UK

Email: r010a15@abdn.ac.uk, angel.cuestaciscar@abdn.ac.uk

The nature of the electrolyte cation is known to affect the Faradaic efficiency and selectivity of CO₂ electroreduction. Singh et al. (J. Am. Chem. Soc. 2016, 138, 13006–13012) recently attributed this effect to the buffering ability of cation hydrolysis at the electrical double layer. According to them, the pKa of hydrolysis decreases close to the cathode due to the polarization of the solvation water molecules between the cation's positive charge and the negative charge on the electrode surface. We have tested this hypothesis experimentally, by probing the pH at the gold-electrolyte interface in situ using ATR-SEIRAS. The ratio between the integrated intensity of the CO₂ and HCO₃⁻ bands, which has to be inversely proportional to the pH, provided a means to determining the pH change in-situ during the electroreduction of CO₂. Our results confirm that the magnitude of the pH increase at the interface follows the trend Li⁺ > Na⁺ > K⁺ > Cs⁺, adding strong experimental support to Singh's et al.'s hypothesis. We show, however, that the pH buffering effect was overestimated by Singh et al., their overestimation being larger the larger the cation.

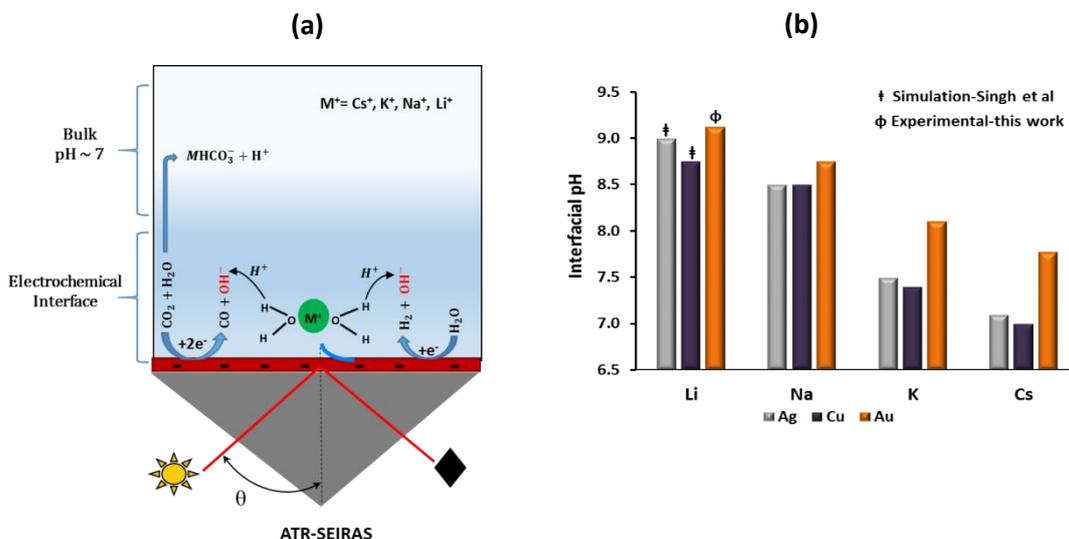


Figure 1: (a) Illustration of cation hydrolysis buffering the interfacial pH during electroreduction of CO₂ (b) Steady-state pH at the metal-electrolyte interface during the electroreduction of CO₂ at -1 V vs. RHE in CO₂-saturated 0.05 M M₂CO₃ solutions (M=Li, Na, K, Cs). pH values for Ag and Cu correspond to those resulting from Singh's et al.'s calculations, while in the case of Au they correspond to our experimental determination using ATR-SEIRAS.

Combined Optoelectronic and Electrochemical Study of Nitrogenated Carbon Electrodes

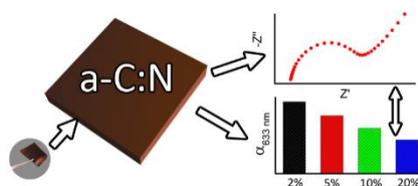
James A. Behan, Serban N. Stamatina, Md. Khairul Hoque, Guido Ciapetti, Federico Zen, Leticia-Esteban Tejeda and Paula E. Colavita

School of Chemistry, CRANN and AMBER Research Centres, Trinity College Dublin, College Green, Dublin 2, Ireland
Email: behanja@tcd.ie, colavitp@tcd.ie

The incorporation of Nitrogen into carbon-based materials has been suggested as a route towards new electrode materials with properties amenable to applications in electrocatalysis¹ and biosensing². Materials based on nitrogen-incorporated carbons have also been suggested for use as support materials in fuel cells due to their corrosion resistance and metal-free ORR activity³.

The realisation of these proposed applications requires a fundamental understanding of the effects of nitrogen incorporation on both the bulk physical properties and the surface chemistry of carbon materials. To this end we have prepared nitrogen-incorporated amorphous carbon thin films with varying N-content via DC magnetron sputtering and characterised them using a combination of optical and electrochemical techniques including X-ray photoelectron spectroscopy, ellipsometry, voltammetry and impedance spectroscopy. Here we present results indicating that low-levels of nitrogenation produce films with lower optical gaps and faster electron transfer kinetics to outer-sphere redox couples compared to unmodified amorphous carbon; higher levels of nitrogen-incorporation decrease the metallic character of the films, ultimately yielding materials with optical and electrochemical properties consistent with disordered cluster aggregates rather than amorphous solids⁴.

In addition to the physical properties of the bulk, surface chemistry is also important for understanding how structural changes induced in carbon materials by nitrogen incorporation may be best controlled to allow for the synthesis of new materials tailored for specific electrochemical applications. We therefore present studies on the electrochemistry of a-C:N electrodes with the surface-sensitive redox probe dopamine as a function of nitrogen content.



References:

1. Yoo, K.; Miller, B.; Kalish, R.; Shi, X., *Electrochem. Solid-State Lett.* **1999**, *2*, 233-235.
2. *Anal. Chem.* **2012**, *84*, 6240-6248.
3. Wang, D.-W.; Su, D., *Energy Environ. Sci.* **2014**, *7*, 576-591.
4. Behan, J. A.; Stamatina, S. N.; Hoque, M. K.; Ciapetti, G.; Zen, F.; Esteban-Tejeda, L.; Colavita, P. E., *J. Phys. Chem. C*, **2017**, *121* (12), pp 6596–6604

Electrowetting without Dielectrics

Robert A.W. Dryfe,^a Hollie V. Patten,^a Deborah J. Lomax,^a Aled T. Williams,^a Pallav Kant,^b Anne Juel^b and Pawin Iamprasertkuin^a

a) School of Chemistry

b) School of Physics & Astronomy

University of Manchester, Oxford Road, Manchester M13 9PL UK

Email: robert.dryfe@manchester.ac.uk

Electrowetting (EW) is a powerful method to achieve external wetting control, with many applications ranging from variable focal-length liquid lenses, electronic paper and the actuation of droplets in lab-on-a-chip devices. Recent work from Manchester has shown that EW can be observed on graphite: unprecedented changes in contact angle are seen for voltages below the electrolysis threshold (50° with 1 V for a water in air, and 100° with 1.5 V for water immersed in hexadecane) that are highly reproducible, stable over hundreds of cycles and free of hysteresis [1]. This enables one to realize EW on a conductor (EWOC), thus enabling the use of voltages that are one or two orders of magnitude lower than EW usually performed in device applications, with a dielectric layer (“EW on a dielectric”, EWOD). Current developments, including the extension of this work to aged/functionalised surfaces and other materials will be discussed [2].

References:

- [1] D.J. Lomax, P. Kant, A.T. Williams, H.V Patten, Y, Zou, A. Juel and R.A.W. Dryfe, *Soft Matter*, **12**, (2016), 8798.
- [2] K. Ounnunkad, H.V Patten, M. Velický, A.K. Farquhar, P.A. Brooksby, A.J. Downard and R.A.W. Dryfe, *Faraday Disc.*, in press, DOI: 10.1039/c6fd00252h

Keynote: Gary Attard

The slowly-evolving picture of the Pt{110} electrode surface: Is there still something new to learn from single crystal platinum voltammetry?

Gary A. Attard,^a Ashley Brew^b, Katherine Hunter^b, Ricardo Martínez-Hincapié^c, Juan Feliu^c, Jonathan Sharman^d and Edward Wright^d

a) Department of Physics, The Oliver Lodge Laboratory, University of Liverpool, Liverpool L69 7ZE, UK

b) School of Chemistry, Cardiff University, Park Place, Cardiff CF10 3AT, UK

c) Instituto de Electroquímica, Universidad de Alicante, Apartado 99, E-03080, Alicante, Spain

d) Johnson Matthey Technology Centre, Blount's Court Road, Sonning Common, Reading, RG4 9NH, UK

Email: attard@liv.ac.uk

It is crucial for a proper understanding of electrocatalysis that reactions at well-defined electrodes are pursued since such studies will inform how structure/activity relationships at 'real' supported electrocatalysts may be elucidated and optimised [1]. However, even a cursory inspection of the published literature pertaining to Pt{110} will highlight the fact that full understanding of the surface structure of "well-defined" Pt{110} is far from complete [2 - 5]. In this presentation, it will be demonstrated that depending on the cooling environment following flame-annealing, several different surface structural phases may be identified corresponding to (1x1) and variously disordered (1x1) and (1x2) reconstructed phases. Each of these phases in turn afford quite different activity in relation to the oxygen reduction reaction (ORR). Furthermore, by utilising stepped Pt{110} electrodes together with CO charge-displacement measurements (and also electrolyte pH/ionic strength studies) it is suggested that one may assign "local" values of the potential of zero charge to the voltammetric peaks observed. The consequences of this assertion for the interpretation of **all** of the complex voltammetric behaviour displayed by clean Pt{hkl} electrodes in aqueous media will be discussed [6].

[1] V. Climent and J.M. Feliu, Thirty years of platinum single crystal electrochemistry, *Journal of Solid State Electrochemistry*, 15 (2011) 1297-1315.

[2] D. Armand, J. Clavilier, Electrochemical behaviour of the (110) orientation of a platinum surface in acid medium: the role of anions, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* 263 (1989) 109-126.

[3] G.A. Attard, A. Brew, Cyclic voltammetry and oxygen reduction activity of the Pt{1 1 0}-(1 × 1) surface, *Journal of Electroanalytical Chemistry* 747 (2015) 123-129.

[4] N.M. Marković, B.N. Grgur, C.A. Lucas, P.N. Ross, Surface electrochemistry of CO on Pt(110)-(1 × 2) and Pt(110)-(1 × 1) surfaces, *Surface Science* 384 (1997) L805-L814.

[5] L.A. Kibler, A. Cuesta, M. Kleinert, D.M. Kolb, In-situ STM characterisation of the surface morphology of platinum single crystal electrodes as a function of their preparation, *Journal of Electroanalytical Chemistry* 484 (2000) 73-82.

[6] G.A. Attard, K. Hunter, E. Wright, J. Sharman, R. Martínez-Hincapié, J.M. Feliu, The voltammetry of surfaces vicinal to Pt{110}: Structural complexity simplified by CO cooling, *Journal of Electroanalytical Chemistry*, 793 (2017) 137-146.

Polymer of Intrinsic Microporosity (PIM) Film Coating Dampens Chaotic Copper Corrosion

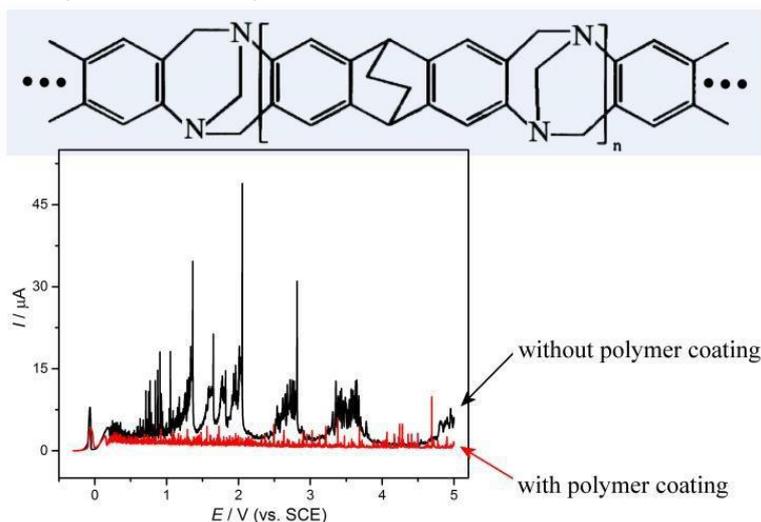
Amelia R. Langley¹, Neil B. McKeown², and Frank Marken¹

¹ Department of Chemistry, University of Bath, Bath BA2 7AY, UK

² School of Chemistry, University of Edinburgh, Joseph Black Building, West Mains Road, Edinburgh, Scotland EH9 3JJ, UK

Email: A.R.Langley@bath.ac.uk

Copper surfaces are known to exhibit oscillatory/chaotic behavior [1,2] under anodic conditions when immersed in salt water. The process can be dissected into the formation of insoluble Cu(I)Cl at the electrode surface followed by re-dissolution as Cu(II)Cl₃⁻ with complex/chaotic dynamics.



Here, the effect of an intrinsically microporous polymer (PIM-EA-TB, see Figure [3,4]) with micropores of typically 1-2 nm diameter coated over the copper surface is investigated. With voltammetry experiments at copper microelectrodes, it is demonstrated that the intrinsically microporous polymer can dampen the oscillatory behaviour depending on the thickness of the polymer coating. A mechanism is proposed.

References:

- [1] H. P. Lee and K. Nobe, *J. Electrochem. Soc.* 132 (1985) 1031-1037
- [2] K. S. Indira, S. K. Rangarajan, K. S. G. Doss, *J. Electroanal. Chem.* 21 (1969) 49-56
- [3] E. Madrid, Y.Y. Rong, M. Carta, N.B. McKeown, R. Malpass-Evans, G.A. Attard, T.J. Clarke, S.H. Taylor, Y.T. Long, F. Marken, *Angew. Chem. Inter. Ed.* 53 (2014) 10751-10754.
- [4] E. Madrid, P. Cottis, Y.Y. Rong, A.T. Rogers, J.M. Stone, R. Malpass-Evans, M. Carta, N.B. McKeown, F. Marken, *J. Mater. Chem. A* 3 (2015) 15849-15853.

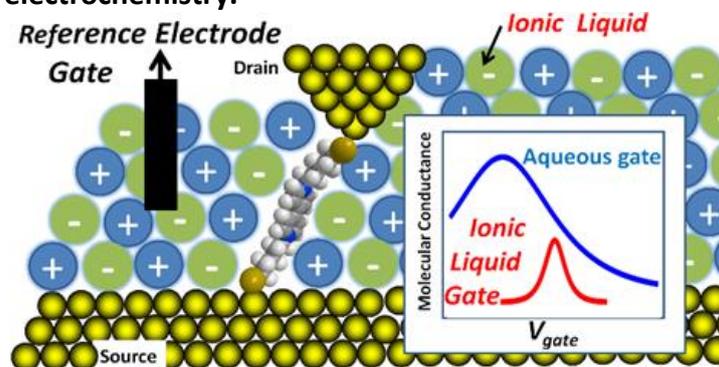
STM Studies of Electrochemical Single Molecule Transistors and Molecular Wires

Richard J. Nichols* and Osorio, H. M.; Cea, P.; Gluyas, J. B. G.; Hartl, F.; Higgins, S. J.; Leary, E.; Low, P. J.; Martín, S.; Tory, J.; Ulstrup, J.; Vezzoli, A.; Milan, D. C.; Zeng, Q.; Catarelli, S. R.; Schwarzacher, W.; Brooke, R., Mao, B.-W.; Yan, J.-W.; Jeppesen, J. O.; Lycoops, J; Kay, N. J.; Haiss, W. and Sedghi, G.

The University of Liverpool, UK

Email: nichols@liv.ac.uk

We have exploited STM based methods for making single molecule measurements under electrochemical potential control in ionic liquid electrolytes.¹⁻⁴ The electrochemical potential can be used to control the redox state of single molecule bridges and switch the electrical conductance from low to higher values. This has been referred to as the “single molecule electrochemical transistor” configuration, with the electrochemical potential “gating” the molecular conductance in the STM nano-gap configuration. Recent results from our group on gating the conductance of single molecules in ionic liquid electrolytes will be discussed including studies of viologens, redox active metal terpyridine molecular wires and pyrrolo-tetrathiafulvalene (pTTF) molecular bridges. Mechanisms of charge transport in the STM nano-gap setup are discussed alongside the advantages of undertaking such single molecule electrochemical measurements in ionic liquids. **Very recent results with semiconductor contacts will also be presented, with potential future applications in semiconductor electrochemistry.**



References

1. Vezzoli, A.; Brooke, R. J.; Ferri, N.; Higgins, S. J.; Schwarzacher, W.; Nichols, R. J., Single-Molecule Transport at a Rectifying GaAs Contact. *Nano Lett.* **2017**, *17* (2), 1109-1115.
2. Zhang, W.; Gan, S.; Vezzoli, A.; Davidson, R. J.; Milan, D. C.; Luzyanin, K. V.; Higgins, S. J.; Nichols, R. J.; Beeby, A.; Low, P. J.; Li, B.; Niu, L., Single-Molecule Conductance of Viologen–Cucurbit[8]uril Host–Guest Complexes. *ACS Nano* **2016**, *10* (5), 5212-5220.
3. Nichols, R. J.; Higgins, S. J., Single Molecule Nanoelectrochemistry in Electrical Junctions. *Acc. Chem. Res.* **2016**, *49* (11), 2640-2648.
4. Osorio, H. M.; Catarelli, S.; Cea, P.; Gluyas, J. B. G.; Hartl, F.; Higgins, S. J.; Leary, E.; Low, P. J.; Martín, S.; Nichols, R. J.; Tory, J.; Ulstrup, J.; Vezzoli, A.; Milan, D. C.; Zeng, Q. Electrochemical Single-Molecule Transistors with Optimized Gate Coupling. *Journal of the American Chemical Society* **2015**, *137*, 14319-14328.

Using X-ray and neutron reflectometry to monitor corrosion mechanisms at the angstrom-level

Mary H. Wood¹, J. Poon¹, D. Madden¹, T. J. Wood², R. J. L. Welbourn², S. M. Clarke¹

¹ University of Cambridge, Cambridge, ²ISIS, Rutherford Appleton Laboratory, Didcot

Email: maryhwood@gmail.com

The corrosion of ferritic steel in salt solutions remains a major problem across a range of industries and is a massive drain on the economies of developed nations (coming in around 3-4 % of their GDP)^{1,2}. Although great effort has been expended into researching its causes and prevention, this has mainly focused on bulk electrochemical or physical methods. X-ray and neutron reflectometry (XRR and NR) are both extremely powerful techniques that allow angstrom-level quantification of the thickness, composition and roughnesses of surface films and hence offer unique opportunities to increase understanding concerning the fundamental surface chemistry underlying corrosion and inhibition mechanisms³.

In this work, XRR and NR were used with complementary techniques such as XPS to study iron films (as a model for ferritic steel) under a range of different corrosive environments and with the addition of potential corrosion inhibitors. NR in particular was used to elucidate the structure of organic species at the interface *in situ*, whereas XRR was more powerful in terms of characterising the changing metal surface. This allowed a detailed breakdown of the time-dependent structural changes caused by corrosion (for example, as shown in Figure 4, the growth of a void under the film surface followed by complete dissolution of the iron layer) as well as a direct comparison of several potential corrosion inhibitors. Some surprising methods for protecting the surface that didn't involve addition of inhibitors but that proved extraordinarily effective were also revealed.

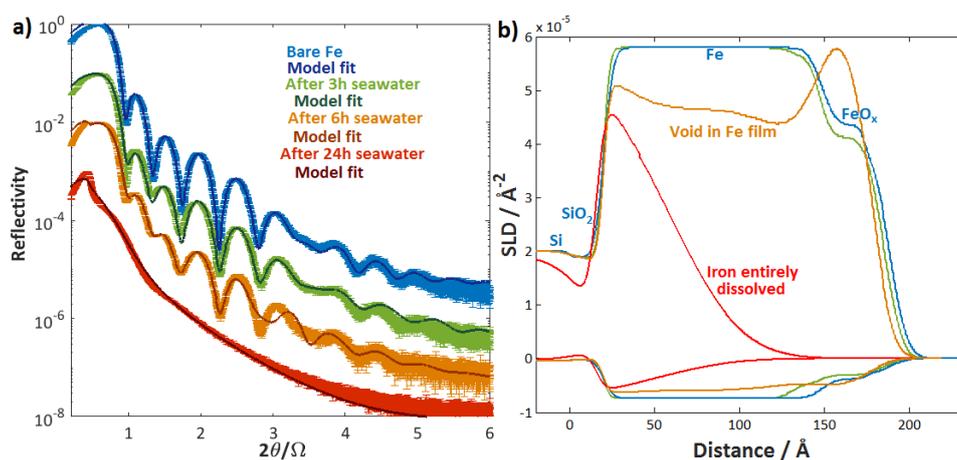


Figure 4a) Example of XRR data for a 20 nm Fe film after various amounts of time soaked in seawater (fits shown as solid lines). b) Scattering length density (SLD) profiles of the fitted models, showing evolution of the iron structure with increasing corrosion.

With thanks to Shell for project funding and to the ISIS neutron source for instrument time.

References

- (1) Mills, A.; Hazafy, D. *Chem. Commun.* **2012**, 48, 525.
- (2) Noël, J. J. In *Neutron reflectometry- a probe for materials Surfaces*; International Atomic Energy Agency, 2004; pp 79–84.
- (3) Wood, M. H.; Welbourn, R. J. L.; Zorbakhsh, A.; Gutfreund, P.; Clarke, S. M. *Langmuir* **2015**, 31, 7062.

Electroless Ni-B plating in a gradient magnetic field.

S. Danilova,^a J. E. Graves,^a L. Bonin,^b V. Vitry,^b A. Cobley^a

*a) The Functional Materials Applied Research Group, Coventry University
Priory Street, Coventry, UK CV1 5FB*

*b) Metallurgy Unit, Engineering faculty, University of Mons
56 Rue de l'Epargne 7000 Mons, Belgium
Email: danilovs@uni.coventry.ac.uk*

Electroless deposited Ni-B is a promising material for the automotive and aerospace industries due to its exceptional hardness. The morphology, grain size and roughness affect the properties of the material. The introduction of a magnetic field during the alloy deposition process has been reported to have effects on the layer formation and therefore the properties of the deposit [1]. The magnetohydrodynamic effect arises when the magnetic field is applied and improves the mass transport in solution during electrochemical deposition, affecting the morphology and crystal structure of the deposit [2]. In addition, patterning has also been observed during electrochemical deposition in a gradient magnetic field [3].

The current work was conducted at the University of Mons, Belgium and Coventry University, UK as a short term scientific mission sponsored by e-MINDS COST MP1407. The Ni-B electroless deposition was performed on a stainless steel substrate in baths of various compositions and using a magnet of 0.2 T strength and 10x10x5 mm size attached behind the test piece.

The deposit showed the distinctive patterning effect (Figure 1 (a)) as well as more uniform layer morphology (Figure 1 (b and c)). This paper will propose the theory underlying these findings and discuss potential industrial applications.

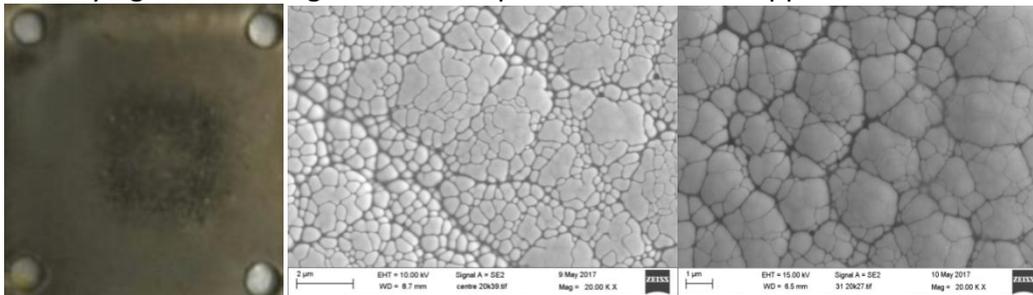


Figure 1. Electroless Ni-B deposition under gradient magnetic field. (a) Optical image of substrate with distinctive pattern effect, (b) SEM image of layer deposited under magnetic field, (c) SEM image of layer deposited without magnetic field.

References

- [1] Y. Yu, G. Wei, X. Hu, H. Ge, Z. Yu, *Surf. Coatings Technol.* 204 (2010) 2669–2676;
- [2] L.M.A. Monzon, J.M.D. Coey, *Electrochem. Commun.* 42 (2014) 38–41;
- [3] P. Dunne, J.M.D. Coey, *Phys. Rev. B - Condens. Matter Mater. Phys.* 85 (2012) 1–21.

Proton conduction pathways in porous organic cage networks and functionalised silica ionogels

Scott Lewis, Ming Liu^(a), Matthew Michie^(a), Linjiang Chen^(a),
Marc A. Little^(a), Sam Y. Chong^(a), Iain M. Aldous^(a), Tom Hasell^(a),
Andrew I. Cooper^(a) and Laurence J. Hardwick^(a)

*Stephenson Institute for Renewable Energy and Department of Chemistry,
University of Liverpool, Liverpool L69 7ZF, UK
Email: slewis10@liverpool.ac.uk*

Organic molecular cage salts containing protonated secondary amine groups show promise as proton conducting electrolytes due to their high water uptake, intrinsic porosity and appreciable ionic conductivity. Herein we report the proton conductivity of reduced amine cage salts with conductivities in the range 10^{-3} - 10^{-2} S cm⁻¹ [1], at temperatures up to 80°C. These cages are formed from reversible imine bond formation and packing of discrete, rigid cage molecules results in a defined microporous structure [2]. Proton conductivity was investigated using the 2-probe AC method of impedance spectroscopy under varying humidity and temperature for various cage systems. The determined activation energies of ca. 0.3 eV indicate a mixed Grotthuss and vehicular method of proton transport and suggest high intrinsic proton transport for some cage materials [1]. Comprehensive simulation studies and structural characterisation using powder XRD, and water uptake measurements suggests that water molecules form clusters within the voids of the charged cage cations and as a result, become polarised which facilitates proton transport. Both molecular dynamic simulation and transference number studies imply that the anionic moieties investigated (for example Cl⁻ and SO₄²⁻) are too large to be mobile and remain fixed around each cage cation.

Inorganic silica gels can be readily synthesised via sol-gel processing of tetraalkyl-orthosilicates in a suitable solvent under acidic or basic conditions [3]. The resulting porous aerogels can be used as a matrix to entrap small molecules and ions to increase the functionality of these gels for applications such as solid electrolytes, sensors, ion exchange resins and as supercapacitors and are thermally stable [3]. We have optimised the sol-gel process to create porous ionogels incorporating low concentrations (<10% wt.) of [4+6] porous proton conducting amine cage salts, which have previously demonstrated appreciable proton conductivity. A series of water-stable ionogels were investigated using electrochemical impedance spectroscopy and the confinement of the cage salts was probed using short angle X-ray scattering (SAXS). Synthesised ionogels exhibited proton conductivity of 10^{-6} - 10^{-4} S cm⁻¹ from room temperature to 150°C.

[1] Liu, M. *et al.*, *Nature Commun.*, **7**, 1–9 (2016).

[2] Tozawa, T. *et al.*, *Nat. Mater.* **8**, 973–8 (2009).

[3] Brachet, M., Brousse, T. & Le Bideau, J.. *ECS Electrochem. Lett.* **3**, A112–A115 (2014).

Trends in oxygen reduction on a Pt-alloy single crystal: acidic versus alkaline media

Back Kim D. Jensen^a, Jakub Tymoczko^b, Aliaksandr S. Bandarenka^c, Ib Chorkendorff^a,
María Escudero- Escribano^a, and Ifan E. L. Stephens^d

a Department of Physics, Technical University of Denmark (DTU), Kgs. Lyngby, Denmark

b Analytical Chemistry – Center for Electrochemical Sciences (CES), Ruhr-Universität Bochum, Germany

*c Energy Conversion and Storage (ECS), Physik-Department, Technische Universität München (TUM),
Germany*

d Department of Materials, Imperial College London, United Kingdom

Email: i.stephens@imperial.ac.uk

Electrochemists have made huge progress in understanding how to tune the reactivity of the electrode-electrolyte interface. Most studies have focused on tailoring the electrode, by modifying the surface electronic structure. However, it is of fundamental importance to understand how to tailor the electrolyte side of the interface. Oxygen reduction is the most studied electrochemical reaction, as it limits fuel cells and metal air batteries.

In our earlier studies, we mapped out the experimental *Sabatier* volcano for the oxygen reduction reaction in 0.1 M HClO₄ using the Cu/Pt(111) near-surface alloy. We experimentally confirmed the theoretical notion that the most optimal catalyst should exhibit OH binding 0.1 eV weaker than Pt(111).[1] However, numerous reports suggest significant divergences in the catalytic performance of noble metals between acid and base. [2,3]

In the current study, we extend our previous studies on the Cu/Pt(111) to alkaline media. By focusing on surfaces with the (111) orientation, we can orthogonalise surface orientation and the reactivity of the surface. Remarkably, we observe that the same trend persists between OH binding and oxygen reduction activity in acid and alkaline media. Moreover, all surfaces show a ~8 fold improvement in activity in 0.1 M KOH, relative to the same surface in 0.1 M HClO₄. At the peak of the volcano, we observe an exceptionally high activity of 107 mA/cm² at 0.9 V with respect to the reversible hydrogen electrode. Curiously, stepped surfaces with the same binding to OH are markedly less active than Pt(111).[3] Taking these findings together, we deduce that in alkaline media, surface orientation may play a non-trivial role on electrochemical kinetics; i.e. binding to the reaction intermediates is not the only effect that controls activity.

[1] Stephens, I. E. L., et al **J. Am. Chem. Soc.** 133, 5485, (2011).

[2] Staszak-Jirkovský, J., et al **ACS Catalysis** 5, 6600, (2015).

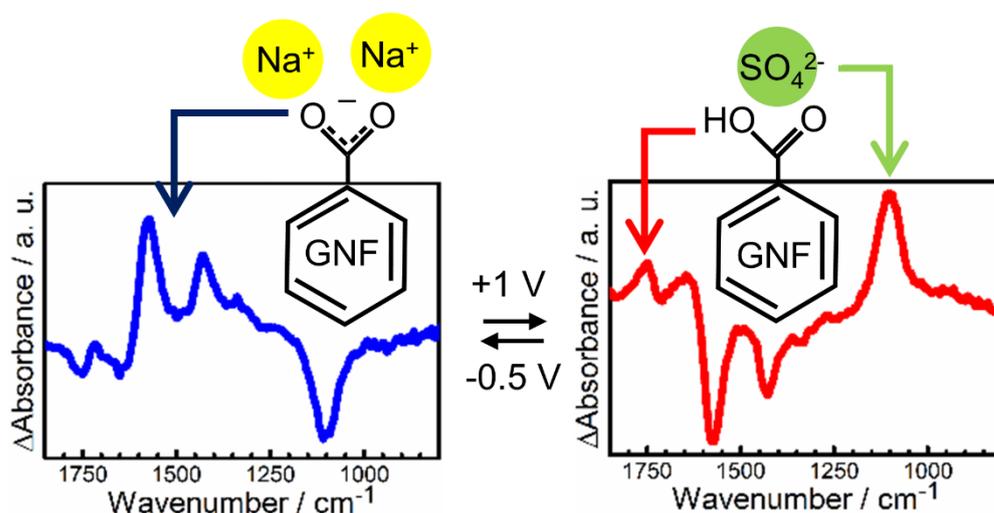
[3] Rizo, R., et al. M. **Physical Chemistry Chemical Physics** 15, 15416, (2013).

Deprotonation of graphene nanoflake electrode edge groups studied using *in situ* IR spectroelectrochemistry

Katherine B Holt,^a Mailis M. Lounasvuori

*a) Department of Chemistry, University College London
Email: k.b.holt@ucl.ac.uk*

The ubiquity of acid moieties at electrode interfaces, as defect sites on carbon electrodes and as polymer electrolytes of solid supercapacitors, makes understanding their response to applied electrode potential an essential area of study. In this study we use *in situ* IR spectroscopy to monitor the protonation state of carboxylic edge groups of graphene nanoflakes as a function of applied potential¹.



Deprotonation of acid groups was found to take place on application of a negative potential, with positive potential resulting in their re-protonation. The deprotonation was found to be induced by a local increase in cation activity at the electrode interface on application of negative potential. The increase in cation activity has the effect of lowering the effective pK_a of the acid groups which induces deprotonation to take place.

The *in situ* measurements allowed concomitant changes in electrolyte composition to be determined. It was found that solution acid species, such as HSO₄⁻ and H₂PO₄⁻ also undergo deprotonation when a negative potential is applied. This is also attributed to the migration of cations towards the electrode increasing their local activity and lowering the effective pK_a of the solution acids. This observation is important as it implies that speciation of acids near a biased electrode can differ significantly from bulk solution and this can be driven purely by cation migration in the absence of adsorption, redox chemistry or pH change.

Reference:

[1] M. M. Lounasvuori, K. B. Holt, *Chem. Commun.* (2017) **53**, 2351.

Study of Oxygen Reduction Reaction by Scanning Electrochemical Microscopy

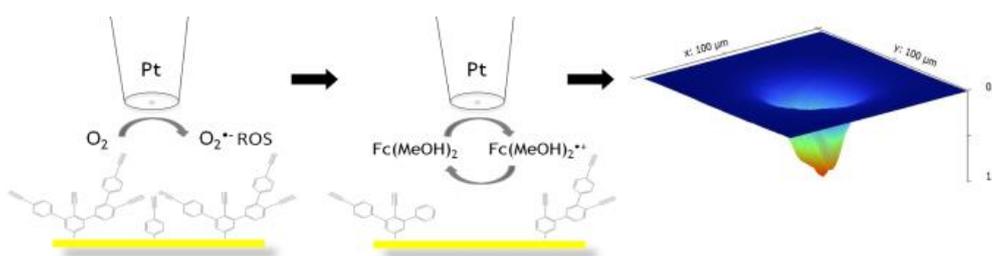
Y. Aceta, Y.R. Leroux, P. Hapiot^a

a) Institut des Sciences Chimiques de Rennes, UMR CNRS 6226, Université de Rennes 1, Equipe MaCSE, Campus Beaulieu, 35042 Rennes Cedex, France
Email: jezebel.aceta@univ-rennes1.fr

Multielectronic O₂ reduction reaction (ORR) and its catalysis is of general importance in natural and industrial processes.¹ The generally admitted description of ORR in water as simple competitive pathways between 2-electron (O₂ to H₂O₂) and 4-electron (O₂ to H₂O) reductions is often inadequate. The electron transfer steps could be accompanied by homogeneous or heterogeneous chemical steps and oxygen-oxygen bond breaking leading to possible numerous intermediates. This chemical reactions are usually so fast that the detection and characterization of intermediates, and thus the establishment of the reaction mechanism remains unknown.²

In this study, we have investigated the reduction of O₂ in water as function of different experimental parameters (pH, potential, additives...) by SECM using a foot-printing strategy.² This approach is based on the use of a sensitive surface to evidence the formation of reactive oxygen species (ROS), for example OH radicals during the ORR.

The role of added scavenger on the production of ROS was also examined. Considering the high reactivity of some of these ROS versus organic and living materials, these studies could have important consequences in several practical situations (biological sensors, fuel cell catalysts, reaction kinetics, porous membrane studies, corrosion mechanisms, etc.) as far as O₂ reduction is concerned.^{3,4}



References

- (1) Bard, A. J. *J. Am. Chem. Soc.* **2010**, *132* (22), 7559–7567.
- (2) Andrieux, C. P.; Hapiot, P.; Saveant, J. *J. Am. Chem. Soc.* **1987**, *109* (12), 3768–3775.
- (3) Noël, J. M.; Latus, A.; Lagrost, C.; Volanschi, E.; Hapiot, P. *J. Am. Chem. Soc.* **2012**, *134* (5), 2835–2841.
- (4) Lhenry, S.; Leroux, Y. R.; Hapiot, P. *Anal. Chem.* **2012**, *84* (17), 7518–7524.

Corrosion

Oral Abstracts

Improvement of sol-gel coatings and their anti-corrosion properties by doping with Titanium precursors

T. Lutzler^{a)*}, A. Alejo-Rodriguez^{b)}, T. Charpentier^{a)}, H. Schneider^{b)}, A. Neville^{a)}

^{a)} *Institute of Functional Surfaces, School of Mechanical Engineering, University of Leeds, Leeds LS2 9JT, United Kingdom*

^{b)} *EPG AG-Succursale France, Parc d'activités communautaire n° 1, 135 Voie Principale, 57450 Henriville, France*
Email: mntl@leeds.ac.uk

Corrosion is a major oilfield flow assurance problem^[1]. Paints and coatings are often used in oil production environment as a barrier to corrosion. In recent studies sol-gel materials draw increasing interest due to many promising properties like hardness, durability, scratch resistance and thermal stability and are gaining more worldwide recognition as an alternative for the preparation of glasses and ceramics at lower temperatures^[2]. Beside the protection of metals and its alloys in corrosive environments, sol-gel-based coatings also exhibit high potential as an alternative to coatings that contain toxic compounds like chromate^[3]. In this project silica inorganic sol-gel coatings were studied in order to follow the evolution of corrosion and to optimize their physico-chemical properties with particular attention to their corrosion resistance properties. To evaluate the protective properties stainless steel 304/304L coupons coated with inorganic coatings with or without doping material were subjected to a corrosive environment. IO is considered as the reference. IM sample was synthesized with the same sol-gel structure and composition and was in addition doped with Titanium precursor. The coatings are a few μm thick. The kinetics of the degradation process were monitored throughout by electrochemical impedance spectroscopy (EIS). Besides EIS, electron microscopy was used to characterize the coating morphology before and after exposition to the corrosive environment. Chemical changes of the coating materials were determined by IR spectroscopy and Scanning Electron Microscopy (SEM). The achieved data allow to understand the failure mechanisms of these coatings and help to improve the formulation to enhance their resistance to corrosion.

[1] Oyeneyin, B. (2014). Integrated sand management for effective hydrocarbon flow assurance. Amsterdam, Elsevier.

[2] Pierre, A. C. (1998). Introduction to sol-gel processing. Boston/Dordrecht/London, Kluwer Academic Publishers.

[3] Zhong, X., et al. (2010). A novel approach to heal the sol-gel coating system on magnesium alloy for corrosion protection. *Electrochimica Acta* 55(7): 2424-2429.

AFM-SECM and Nanoelectric Liquid Imaging for Corrosion Research

Hao Sun,^a Shawn Qu,^b Anyang Cui,^c Yufeng Dai,^b Zhigao Hu,^c Khizar Sheikh^a, Zhuangqun Huang,^a Peter De Wolf^a

^a Bruker Nano Surfaces, 112 Robin Hill Road, Santa Barbara, California, CA 93117 USA

^b Huawei Technologies Co., Ltd., Shenzhen, Guangdong, China 518129

^c Department of Electronic Engineering, East China Normal University, Shanghai, China 200241

Corrosions often are redox reactions that involve metal oxidation by dioxygen, proton or water, and result in the release of hydroxyl groups, metal cations, or hydrogen. Localized processes, e.g. pitting, crevice, and galvanic corrosions, are primary forms, while even global uniform corrosion occurs heterogeneously on micro- or nanoscale. These local reactivity heterogeneities are the consequence of the local differences in structural, mechanical, electrical, and/or electrochemical properties. Therefore, approaches capable of simultaneously capturing correlated multidimensional information on nanoscale are highly desired. In addition, in these dynamic processes, *in situ*, non-invasive methodologies are also highly desired.

We have recently developed batch-fabricated, high-quality and robust nanoelectrode probes with the exposed Pt-coated tip apex of ~200 nm height and the end tip diameter of ~50 nm. These nanoelectrode tips are designed for Atomic Force Microscopes (AFM) platform to enable the AFM-based scanning electrochemical microscopy (SECM). AFM-SECM provides high-resolution, highly-multidimensional information. For example, PeakForce SECM and Force Volume SECM simultaneously images surface topography, quantitative nanomechanics, electrochemistry (at < 100 nm resolution), and tip-sample contact current.^{1,2} The nanoelectrode probe is also the critical enabler of nanoelectric measurements in liquid, such as conductivity, surface potential and piezo response imaging in electrolyte environment.

In this talk, we will present the recently-developed nanoelectrode probe, a variety of AFM-SECM modes, nanoelectric liquid studies, and their applications in corrosion research. Examples discussed here include surface protection, reactivity hot spots revealed by *in situ* product detection, deposition and the subsequent stripping of metal products on the nanoelectrode tip, and nanoelectric liquid imaging of model samples. This work demonstrates the versatility of this suite of new techniques for corrosion research.

References:

- 1 Nellist et al., *Nanotechnology*, 2017, **28**, 095711.
- 2 Huang et al., *Microscopy Today*, 2016, **24**, 18.

Effect of the use of pulse plating techniques in electrodeposited Sn-Cu Coatings for Pb-free, environmentally-friendly applications

Dr Andrew Cobley, Dr Liang Wu

*The Functional Materials Research Group, Centre for Manufacturing and Materials Engineering
Coventry University, Coventry, United Kingdom
Email: a.cobley@coventry.ac.uk*

The electrodeposition of lead containing alloys have found many industrial applications including electronics and other applications. However, lead is very harmful to health and the environment and the Restriction of Hazardous Substances Directive (RoHS) has been in force in Europe since 2003 restricting the use of certain hazardous substances (e.g. lead, cadmium, mercury etc.) in electrical and electronic equipment and this is likely to be extended to other industrial sectors. For this reason there is intensive research to find alternatives to lead alloys and one favourable candidate is Sn-Cu. This paper will describe a study carried out to obtain a deeper understanding of some of the factors affecting Sn-Cu electroplating. Experimental work, by means of Hull Cell tests, ultrasonic agitation and pulse plating, has been undertaken to understand the effect of these factors on the properties of the Sn-Cu coatings. A number of advanced analytical techniques, including scanning electron microscope (SEM), energy dispersive x-ray spectroscopy (EDS) and white light scanning interferometry (WLS), have been used to evaluate the characteristics of the Sn-Cu coatings, in terms of their surface morphology, chemical composition and microstructure.

It was found that that pulse plating techniques combined with high speed magnetic stirring during deposition had a strong effect on the characteristics of the Sn-Cu electrodeposits and, in the short term, on Sn whiskers developing from the deposit.

This work is funded via the EU H2020 Fast Track to Innovation programme.

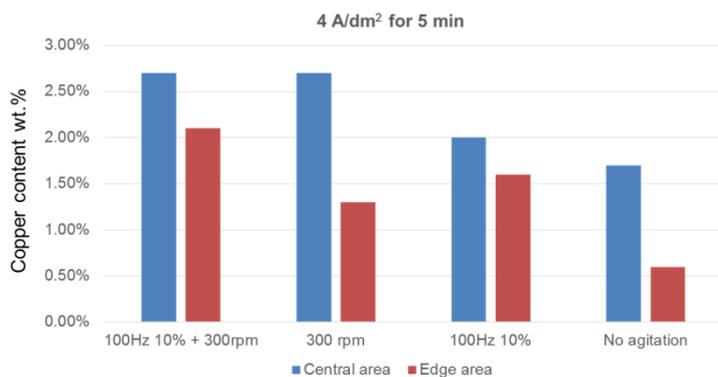


Figure 1. Effect of pulse plating on copper content of Sn-Cu alloy electrochemical deposition. All samples plated at 4 A/dm² for 5 minutes

Effect of surface roughness on pitting behaviour of X65 carbon steel in saturated CO₂ environment

Sikiru Mohammed, Yong Hua, R. Barker, A. Neville

*Department of Mechanical Engineering
University of Leeds LS2 9JT, UK
Email: mnsam@leeds.ac.uk*

Surface finishing of steel can be interpreted in terms of roughness which may vary based on demand specifications. Pitting investigations are often conducted using polished samples which are not true reflection of in-service applications [1]. Machining and surface finishing impact on steel roughness which has been reported to influence pitting in low carbon steel [2]. Roughness on mild steel varies depending on speed and rake angle utilised during turning operations while corrosion tests revealed higher pit depth for rough surface compared to smooth surface [2].

Burstein et al. [3] examined the influence of surface roughness on metal stable pitting of stainless steel. They reported that smooth surfaces have low chance of metastable pitting but that emerged metastable pits have high probability for survival. Chen et al. [4] study on influence of SRB and surface roughness on carbon steel pitting revealed that surface roughness play significant role in carbon steel pitting. Eyu et al. [5] assessed the effect of surface roughness on carbon steel employed for coal steam application and observed that corrosion potential decreased as surface roughness increased; indicating higher ferrite dissolution with increase in roughness. Their work as well reported higher pitting with increase in surface roughness. Melchers et al. [6] work on mild steel corrosion in marine environment reported that surface roughness influence carbon steel pitting only at the early stage. FeCO₃ and Fe₃C are the common corrosion products formed on low carbon steel. FeCO₃ film adheres to steel surface and retards corrosion under suitable conditions but pitting could still progress beneath FeCO₃ film. There is yet no known literature comparing the influence of surface roughness on pit initiation/propagation beneath formed FeCO₃ and under film-free conditions.

This work therefore investigated the effect of surface finishing on pitting beneath FeCO₃ film formed on API 5L X65 (UNS K03014) carbon steel as well as under film-free conditions in saturated CO₂ environment. X65 carbon steel was polished to 3 different finishing: 120 grit; 1,200 grit; and 0.25 μ m. LPR/OCP measurements were conducted for the different samples under 3.5 wt% NaCl, 80°C up to 96h at pH3.8 and pH6.6. Top view SEM image was observed before cleaning sample in Clarke's solution followed by surface profilometry of corroded sample surface. Results revealed that pitting progressed beneath both Fe₃C and FeCO₃ films with less pitting recorded for FeCO₃ films. As expected, pitting was observed to increase as surface roughness increased.

Keywords: Carbon steel, surface roughness, sweet corrosion, pitting, profilometry

References

- [1] G. Hinds, L. Wickstrom, K. Mingard, and A. Turnbull, "Impact of surface condition on sulphide stress corrosion cracking of 316l stainless steel," *Corrosion Science*, vol. 71, pp. 43-52, 2013.
- [2] M. Prakash, S. Shekhar, A. Moon, and K. Mondal, "Effect of machining configuration on the corrosion of mild steel," *Journal of Materials Processing Technology*, vol. 219, pp. 70 - 83, 2015.
- [3] G. Burstein and P Pistorius, "Surface roughness and the metastable pitting of stainless steel in chloride solutions," *Corrosion*, vol. 51, no. 5, pp. 380-385, 1995.
- [4] Y Chen, R. Howdyshell, S. Howdyshell, and L.-K. Ju, "Characterizing pitting corrosion caused by a long-term starving sulfate-reducing bacterium surviving on carbon steel and effects of surface roughness," *Corrosion*, vol. 70, no. 8, pp. 767-780, 2014.
- [5] G. D. Eyu, G. Will, W. Dekkers, and J. MacLeod, "Effect of hydrodynamics and surface roughness on the electrochemical behaviour of carbon steel in CSG produced water," *Applied Surface Science*, vol. 357, Part A, pp. 506 - 515, 2015.
- [6] R. Melchers and R. Jeffrey, "Surface roughness effect on marine immersion corrosion of mild steel," *Corrosion*, vol. 60, no. 7, pp. 697-703, 2004.

Towards realistic atmospheric aerosol deposits – automated ultrasonic deposition

Angus J. M. C. Cook,^a Alison Davenport^a

a) School of Metallurgy and Materials, University of Birmingham, Edgbaston, West Midlands, UK, B15 2TT

Email: amc910@bham.ac.uk

The study of atmospheric corrosion, where contaminants collect on metal surfaces through aerosol deposition, has previously been investigated using a variety of methods with various benefits and drawbacks, such as thin-film electrochemistry, high throughput droplet tests, and salt-fog style experiments.(1-3)

Ultrasonic plates have been used to more accurately replicate the process of atmospheric aerosol deposition through solution atomisation; the duration and intensity of the ultrasonic pulse may be accurately controlled, and result in a controllable droplet size profile.(4) In this paper we extend the use of an ultrasonic atomiser to create an automated, localised aerosol deposition system, capable of repeatable deposition profiles over a contained area. This allows for high-throughput, realistic spray tests to be undertaken

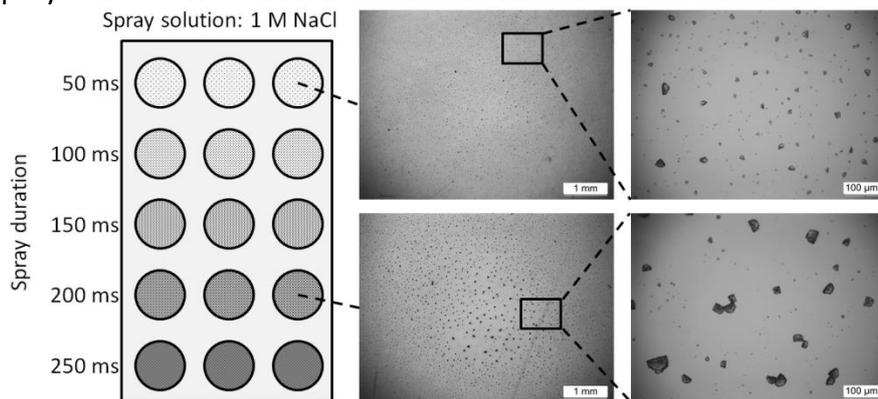


Figure 5 Example deposition scheme over a single sample, with micrographs of representative dry NaCl deposits

1. Nishikata A, Ichihara Y, Tsuru T. AN APPLICATION OF ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY TO ATMOSPHERIC CORROSION STUDY. *Corrosion Science*. 1995;37(6):897-911.
2. Cook AJMC, Padovani C, Davenport AJ. Effect of Nitrate and Sulfate on Atmospheric Corrosion of 304L and 316L Stainless Steels. *Journal of The Electrochemical Society*. 2017;164(4):C148-C63.
3. de la Fuente D, Bohm M, Houyoux C, Morcillo M, Rohwerder M. Methods for salt contamination of steel corrosion products: A characterization study. *Mater Corros*. 2007;58(10):781-8.
4. Oltra R, Colard L, Bonzom R. A novel methodology to study localized corrosion under atmospheric simulated corrosion conditions: Toward a continuous monitoring of the corrosion damage on AA2024. *Materials and Corrosion*. 2017;68(3):311-5.

Characterisation of Corrosion Products of a Ti-Based Metallic Glass in Artificial Pits by In Situ Synchrotron X-ray Diffraction

P. F. Gostin^a, Y. Zhang^a, A. Cook^a, A. Morrell^b, A. Liens^c, K. Ignatyev^d, M. Stoica^e, O. Addison^a, A. Davenport^a

a) University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom

b) Aston University, Birmingham B4 7ET, UK

c) INSA Lyon MATEIS, CNRS, UMR 5510, F-69621 Villeurbanne, France

d) Diamond Light Source, Didcot, Oxfordshire OX11 0DE, United Kingdom

e) ETH Zurich, Vladimir-Prelog-Weg 4, Zurich 8093, Switzerland

Email: p.gostin@bham.ac.uk

Current standard corrosion tests of metallic biomaterials are carried out in vitro in simulated body conditions on bulk components or specimens. These test conditions may not be sufficient to predict the actual behaviour of an implant in vivo. Indeed, it was demonstrated recently that titanium implants can corrode in the absence of wear, generating pro-inflammatory corrosion products leading to revision surgery [1]. The observed corrosion products may have been produced through a localized form of corrosion called mechanically assisted crevice corrosion. Conventional corrosion testing on passive surfaces is not able to predict those corrosion products. More aggressive tests like artificial pit methods, provide more realistic conditions leading to corrosion products similar to the ones found in vivo. Synchrotron X-ray methods can be employed to identify and characterise in situ such corrosion products [2].

Titanium-based metallic glasses hold promise for use in small implants due to their high yield strength. So far, their corrosion behaviour has been characterised using standard polarisation methods on passive bulk specimens. Most of them are passive and have a relatively high pitting corrosion resistance in simulated body conditions.

In this work, we use in situ synchrotron X-ray diffraction to characterise corrosion products generated by a Ti-based bulk metallic glass, i.e. Ti₄₀Zr₁₀Cu₃₄Pd₁₄Sn₂ (at.%) [3], inside artificial pits formed in 0.9% NaCl (+ 4% albumin; + 0.1% H₂O₂; + 4% albumin + 0.1% H₂O₂). In all electrolytes, the pit cavity contains a black layer, predominantly Pd, with PdCl₂ in some cases, and closer to the interface CuCl typically within ≤100 μm. This suggests Pd nanoparticles may be generated by the glassy Ti₄₀Zr₁₀Cu₃₄Pd₁₄Sn₂ alloy during service. The effect of Pd nanoparticles on cell behaviour will be determined in future work.

1. Addison, O., et al., *Do 'passive' medical titanium surfaces deteriorate in service in the absence of wear?* Journal of the Royal Society, Interface, 2012. **9**(76): p. 3161-3164.
2. Rayment, T., et al., *Characterisation of salt films on dissolving metal surfaces in artificial corrosion pits via in situ synchrotron X-ray diffraction.* Electrochemistry Communications, 2008. **10**(6): p. 855-858.
3. Zhu, S.L., X.M. Wang, and A. Inoue, *Glass-forming ability and mechanical properties of Ti-based bulk glassy alloys with large diameters of up to 1 cm.* Intermetallics, 2008. **16**(8): p. 1031-1035.

Analysis of X65 Carbon Steel Surfaces After Erosion-Corrosion Testing Using a Submerged Impingement Jet

Joshua Owen^a, Richard Barker^a, Anne Neville^a

a) Institute of Functional Surfaces (IFS), School of Mechanical Engineering, University of Leeds, Leeds, LS2 9JT, UK

Email: mn09jjo@leeds.ac.uk

Erosion-corrosion in the oil and gas industry, caused by the mechanical removal of material due to the impingement of sand particles and carbon dioxide (CO₂) corrosion, is a significant problem that can result in high degradation rates of carbon steel pipelines. Erosion-corrosion material loss is typically greater than the sum of the individual erosion and corrosion components, due to the interaction between the two wear mechanisms, resulting in an enhanced total material loss. Erosion-corrosion research has shown how parameters such as sand concentration and flow velocity affect the contributions of corrosion, erosion, corrosion-enhanced erosion and erosion-enhanced corrosion to total erosion-corrosion material loss. However, further investigation into the causes of corrosion-enhanced erosion and erosion-enhanced corrosion of carbon steel in conditions representative of oil and gas pipe flow conditions is required.

This work presents analysis of X65 carbon steel surfaces after erosion-corrosion tests in a submerged impingement jet (SIJ). The SIJ is capable of replicating harsh erosion-corrosion operating conditions, with high flow velocities and sand concentrations (20m/s and 1000mg/l) used to create a highly erosive and corrosive environment to investigate the interactions between erosion and corrosion. Computational fluid dynamics (CFD) was used to predict the trajectories of sand particles through the SIJ nozzle to determine impact angles and impact velocities on the surface of the X65 sample. Various surface analysis techniques were used to examine the surfaces of the carbon steel samples after erosion-corrosion tests to give a better understanding of the causes of corrosion-enhanced erosion and erosion-enhanced corrosion and how the interaction between corrosion and erosion contribute to the total erosion-corrosion wear of carbon steel.

Potentiodynamic Anodic Polarisation Parameters as Indicators to Erosion-Corrosion of Stainless Steel

Mohammed Nabeel Majeed, Anne Neville, Richard Barker

Institute of Functional Surfaces (IFS), School of Mechanical Engineering, University of Leeds, LS2 9JT, Leeds, UK.

Email: mnmnm@leeds.ac.uk

Most of the studies that have dealt with the issue of erosion-corrosion resistance of stainless steels have focused on investigating the effect of influencing parameters such as flow velocity, sand loading and impact angle amongst others. These parameters are mostly linked to the resistance of a material to erosion. It is known that a corrosive environment can exacerbate erosion. Temperature is known to play a noticeable role in corrosion but only few published literature assess the effect of temperature on erosion-corrosion.

It is known that the corrosion resistance of corrosion resistant alloys reduces when the Critical Pitting Temperature (CPT) is reached. There is no literature that has examined the corrosion resistance of materials at their CPTs under erosion circumstances. This work therefore aims to investigate the effect of temperature (below and at CPT) on the erosion-corrosion of stainless steels in a (10% NaCl) CO₂-Saturated oilfield environment. It is known that erosion-corrosion resistance depends on the ability of the material to re-passivate after impact by sand and so if the temperature is above the CPT, this will be changed. The erosion-enhanced corrosion of UNS S32760 and UNS S31803 stainless steels at 20 m/s flow velocity and 1500 ppm sand concentration at different temperatures (25, 48 and 61) °C was evaluated by in-situ electrochemical measurements using Submerged Impinging Jet (SIJ). A potentiodynamic anodic polarisation was used to evaluate the corrosion resistance parameters. Results showed that correlation exists between the erosion-enhanced corrosion and static corrosion resistance parameters of the studied materials.

Finite Element Modelling of Corrosion Product Deposition in Nuclear Plants

Jiejie Wu^a, Nicholas Stevens^a, Brian Connolly^a, Andy Banks^b, Andrew Powell^b, and Lara-Jane Pegg^b

a) The University of Manchester, UK

b) Rolls-Royce Plc., UK

Email: jiejie.wu@manchester.ac.uk

Corrosion Related Unidentified Deposition (CRUD) in nuclear power plants can cause severe issues due to the corrosion of the major metal alloy components of piping and tubing under high temperature, high pressure water environments, as shown Fig 1. The corrosion products can become deposited on complex flow geometries. These deposits reduce heat transfer efficiency, cause Tube Support Plate (TSP) blockage and Flow Induced Vibration (FIV), and generate occluded sites where radioactive species (such as Co60) and water treatment chemicals (e.g. LiOH, B(OH)₃) can accumulate. Such uncontrolled chemistry can accelerate the localised corrosion, which may lead to the reduction of tube wall thickness, cladding cracking, fuel leakage and subsequently increased radiation doses for plant workers [2].

The primary objective of this work is to facilitate the development of an all-inclusive deposition model, which will reproduce the morphology of deposits found in actual plants and assist in elucidating the electrokinetic mechanism. In this paper the development and verification of an electric model will be presented. In the model, coupled anode and cathode regions were found at the inlet of a pipe restriction, associated with a region of recirculating flow following the front facing step (FFS), as shown in Fig 2. The corresponding current densities and overpotential at the metal/solution interface were calculated. The coupled anode and cathode may explain the observed deposition process – generating deposits at the front facing step first, followed by a region free of deposits and then repeating ripples of deposited material. At the restriction outlet, a cathode was found.

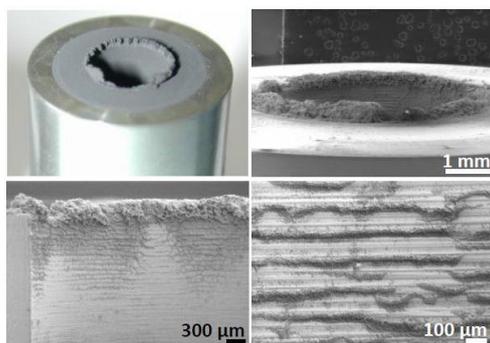


Fig 1. Deposits on Alloy 600 TT in secondary coolant chemistry (T=275°C, P=90 bar) [1]

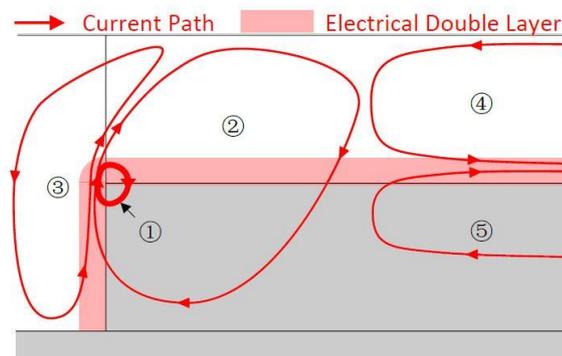


Fig 2. Schematic current path between solution and metal at the inlet of a restriction

[1] M. Guillodo, M. Muller, T. Barale, M. Foucault, "Singular Deposit Formation in PWR due to Electrokinetic Phenomena – Application to SG Clogging," in *6th CNS International Steam Generator Conference*, 2009.

[2] S. Odar and P. Rudling, "Crud in PWR / VVER coolant Volume I – Sources, Transportation in Coolant, Fuel Deposition and Radiation Build-up," ANT International, 2014.

Novel assessment of atmospheric corrosion of brass under sodium chloride-containing water droplets using the scanning Kelvin probe

A. Nielsen, G. Williams, N. Cooze, P.C. Dodds, P. Ansell & E. Strutt

Swansea University, Swansea, UK

Email: 523533@swansea.ac.uk

Imitating gold at a fraction of the cost is an attribute of brass that has driven watchmakers and minters to utilise this alloy, providing their products with desirable aesthetics while being commercially feasible. Unfortunately, tarnishing under atmospheric conditions reveals the imitator all too soon. This study aims to simulate and measure a fundamental corrosion mechanism on brass.

As a NaCl water droplet becomes deficient in oxygen, a differential aeration cell is established whereby cathodic oxygen reduction becomes preferable at the droplet circumference. This region draws sodium cations to counteract the electronegativity associated with an accumulation of hydroxide anions producing a secondary spreading phenomenon – originating at the droplet perimeter and proceeding radially outside its boundaries.

A combination of time-lapse photography and height-regulated scanning kelvin probe (SKP) potentiometry is used to study cathodic secondary spreading phenomenon, following exposure to NaCl containing water droplets. The rates at which these highly alkaline electrolytic films proceed from the droplet edge are measured and are shown to follow parabolic kinetics. NaCl droplet concentrations ranging 0.1 – 5 mol/dm³ exhibit significant rates of secondary spreading as shown using time-dependent E_{corr} vs distance plots, though visual analysis was inadequate in measuring similar rates at lower NaCl concentrations. Cl⁻ sequestering corrosion product under the droplet coupled with migration of Na⁺ ions from the droplet bulk lower the solute concentration causing progressive evaporation under constant humidity, shown to be most extreme at lower NaCl droplet concentrations.

Preferential Weld Corrosion of High Strength Pipeline Steels

N. Nofrizal^{1,2}, K. Georgarakis¹ and S. A. Impey¹

¹*Cranfield University, Bedfordshire, England*

²*Ministry of Energy and Mineral Resources, Indonesia*

*Email: n.nofrizal@cranfield.ac.uk; k.georgarakis@cranfield.ac.uk s.a.impey@cranfield.ac.uk**

The preferential or selective corrosion of weldments can occur due to differences in chemical composition and microstructure between the parent material (PM), heat affected zone (HAZ) and weld metal (WM). A potential difference and galvanic currents generated in the weldment in different environments can sometimes lead to serious localised corrosion.

In practice, the galvanic currents are generally controlled by the addition of a corrosion inhibitor and by ensuring that the composition of the weld metal is selected is slightly more-noble than the parent material. However, it has been shown that a current reversal occurs in some conditions, which result in the weld material becoming more active than the parent metal and severe attack of the weld occurs.

The aim of the project is to study the effect of flow rates on preferential weld corrosion in high strength pipeline steel by investigating the hydrodynamic conditions under which current reversal takes place.

A submerged jet-impingement flow loop enabled a weldment in X65 carbon steel (parent material, weld metal and heat affected zone) to be evaluated at flow rates of 0, 5 and 10 m/s, in brine solution saturated with CO₂ at 1 bar. The self-corrosion rate and galvanic currents from the weldment regions were monitored using linear polarisation resistant measurements and zero-resistance ammeters. Electrochemical impedance spectroscopy was used to complement the LPR measurements and confirm the self-corrosion rates of each part of the weldment in different environments. The total corrosion rates were determined and the effects of oxygen and efficiency of a typical oilfield corrosion inhibitor on this form of corrosion are discussed. The role of surface films that form in brine containing dissolved carbon dioxide will be examined. The research will support corrosion prevention activities and make an important contribution to corrosion control in the oil and gas industries operating in Indonesia and elsewhere. In this way, it is envisaged that the research will provide advances in terms of improved safety, equipment reliability and associated economic benefits.

Key words: weld corrosion, X65 carbon steel, inhibitor, carbon dioxide

**Correspondence Author*

Influence of Ca^{2+} ions on CO_2 corrosion of X65 carbon steel at elevated temperature

Amir Shamsa^a, Yong Hua^a, Richard Barker^a, Evgeny Barmatov^b, Trevor L. Hughes^b, Anne Neville^a

a) Institute of Functional Surface (IFS), School of Mechanical Engineering, University of Leeds, Leeds. LS29JT, UK

*b) Schlumberger Gould Research Center, Cambridge, CB30EL, UK
Email: pm12a2s@leeds.ac.uk*

The effect of Ca^{2+} ions on the corrosion behaviour of carbon steel in a CO_2 -containing sodium chloride solution was evaluated using the mass loss technique. Both general and localised corrosion behaviour was investigated over periods from 6 to 96 h at both 80°C and 150°C. In the absence of Ca^{2+} ions, high corrosion rates of 8.6 mm/year and 9.8 mm/year were observed after 6 h of exposure at 80 and 150°C, respectively. Film formation was already recorded at the higher temperature under these conditions. The general corrosion rates after 96 h reduced to 2.5 mm/year and 0.59 mm/year for 80 and 150°C due to the formation of crystalline iron carbonate (FeCO_3). In the presence of 5000 ppm Ca^{2+} ions there was more significant effect on the general corrosion rate at the lower temperature of 80°C where the protection afforded by the corrosion product layer was reduced. The extent of localised/pitting corrosion increased through the addition of Ca^{2+} ions at 80°C, indicating that Ca^{2+} plays a role in promoting localised corrosion (as chloride content was maintained compared to NaCl experiments). However, at higher temperature Ca^{2+} addition made little difference to general and localised corrosion rates. Results gathered from scanning electron microscopy and X-ray diffraction indicated that the addition of 5000 ppm of Ca^{2+} modified the corrosion product morphology at both temperatures from surfaces covered entirely by FeCO_3 to surfaces covered by iron-calcium carbonate and calcium carbonate.

Comparison of two electrochemical methods (ENM and EIS) for detection of Corrosion under Insulation (CUI)

Tian Yang Lan and Douglas J Mills

Faculty of Arts, Science and Technology, University of Northampton, Northampton, UK

Email: Douglas.Mills@Northampton.ac.uk, TianYang Lan: lantianyang1@gmail.com

Corrosion Under Insulation (CUI) is corrosion that occurs on the metal (normally steel) substrate underneath a heat insulating material. This can develop and progress quickly dependent on the available moisture, oxygen, contaminants and the temperature. CUI is hard to find because the insulation covers all the corrosion signs. Removing and reinstating insulation is a very costly way of inspecting for CUI. So the aim of this work is to develop a good inspection method to identify CUI. Initially an Electrochemical technique is being investigated eg EIS (Electrochemical Impedance Spectroscopy) or ENM (Electrochemical Noise Measurement). This depends on a good ionic path which may exist already or can be created by applying a probe eg a wet pad to the outside of the pipe. The real world situation has been being simulated in the lab by laying a detached piece of vinyl coating whose DC resistance is known and constant on top of different materials which are at different corrosion stages and investigating their electrochemical response. The three types of substrate used are : 1) clean stainless steel, 2) clean carbon steel, 3) rusty carbon steel. The way the EIS data has been analysed is to compare the impedance and phase data at particular frequencies and see if there are any significant differences. Regarding ENM results, the data has been treated to remove drift and spikes and the values of resistance noise (R_n), voltage noise (V_n) and current noise (I_n) have been calculated and then been compared to see if the level of corrosion can be related to one or more of these numbers. Future work will be to investigate a non-electrochemical method eg pulsed eddy current and then move on from model experiments in a lab environment to investigate real insulation on real pipes.

Corrosion control of magnesium alloys with its hydroxide (using a hydrothermal route).

Yading. Wang,^a Andrew. Pidcock,^a Susan. Impey^a

*a) School of Aerospace, Transport and Manufacturing, Cranfield University
Email: yading.wang@cranfield.ac.uk*

Magnesium-based alloys are the lightest engineering alloys with energy saving potential due to the favourable strength to weight ratio. However, the high chemical activity of magnesium can cause corrosion problems. Various protective coating methods are reported to improve the corrosion resistance of magnesium alloys such as conversion coatings, anodising, electrochemical and electroless plating, gas phase deposition and organic coatings[1][2].

The development of a Mg(OH)₂ coating on magnesium alloys by a hydrothermal route has recently been explored by Ishizaki and Zhu[3][4]. This coating not only provides protection but is also environmentally friendly. The research reported here concerns hydrothermal coatings deposited on an AZ31B magnesium alloy with de-ionised water at 120°C and 160°C. Coating thicknesses were measured and microstructure was characterised by scanning electron microscopy. The relationship between the thickness and heat treatment time was determined. X-ray diffraction and energy-dispersive X-ray spectroscopy was used for identification. The corrosion behaviour was studied by immersing hydrothermal coated samples into 3.5%wt NaCl solutions for 24 hours and/or 48 hours. Open-circuit-potentials and electrochemical-impedance-spectroscopy was used to evaluate the corrosion resistance of the hydrothermal coatings with respect to immersion time. The hydrothermal coating significantly improved the corrosion resistance of Mg alloy samples and the results and behaviour are discussed.

*(This abstract is to be submitted for the **Corrosion Science Symposium**)*

Reference

- [1] J.E. Gray, B. Luan, Protective coatings on magnesium and its alloys - A critical review, J. Alloys Compd. 336 (2002) 88–113. doi:10.1016/S0925-8388(01)01899-0.
- [2] S. Abela, Protective Coatings for Magnesium Alloys, Magnes. Alloy. - Corros. Surf. Treat. (2011). doi:10.5772/14100.
- [3] T. Ishizaki, S. Chiba, K. Watanabe, H. Suzuki, Corrosion resistance of Mg–Al layered double hydroxide container-containing magnesium hydroxide films formed directly on magnesium alloy by chemical-free steam coating, J. Mater. Chem. A. 1 (2013) 8968. doi:10.1039/c3ta11015j.
- [4] Y. Zhu, Q. Zhao, Y.H. Zhang, G. Wu, Hydrothermal synthesis of protective coating on magnesium alloy using de-ionized water, Surf. Coatings Technol. 206 (2012) 2961–2966. doi:10.1016/j.surfcoat.2011.12.029.

Optical Microscopic In-situ Observation of Crevice Corrosion of a Duplex Stainless Steel

So Aoki,^a Jun'ichi Sakai^b

a) Japan Atomic Energy Agency

b) Waseda University

Email: aoki.so@jaea.go.jp

Introduction

Due to the characteristic γ/α duplex phase structure and the special compositional arrangement, Duplex stainless steels (DSS) have excellent corrosion resistance and mechanical properties without sacrificing economic performance. Therefore, DSS are used in severe corrosive environments like high chloride concentration solutions, oil and gas wells. However, it has been reported that DSS suffers from crevice corrosion in the seawater applications. The purpose in this study is to clarify dissolution behaviour on crevice corrosion of DSS by means of optical microscopic in-situ observation and electrochemical measurements to elucidate the crevice corrosion mechanism.

Experimental Procedure

Specimen used in this study was a DSS UNS S31260 (25Cr-7Ni-3Mo-0.15N mass%). Solution was 0.6 M NaCl (50±5 °C). The metal / poly methyl methacrylate (PMMA) crevice was prepared between the specimen and a transparent PMMA cell wall with Ti bolts and nuts. Thus, micro dissolution behaviour of crevice corrosion on a specimen surface was observed in-situ by means of an optical microscope. The specimens were immersed in the solution, and then they were held at 0 mV vs.SCE. Corrosion area was taken a photograph every 15 s by the microscope during the potentiostatic test.

Results

The crevice corrosion initiated just beneath the edge of PMMA washer, it grew concentrically toward the outside direction of the crevice with time. On the early stage of the crevice corrosion growth, γ phase had already dissolved preferentially at the outer part of the corrosion area. And then α phase of this area started dissolving with corrosion area extending. Finally, α phase dissolved preferentially at that area. Bubble evolution was observed around the corrosion area, and the bubble moved toward the outside of the crevice.

Discussion

The galvanic cell between inside crevice anode and outside crevice cathode consisted of IR drop with large solution resistance is induced, because of tight shape of the crevice. As a result of the IR drop, potential gradient form from the outside to the inside in the crevice. Dissolved metal ions decrease solution pH by its hydrolysis. The bubble observed around the corrosion area was probably hydrogen gas proceeded from the reduction reaction of hydrogen ions. It seems that the low pH solution diffused toward the outside direction of the crevice. It is for these reasons that the distribution of the dissolution behavior¹⁾⁻²⁾ was observed inside the crevice in this study.

References

- 1) So Aoki et al., *Corrosion Engineering*, 60, 272 (2011).
- 2) So Aoki et al., *Corrosion Engineering*, 64, 317 (2015).

Comparison of corrosion behaviour of X65 steels in water-containing supercritical CO₂ environments with NO₂/O₂

Yong Hua^a, Richard Barker^b and Anne Neville^b

*University of Leeds, Leeds
Email: leo.huayong@gmail.com*

Corrosion experiments were performed on X65 carbon steel in water-supercritical CO₂ (SC-CO₂) and under-saturated SC-CO₂ conditions at 80 bar and 35°C in the presence of 100 ppm (mole) NO₂ and 1000 ppm O₂. Results indicated that no corrosion occurs in dry conditions, and the reduction in water concentration from 1770 to 300 ppm results in the general corrosion rate reducing from 0.68 to 0.05 mm/year. There is no significant difference in the extent of localized corrosion observed on the surface. Pitting (or localized attack) rates for X65 ranged between 0.65 and 0.51 mm/year by varying the water concentrations between 1770 and 300 ppm in the presence of 100 ppm NO₂ and 1000 ppm O₂. For water-saturated CO₂ conditions, the general corrosion rate was 0.3 mm/year after 48 hours and approximately 20 times lower than the pitting/localized corrosion rate of 6.8 mm/year recorded in the presence of 100 ppm NO₂ and 1000 ppm O₂. Only crystalline FeCO₃ was observed on the surface in water-saturated CO₂ condition with or without adding 100 ppm NO₂ and 1000 ppm O₂. The introduction of both 100 ppm NO₂ and 1000 ppm O₂ inhibited the formation of crystalline FeCO₃ for under-saturated conditions.

Additional tests involving solution replenishment over 48 hours in the water-saturated system containing 3ml, 40ml and 100ml solutions were also conducted and indicated that no significant difference in general corrosion rates occurred through adding more water in the system, but the localized corrosion rate reduced from 6.8 to 5.2 mm/year if the water condition increased from 3ml to 100ml in the system.

Analysis of corrosion products formed on the steel surface was performed using X-ray diffraction, X-ray photoelectron spectroscopy, Raman and Scanning electron microscopy. The results suggest that the 100 ppm NO₂ and 1000 ppm O₂ would dissolve into the aqueous water phase quickly and can cause high localized corrosion in water-saturated CO₂ conditions. However, the localized corrosion rate observed in under-saturated condition is far less than that in water-saturated CO₂ condition.

Comparative Studies of corrosion Behaviour of Casting and Laser-treated Mg-1Ca Alloy in Simulated Body Fluid and 0.9 wt% NaCl Solution

Yuxiang Liu, Michele Curioni and Zhu Liu

School of Materials, The University of Manchester, Manchester, M13 9PL, UK

Email: yuxiang.liu-2@postgrad.manchester.ac.uk

Magnesium alloys used as biodegradable medical implants in physiological environment experience complex forms of corrosion, compared with those in a solution only containing chloride ions. In this study, we performed a comparative study on corrosion behaviour of Mg-1Ca alloy in simulated body fluid (SBF) and in 0.9 wt% NaCl solution, and investigated the effects of laser surface melting.

The results showed that the main corrosion products formed on the cast alloy are MgO and Mg(OH)₂ in 0.9 wt% NaCl solution, whereas thick, multilayer Calcium/Magnesium phosphates are formed in SBF solution on top of the MgO. In the SBF solution, for the first two hours, the magnesium hydroxide dominated the whole Mg alloy surface, and phosphates started to build up for longer immersion times. The formation of multilayer phosphates provided a partial protection for the alloy against further corrosion. Such protection was absent in the 0.9 wt% NaCl solution due to the dissolution of MgO and Mg(OH)₂.

Excimer laser surface melting in ambient atmosphere induced calcium-rich magnesium solid solution and generated a layer of MgO on the alloy surface. The laser-treated surface was immediately covered by a Calcium/Magnesium phosphates layer, once exposed in the SBF solution, leading to a remarkable decrease in corrosion rate. In 0.9 wt% solution, the laser treated alloy exhibited much less improvement.

Investigating Corrosion Using High-Speed AFM

Stacy Moore¹, Robert Burrows^{1,2}, Loren Picco^{1,2}, Tom Scot¹, Oliver Payton^{1,2}, Alice Laferrere¹

1 University of Bristol, Bristol, 2 National Nuclear Laboratory, Gloucester.

Email: stacy.moore@bristol.ac.uk

The unpredictable nature of stress corrosion cracking (SCC) calls for further research into the mechanisms under which SCC and other forms of destructive corrosion occur. Observation of crack initiation at the nanoscale could give valuable insight into the processes that take place within metals during SCC.

Atomic force microscopes (AFMs) build up topographic maps of a surface by measuring the mechanical response of a sharp probe as it moves across the sample. They are capable of high-resolution imaging of structures and the measurement of mechanical properties at nanometre scales in varying gaseous, liquid and vacuum environments[1]. As a result, AFMs are considered one of the most versatile tools in nanoscience. However, a typical map is formed over a period of 100-1000 seconds, with a finite number of pixels per image, limiting it to static snapshots over small scan areas[2].

The clear potential of AFM quickly gave rise to considerable effort to enhance the image rate and address other limitations, ultimately resulting in the development of high-speed atomic force microscopes (HS-AFMs)[2]. The HS-AFM developed at Bristol Nano Dynamics Ltd. operates at speeds orders of magnitude faster than conventional AFMs, and is capable of capturing multiple frames per second. This allows for direct observation of dynamic events in real-time, with nanometre lateral resolution and subatomic height resolution[2]. Furthermore, HS-AFM is a valuable tool for studying solid-liquid interfaces and as such has the potential for *in situ* corrosion studies[2]. Additionally, the high pixel rate of the HS-AFM means it is capable of mapping macro-sized areas with nanoscale resolution, for detailed pre- and post-corrosion comparisons. The applications for HS-AFMs are still relatively unexplored, and advances in HS-AFM technology are ongoing.

Investigations were carried out into corrosion mechanisms of thermally sensitised AISI 304 stainless steel using the contact mode HS-AFM. Hardness induced topological maps of the surface have been produced, in which chromium carbide precipitation can be clearly seen by means of proper surface preparation[3]. Furthermore, a micro strain rig was custom built such that samples could be imaged under stress, alongside corrosive conditions, for investigations into SCC initiation. Laferrere et al. have previously demonstrated the use of HS-AFM to image nanoscale corrosion events, with parallel electrochemical control[4]. The research carried out builds upon this previous investigation, further substantiating the capability and potential of HS-AFM for applications in materials and corrosion science.

References:

- [1] O. Payton, et al., *Nanotechnology*, vol. 23, no. 20, p. 205704, 2012.
- [2] O. Payton, et al., *International Materials Reviews*, vol. 61, no. 8, pp. 473–494, 2016.
- [3] A. D. Warren, et al., *Microscopy Today*, vol. 24, no. 03, pp. 52–55, 2016.
- [4] A. Laferrere, R. Burrows, et al., “In situ imaging of corrosion processes in nuclear fuel cladding.” *Corrosion Engineering Science and Technology* (Accepted for publication, DOI: 10.1080/1478422X.2017.1344038.)

Using the Scanning Droplet Cell to Accelerate the Formation of Copper Patina Detected in the Marine Environment

Mr Matthew Kitchen¹, Dr Oliver Lewis¹, Dr Hywel Jones¹, Dr Alistair Finnie²

¹Sheffield Hallam University, Howard Street, Sheffield, United Kingdom

²AkzoNobel/International Paints Ltd, Felling, Gateshead, Tyne & Wear United Kingdom
Email: m.kitchen@shu.ac.uk

When copper is exposed to the marine environment it reacts with chloride ions to form a copper patina which usually has a green/blue appearance (Marušić, Otmačić-Ćurković, Horvat-Kurbegović, Takenouti, & Stupnišek-Lisac, 2009). The copper patina that forms tends to consist of the crystalline phases; atacamite, paratacamite or clinoatacamite, all of which are complex copper hydroxychlorides ($Cu_2Cl(OH)_3$) (Graedel, Nassau, & Franey, 1987). In certain circumstances patination may not be desirable (Bastidas, Criado, Fajardo, & La Iglesia, 2013) therefore it is important to understand the process of patination and the mechanisms by which the different phases form.

Using the Pourbaix diagram for copper in sea water it was found that a neutral pH would allow the formation of a copper hydroxychloride. However, maintaining a constant pH while polarising copper to generate patina products is difficult in a static solution. Therefore to maintain the neutral pH while applying a potential, the Scanning Droplet Cell (SDC) was used. The SDC provides a localised environment from which corrosion measurements can be made, under a constantly refreshed droplet of solution.

By comparison, when polarising copper in a static solution with the three electrodes in the same solution the pH was noted to become more alkaline. Similarly, when separating the counter electrode from the working and reference electrode using a salt bridge the solution containing the working electrode became more acidic. XRD analysis found that when polarising copper in a static solution clinoatacamite was formed. However polarising copper under the SDC formed nantokite on the surface of the copper coupon, while paratacamite was detected in the waste solution. These results help to identify the conditions required to form the different phases of copper hydroxychloride.

References

- Bastidas, D. M., Criado, M., Fajardo, S., & La Iglesia, V. M. (2013). Copper deterioration: causes, diagnosis and risk minimisation. *International Materials Reviews*, 99-127.
- Graedel, T. E., Nassau, K., & Franey, J. P. (1987). Copper Patinas Formed in the Atmosphere - I Introduction. *Corrosion Science*, 27(7), 639-657.
- Marušić, K., Otmačić-Ćurković, H., Horvat-Kurbegović, Š., Takenouti, H., & Stupnišek-Lisac, E. (2009). Comparative studies of chemical and electrochemical preparation of artificial bronze patinas and their protection by corrosion inhibitor. *Electrochimica Acta*, 7106-7113.

Energy & Environmental

Poster Abstracts

New Mechanical Route for Screening OER Catalysts

Michelle P. Browne^a and Andrew Mills.^a

a) School of Chemistry and Chemical Engineering, Queens University Belfast, UK.

Email: M.Browne@qub.ac.uk

The search for new, highly active, inexpensive electrochemical water splitting catalysts is of growing interest since the latter are a key component in solar-driven water-splitting solar cells. In such cells, whilst H₂ is produced on the cathode, it is the reaction on the anode, the Oxygen Evolution Reaction (OER) which is the most kinetically demanding step in the overall process.¹ The screening of OER materials routinely involves fabricating thin films of the catalysts on conducting substrates from powder dispersions.² This process can be extremely time consuming and produce results which are often hard to compare and reproduce, due to a variety of reasons, including mass loading effects. In this study, a novel mechanical route for producing reproducible electrodes of new OER catalysts in powder form is described. These electrodes can then be readily utilised in a rotating disc electrode (RDE).

In order to test our mechanical fabrication procedure, RuO₂, was synthesised by the Adams method, and used as the active OER material.^{1, 3} The RDE electrodes were produced by pressing a known amount of Pt powder with Ru Adams, and minimal amount of PTFE binder powder on top, using an infra-red die and hydraulic press. The resulting Ru/PTFE and Pt layered disc is illustrated in Fig. 1(a) and (b). The Ru/PTFE/Pt disc has exceptional OER properties when compared to literature values for RuO₂; e.g. the overpotential at 10 mA cm⁻² is 0.26 V, Fig. 1(c), and exhibits a Tafel slope of 30 mV dec⁻¹.¹ Additionally, this mechanical technique provides a facile and reproducible route for OER electrode fabrication from powders. Thus this approach allows for the rapid screening of any new potential OER material, which will also be explored in this study.

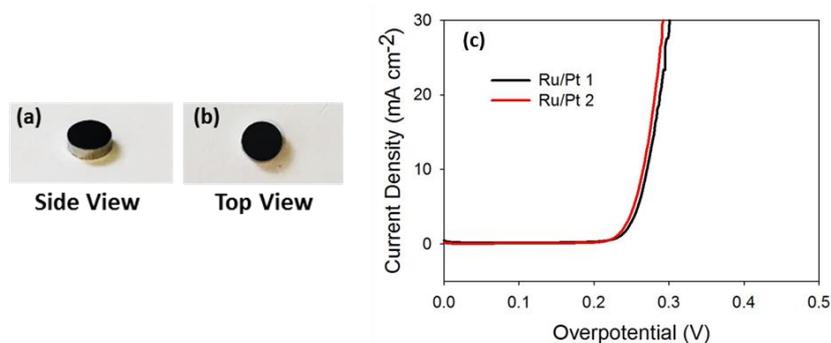


Figure 1 (a) XRD analysis of the Ru Adams with COD reference pattern for RuO₂ (b) Picture of the pressed Ru Adams top and Pt powder disc and (c) OER Linear sweep voltammograms.

1. M. P. Browne, H. Nolan, G. S. Duesberg, P. E. Colavita and M. E. G. Lyons, *ACS Catalysis*, 2016, **6**, 2408-2415.
2. M. P. Browne, J. M. Vasconcelos, J. Coelho, M. O'Brien, A. A. Rovetta, E. K. McCarthy, H. Nolan, G. S. Duesberg, V. Nicolosi, P. E. Colavita and M. E. G. Lyons, *Sustainable Energy & Fuels*, 2017, **1**, 207-216.
3. A. Mills and C. O'Rourke, *Chem. Commun.*, 2016, **52**, 7727-7730.

Electrochemical Behaviour of H_3PO_3 on Pt Electrode in Hot Concentrated H_3PO_4 Electrolyte

Michal Carda^a, Martin Prokop^a, Tomas Bystron^a, Martin Paidar^a, Karel Bouzek^a

*a) University of Chemistry and Technology Prague, Technicka 5, 16628, Praha 6, Czech Republic
Email: prokopm@vscht.cz*

Concentrated H_3PO_4 represents the most widely utilised proton-conductive phase in membranes for high temperature proton-exchange membrane fuel cells (HT PEM FC) operating at 120-200 °C. Acid is usually immobilized in polybenzimidazole-type polymer.

However, application of H_3PO_4 is connected with several drawbacks. Firstly, its aggressive nature leading to corrosion of Pt catalyst is widely known. Secondly, adsorption of $\text{H}_2\text{PO}_4^{2-}$ anions on Pt surface negatively influences kinetics of O_2 reduction reaction. The stability of H_3PO_4 is also an issue, though this fact is not widely known. In particular, H_3PO_4 is at elevated temperature reduced at Pt surface by H_2 to phosphorus impurities. Understanding of this process is still far insufficient, although Pt-P and H_3PO_3 were already confirmed as the products of H_3PO_4 reduction [1]. Effect of these impurities on HT PEM FC performance has not been investigated yet. Our previous work was focused mainly on H_3PO_3 electrochemical behaviour on Pt electrode in aqueous electrolytes at ambient temperature [2].

The goal of this work is to qualitatively describe electrochemical behaviour of H_3PO_3 on polycrystalline bulk Pt electrode in 99% H_3PO_4 electrolyte. These conditions are directly relevant to HT PEM FC operation. Measurements were performed using voltammetry techniques in a specially designed electrochemical cell. Impact of H_3PO_3 concentration and electrolyte temperature on shape of measured voltammograms was studied as well as H_3PO_4 stability at various temperatures. Results pointed out several important features of H_3PO_3 electrochemical behaviour on the Pt which will be presented. This data can eventually contribute to optimisation of HT PEM FC operational regime and, quite possibly, even to increase of its lifetime.

Financial support by the FCH JU within the framework of the DEMSTACK project, contract No. 325368, by MSMT CR project No. 7HX13002 and financial support from specific university research (MSMT No 20-SVV/2017) is gratefully acknowledged.

[1] W.H. Doh, L. Gregoratti, M. Amati, S. Zafeiratos, Y.T. Law, S.G. Neophytides, A. Orfanidi, M. Kiskinova, E.R. Savinova, Scanning photoelectron microscopy study of the Pt/phosphoric-acid-imbibed membrane interface under polarization, *ChemElectroChem*, 1 (2014) 180-186.

[2] M. Prokop, T. Bystron, M. Paidar, K. Bouzek, H_3PO_3 electrochemical behaviour on a bulk Pt electrode: adsorption and oxidation kinetics, *Electrochimica Acta*, 212 (2016) 465-472.

Electrochemical CO₂ reduction and formic acid oxidation on Pd_{ML}Pt(111) and Pd_{ML}Pt(100) electrodes

Xiaoting Chen and Marc T. M. Koper

Leiden Institute of Chemistry, Einsteinweg 55, 2333 CC, Leiden, The Netherlands

Email: x.chen@lic.leidenuniv.nl, m.koper@chem.leidenuniv.nl

Formic acid oxidation occupies an important role in fuel cell technology and has been considered as a model reaction for providing a simplified example of more complex organic molecules that can also be applied to this field. Although general agreement exists that Pd is more active towards formic acid oxidation than Pt and Au, the true nature of the underlying reaction mechanism is still open for discussion. As the reverse reaction, efficient production of formic acid from CO₂ reduction has been reported on PtPd nanoparticles from our previous study. We study here the formic acid oxidation on epitaxially grown Pd monolayer on Pt(111) and Pt(100) single crystals by means of cyclic voltammetry with rotating electrodes and online electrochemical mass spectrometry. Our results show that Pd_{ML}Pt(111) exhibits enhanced formic acid oxidation activity at low potential without CO poison formation and considerably lower overpotential for the reduction of CO₂ to formic acid. In the case of Pd_{ML}Pt(100), we find the unique mass transport controlled formic acid oxidation for the first time. These new research results help to understand elementary steps during the conversion of CO₂ and formic acid on Pd based catalysts and highlights the effects of electrolyte pH and surface structure.

Control of Thickness and Morphology of Poly-(3,4-ethylenedioxythiophene) by Electrochemically Growth (E-PEDOT) and Manipulation of its Conductive State for Use as Anodic Buffer Layer in Organic Photovoltaic Cells

J. A. Del-Oso^{a,b}, B. A. Frontana-Uribe^b, J. L. Maldonado^c and M. Rivera-Hernández^d

^a Universidad Autónoma de la Ciudad de México, Prolongación San Isidro No. 151, San Lorenzo Tezonco, Ixtapalapa, 09790, México City, México.

^b Centro Conjunto de Investigación en Química Sustentable UAEMéx-UNAM, Carretera Toluca-Atzacmulco Km 14.5, San Cayetano-Toluca, Estado de México, México.

^c Centro de Investigaciones en Óptica A.P. 1-948, 37000 León, Gto., México.

^d Instituto de Física, Universidad Nacional Autónoma de México, Apdo. Postal 20-364, 01000, México City, México.

Email: alfredo.deloso@uacm.edu.mx

This contribution presents the electrochemical growth and manipulation in the conductance, thickness and morphology of the polymer film poly[3,4-ethylenedioxythiophene] electrochemically (CV or CA) obtained (E-PEDOT), from the monomer 3,4-ethylenedioxythiophene (EDOT)¹ onto the transparent conductive anode indium-tin oxide (ITO). For this study, different mixtures of anhydrous organic solvents were used, resulting in low polymerization kinetics of the monomer EDOT² in Toluene-Acetonitrile (4:1, v/v). Also was found which a low concentration of the monomer and a suitable potential of electropolymerization, allowed us to gain better control the growth of the polymer.³ Finally, these E-PEDOT films were used as buffer layers in organic photovoltaic cells (OPVs) with bulk heterojunction architecture and their performance was compared with those constructed with the classical spin cast deposited PEDOT:PSS buffer.

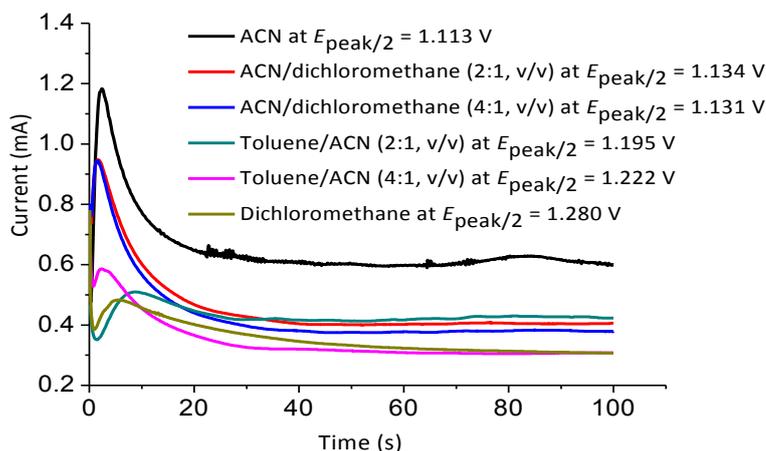


Figure 1. Potentiostatic polymerization of EDOT, in the different organic media at the anodic half-peak potential ($E_{\text{peak}/2}$)

References:

- [1] Nasybulin, Eduard; Wei, Shu; Cox, Marshall; Kymissis, Ioannis; Levon, Kalle. *J. Phys. Chem. C*, **2011**, *115*, 4307. [2] Nasybulin, Eduard; Wei, Shu; Kymissis, Ioannis; Levon, Kalle. *Electrochim. Acta*. **2012**, *78*, 638. [3] Lyutov, Vladimir; Efimov, Igor; Bund, Andreas; Tsakova, Vessela. *Electrochim. Acta*. **2014**, *122*, 21.

Synthesis of highly durable and methanol tolerant Pt catalyst for oxygen reduction reaction by ultraspray method

Carlota Domínguez^a, Md. Khairul Hoque^a, Michelle P. Browne^a, Leticia Esteban-Tejeda^a,
Corbin K. Livingston^b, Kevin M. Metz^b, Paula E. Colavita^a

*a) School of Chemistry and Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN), Trinity College Dublin, Dublin, Dublin 2, Ireland. b) Department of Chemistry, Albion College, 611 E. Porter Street, Albion, Michigan 49224, United States
Email: dominguc@tcd.ie*

Direct methanol fuel cells (DMFCs) are attractive for their possible implementation in portable applications, due to the high energy density of methanol, and their relatively high energy-conversion efficiency. Despite the potential commercialisation of DMFCs, the sluggish kinetics of the oxygen reduction reaction (ORR) that occurs at the cathode is slowing down their development [1]. Current state-of-the-art of catalysts for ORR, highlights Pt-based materials as the most efficiency catalysts in terms of activity [2] although further improvements in their durability are necessary [3]. Additionally, DMFCs might suffer the problem of methanol crossover, the non-reacted methanol permeates the cathode compartment through the polymer membrane causing a decrease in the performance of the cathode catalyst. Therefore, the improvement in the durability and the tolerance to methanol crossover of Pt catalysts are the main challenges for large scale commercialisation of DMFCs.

Herein, we report an ultrasonic spray pyrolysis (USP) method combined with annealing process for the synthesis of active and highly durable platinum nanoparticles embedded in carbon microspheres (PtNP@CMs) as electrocatalysts for ORR. Materials prepared also showed excellent tolerance to methanol crossover in acid environments. The catalytic activity for the ORR has been strongly influenced by the Pt loading used as precursor, resulting in an effective method of synthesis for the reduction of the Pt content in the final catalysts. Moreover, low Pt loadings and higher heat treatments yield high durable catalysts for the ORR in acid environments. Notably, the most durable PtNP@CM catalyst synthesised display no statistical difference in mass activity after 3500 cycles. The better stability of this catalyst might be promoted by the fact that Pt nanoparticles are more embedded in the spherical carbon structures, based in microscopy analysis. Furthermore, the most active catalysts showed an excellent tolerance to the addition of 3 M of methanol measured via a current-time (i-t) chronoamperometric method at 0.55V. We discuss the structural and chemical properties that might be at the origin of the excellent durability. The intrinsic scalability of the proposed synthetic method holds promise for commercial applications of these materials.

References

- [1] Gasteiger, H.A., et al., *Appl. Catal. B*, 2005. 56, 9. [2] Chen, C., et al., *Science*, 2014. 343, 1339. [3] Escudero-Escribano, M., et al., *J. Am. Chem. Soc.*, 2012. 134, 16476.

Versatile 3D-Printed Electrodes for Electrochemical Flow Reactors

L.F. Arenas, C. Ponce de León, F.C. Walsh.

*Electrochemical Engineering Laboratory, Energy Technology Group, Faculty of Engineering and the Environment, University of Southampton SO17 1BJ, UK
Email: lfam1g13@soton.ac.uk*

Porous electrodes in flow-by configuration afford significantly higher active surface area, mass transport and space time yield in comparison to planar electrodes. These electrodes are applied in numerous industrial processes, including inorganic and organic electrosynthesis, treatment of process streams, metal recovery and electrolysis reactions. In this contribution [1], we present a novel 3D-printed flow reactor electrode with a complex, intricate geometry impossible to replicate by computer numerical control (CNC) machining or other classical manufacturing methods. Such 3D-printed electrodes offer an alternative to the currently available metal and carbon-based meshes, foams and felts, delivering a new genre of free-form porous electrodes having tailored composition, catalytic activity, active surface area, fluid flow characteristics and mass transport properties.

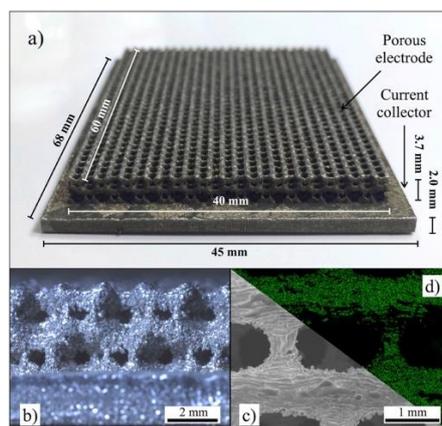


Fig 1. 3D-printed Ni/SS porous electrode. a) the macro structure, b) micrograph of the electrode, c) SEM of an individual pore, d) nickel EDS mapping for the same pore opening.

The mass transport characteristics of a Ni/SS 3D-printed porous electrode compare well and exceed those observed in typical planar, mesh and RVC electrodes. This opens the possibility to employ geometrically complex structures produced by additive manufacturing techniques as high performing, robust electrodes in specialised electrochemical flow reactors. Electrodes having different roughness, microstructure, orientation, composition, electrocatalysis and fluid flow environment can be 3D-printed.

[1]. L.F. Arenas, F.C. Walsh, C. Ponce de León (2017) 3D-printed porous electrodes for advanced electrochemical flow reactors: A Ni/stainless steel electrode and its mass transport characteristics. *Electrochemistry Communications*, 77: 133-137.

Targeting the Electrochemical Activity of Biofilms

Emma Knowles^a, Ritu Katakya^{a*}, Gary Sharples^a, Kasid Khan^a

^aDepartment of Chemistry, Durham University, South Rd, Durham, DH1 3LE
Email: ritu.katakya@durham.ac.uk

Microbial fuel cells (MFCs) have sparked interest within the portable electronics industry where bacteria can be used to power low energy devices through the formation of a redox-active biofilm at an electrode surface. This study explores supercapacitors and targets the electrochemical activity of biofilms to harness the energy that bacteria produce. This could significantly increase the energy that can be generated in applications involving MFCs and potentially provide an alternative renewable fuel source for use in small electronics. A supercapacitor was designed and different carbon-based electrode materials were prepared and tested including carbon nanotubes, graphite and graphene oxide. The electrode materials were also modified with MnO₂ and a redox-active *Pseudomonas Fluorescens* biofilm was grown on electrode surfaces. A range of electrochemical techniques were then employed to quantitatively study the redox activity of the biofilms and determine the bacterial contribution to charge storage. These techniques included cyclic voltammetry, galvanostatic charge/discharge measurements, differential pulse voltammetry and electrical impedance spectroscopy. The outcome of the investigation has shown promising results. The specific capacitance of the MnO₂-modified CNT supercapacitor for example, increased significantly from $79 \pm 7 \mu\text{F g}^{-1}$ in the absence of bacteria, to $170 \pm 9 \mu\text{F g}^{-1}$ after the formation of a 72-hour biofilm. These results indicate that bacterial biofilms could well be the future for energy production in small electronic devices.

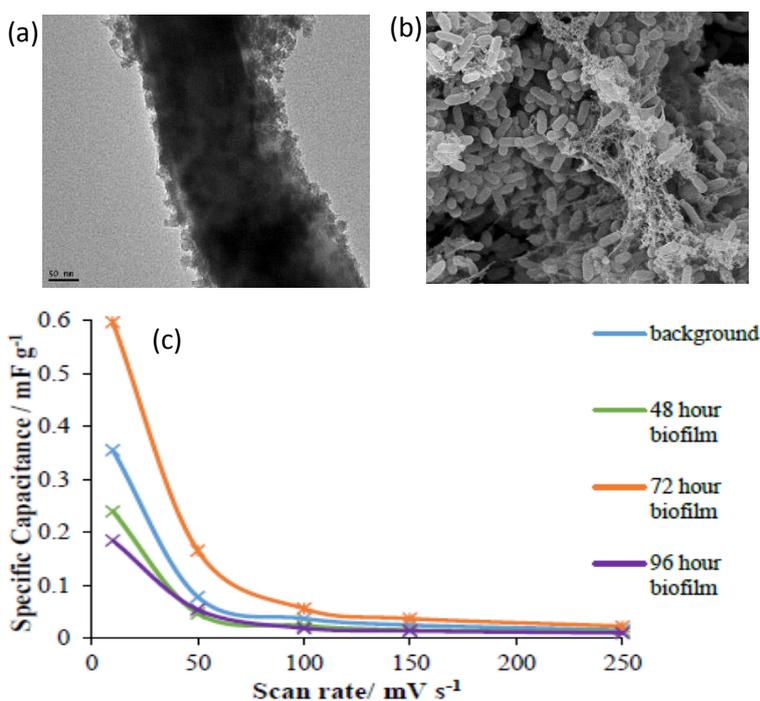


Figure 6. a) TEM image showing the uniform deposition of MnO₂ at the surface of a CNT b) SEM image showing formation of biofilm after 48 hours on CNT:MnO₂ (4 to 1 by mass), c) Comparing the specific capacitances of the supercapacitor in the absence and presence of a biofilm at different scan rates

Capacitive Properties of Nitrogen Doped Amorphous Carbon Materials for Electrocatalytic Applications

Md. Khairul Hoque, James A. Behan, Serban N. Stamatina, Federico Zen, Paula E. Colavita

School of Chemistry, Trinity College Dublin, College Green, Dublin 2, Ireland

Email: hoquemk@tcd.ie

Non-crystalline carbon materials play an important role in electrochemical energy storage and energy conversion technologies.¹ Disordered graphitic carbon scaffolds structures typically result in excellent performance in capacitive and electrocatalytic applications.² Nitrogenation of the carbon matrix is an effective way of introducing disorder in different forms, including changes in morphology, electronic structure and surface functional groups.³ However, it is not well understood how to control the interplay between these effects in electrochemical applications. The aim of this project is to improve our understanding of how compositional changes in the carbon translate into different electrochemical properties by synthesising nitrogenated amorphous carbons (a-C:N) with smooth topography but different levels of nitrogenation. a-C:N electrodes were deposited via sputtering deposition and characterised by XPS, Raman spectroscopy and determination of capacitive properties. In this study the synthesis of N doped amorphous carbon is discussed in addition to how annealing affects the properties of N-doped amorphous carbons. The capacitive properties of deposited a-C:N electrodes were investigated in aqueous and organic electrolytes. XPS studies reveal that the density of N-sites increases with the amount of nitrogen gas used in the deposition, while annealing has the effect of reducing N-site concentration. Raman studies reveal that initial N-doping and disorder can affect the number and size of sp^2 clusters of a-C. Capacitive properties of these electrode materials were analysed by using Electrochemical Impedance Spectroscopy (EIS). Capacitance of amorphous carbon increases with N-doping. Annealing at 900 °C for 1 h also decreases the capacitance of N doped amorphous carbon electrodes. These results are important for an improved understanding of nitrogenated carbon materials for energy conversion and other applications.

References

1. Robertson, J., Diamond-like amorphous carbon. *Materials Science and Engineering: R: Reports* **2002**, 37 (4–6), 129-281.
2. Wood, K. N.; O'Hayre, R.; Pylypenko, S., Recent progress on nitrogen/carbon structures designed for use in energy and sustainability applications. *Energy & Environmental Science* **2014**, 7 (4), 1212-1249.
3. Behan, J. A.; Stamatina, S. N.; Hoque, M. K.; Ciapetti, G.; Zen, F.; Esteban-Tejeda, L.; Colavita, P. E., Combined Optoelectronic and Electrochemical Study of Nitrogenated Carbon Electrodes. *The Journal of Physical Chemistry C* **2017**.

Transition Metal Coordination Complexes with Redox Non-Innocent Ligands for Flow Battery Energy Storage

Craig Armstrong, Dr Kathryn Toghil

Department of Chemistry, Lancaster University,
Lancaster, United Kingdom, LA1 4YB

Email: c.armstrong@lancaster.ac.uk, k.toghil@lancaster.ac.uk

Due to inherent, and often unpredictable intermittency in renewable technologies, a network dependent on such electricity is not feasible. To be completely reliant on renewables whilst still guaranteeing an uninterrupted supply, efficient grid-scale energy storage devices are necessary, to store excess energy at off-peak times for use when demand increases. Redox-flow-batteries (RFBs) are electrochemical energy storage devices which are suitable for grid-scale energy storage due to their easily scalable design; RFBs store complementary redox materials, dissolved in liquid electrolytes, in separate storage tanks which are cyclically pumped through a flow-cell stack where they are reversibly charged or discharged. Hence, RFBs decouple battery power and capacity allowing either property to be independently scaled; by increasing the electrode area or electrolyte volume respectively.¹ Furthermore, RFBs offer long lifetimes, high energy efficiencies and require low maintenance due to their simple modular design making them attractive for various applications including back-up and off-grid installations.

Aqueous flow batteries such as the all-vanadium RFB have achieved commercial success however their energy densities have reached the maximum that can be reasonably achieved, $\cong 33 \text{ W h L}^{-1}$, due to the narrow 1.23 V electrochemical window of water and maximal solubility of their redox material.² In contrast, non-aqueous RFBs can theoretically achieve much higher energy densities by use of solvents which offer larger stability windows (acetonitrile is stable over 5 V for example), and redox materials which undergo multiple electron transitions at high redox potentials. Many non-aqueous systems have been studied thus far, utilising a wide range of chemistries from small organic molecules to transition metal coordination compounds,³ however significantly higher energy densities than aqueous RFBs have not yet been realised due to low solubilities and cell potentials which do not fully exploit the solvent stability window. The work by our group aims to surpass these limitations by utilising transition metal complexes with redox 'non-innocent' ligands which are capable of multiple electron transfers.⁴ Such ligands are known to be redox active and interfere with the metal electronic states, imparting a degree of electron delocalisation across the molecule, allowing numerous oxidation states to be accessed.⁵ Hence, a single species, two or three electron battery may be created with double or triple the energy density of previously studied non-aqueous RFBs.

- 1 A. Z. Weber, M. M. Mench, J. P. Meyers, P. N. Ross, J. T. Gostick and Q. Liu, *J. Appl. Electrochem.*, 2011, **41**, 1137–1164.
- 2 Y. Huang, S. Gu, Y. Yan and S. F. Y. Li, *Curr. Opin. Chem. Eng.*, 2015, **8**, 105–113.
- 3 J. Noack, N. Roznyatovskaya, T. Herr and P. Fischer, *Angew. Chemie Int. Ed.*, 2015, **54**, 9776–9809.
- 4 P. J. Cappillino, H. D. Pratt, N. S. Hudak, N. C. Tomson, T. M. Anderson and M. R. Anstey, *Adv. Energy Mater.*, 2014, **4**, 1300566.
- 5 R. Eisenberg and H. B. Gray, *Inorg. Chem.*, 2011, **50**, 9741–9751.

Synthesis and Electrochemistry of Advanced Electrocatalysts Based on Ternary Metal Nitrides

Penny Whalley,^a Andrew Hector,^a Andrea Russell,^a Andy Dent^b

a) University of Southampton

b) Diamond Light Source

Email: psw1d15@soton.ac.uk

Recently, attention is being drawn to ternary metal nitrides as new applications for them arise. Metal nitrides have attracted much interest in terms of their structural type and their activity as catalysts in a number of reactions.

Electrochemical systems are currently heavily dominated by expensive noble metals, hence transition metal nitrides have been applied to various electrochemical systems such as fuel cells as a viable alternative¹. Bonding and structural features contribute to their attractive electronic conductivity and catalytic activity, whilst their high melting points and resistance against corrosion make them an attractive choice with regards to electrode materials².

In this work, a range of compounds have been synthesised by adding small cobalt additions (between 0 % and 20 %) to the parent phase $\text{Ni}_2\text{Mo}_3\text{N}$, using a modification of the Pechini method³. XRD analysis showed a single phase with a linear increase in lattice parameter as further cobalt is doped into the system. Particle sizes of 90 nm were calculated.

The compounds synthesised show a good activity towards the hydrogen evolution reaction, showing an attractive onset potential and high activity. Initial analysis suggests the 15 % cobalt sample ($\text{Ni}_{1.7}\text{Co}_{0.3}\text{Mo}_3\text{N}$) possesses the most desirable activity towards the HER, with a more positive onset potential and greater activities.

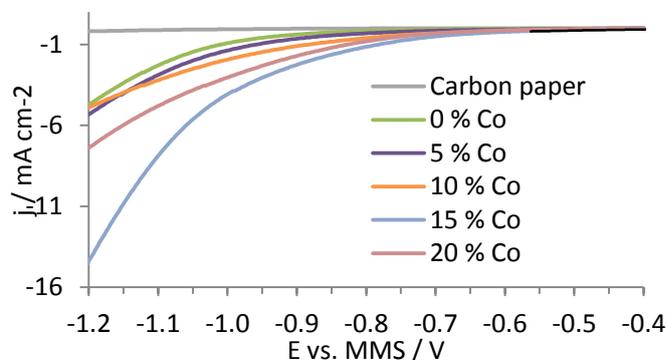


Figure 7 Linear sweeps of electrodes in 0.1 M H_2SO_4 , purged with N_2 (ca. 30 min.) prior to measurements being taken. Scan rate 5 mV s^{-1} .

X-ray absorption spectroscopy (XAS) suggested the incorporation of cobalt into the structure made both metal centres redox active, as oxidation was seen of the molybdenum, cobalt and nickel at open circuit potential with subsequent reduction at more negative potentials. These results were not, however, seen for $\text{Ni}_2\text{Mo}_3\text{N}$.

1. Ham, D. J.; Lee, J. S. (2009) *Energies* 2 (4), 873-899.
2. Chen, J. G. G. (1996) *Chemical Reviews* 96 (4), 1477-1498.
3. Pechini, M. P. Method of preparing lead and alkaline earth titanates and niobates and coating method using the same to form a capacitor. US 3330697 A (1967).

Catalytic Activity of Electrodeposited MoS₂ Films for Hydrogen Evolution

Jo J. L. Humphrey,^a Michael A. O'Connell^a and Andrew J. Wain^a

a) National Physical Laboratory, Hampton Road, Teddington, Middlesex, TW11 0LW

Email: jo.humphrey@npl.co.uk

Electrolysers are expected to play a major role in the green hydrogen economy, as they offer a clean and sustainable approach to the production of hydrogen fuel. These devices utilize (renewable) energy to split water, with catalysts required to efficiently generate oxygen at the anode and hydrogen at the cathode. In the latter case, platinum is regarded as the benchmark due to its high activity and stability.¹ However, there is a need substitute this critical metal catalyst with earth-abundant alternatives, in order to reduce device costs and improve sustainability. In recent years, molybdenum disulphide has received much attention as one such alternative to platinum for the hydrogen evolution reaction (HER).²

In addition to chemical and physical routes, amorphous and nanostructured MoS₂ and MoS₃ films can be prepared by electrodeposition, with the stoichiometry and structure of the final catalyst being dependent on the deposition parameters.^{3,4} In this work we compare the HER behaviour of MoS₂ films prepared by various electrochemical approaches including cyclic voltammetry, constant potential electrolysis and rapid potential pulsing. We demonstrate that the catalytic activity and short-term stability of the film is governed largely by film thickness, which can be controlled by the number of voltammetric cycles or deposition time (Fig. 1).

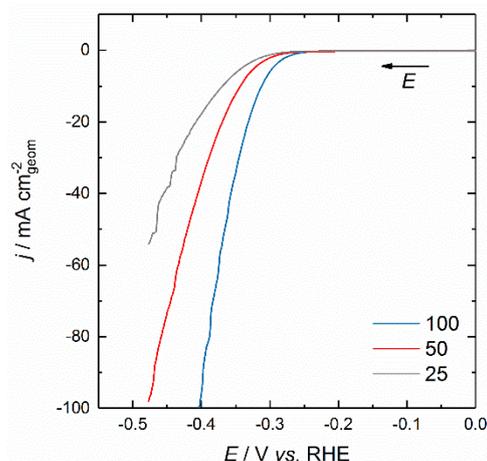


Fig. 1: Linear sweep voltammograms of HER at electrodeposited MoS₂, measured at a scan rate of 5 mV s⁻¹ in H₂-saturated 0.5 M H₂SO₄, under rotation at 1600 rpm. The catalyst films were deposited on glassy carbon substrates by cyclic voltammetry; the legend indicates the number of CV cycles used to prepare the films.

In addition to HER testing using a rotating disk electrode, we use Atomic Force Microscopy and Raman spectroscopy to monitor the catalysts *in situ*, enabling the performance metrics of the films to be correlated with their chemistry and morphology.

References

1. McCrory, C. C.; Jung, S.; Ferrer, I. M.; Chatman, S. M.; Peters, J. C.; Jaramillo, T. F., *Journal of the American Chemical Society* **2015**, *137* (13), 4347-4357.
2. Jaramillo, T. F.; Jørgensen, K. P.; Bonde, J.; Nielsen, J. H.; Horch, S.; Chorkendorff, I., *science* **2007**, *317* (5834), 100-102.
3. Morales-Guio, C. G.; Hu, X., *Accounts of chemical research* **2014**, *47* (8), 2671-2681.
4. Ambrosi, A.; Pumera, M., *ACS Catalysis* **2016**, *6*, 3985-3993.

Developing magnetic resonance imaging (MRI) for studying batteries

Yasmeen M. AlZahrani, Joshua M. Bray, Melanie M. Britton

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

Email: yxa676@student.bham.ac.uk

There is significant interest in the development of improved energy storage devices, in particular, the development of high performance advanced batteries. In order to improve such energy storage devices, a full understanding of the distribution of chemical species, ion transport, side reactions and structural changes of the electrodes, *in operando*, is required.

Magnetic resonance imaging (MRI) is a promising tool to visualize and understand the electrochemical processes inside batteries and it can provide significant insight in a non-invasive way¹. There have been ⁷Li MRI studies of lithium-ion batteries²⁻⁴. Potential replacements for Li-ion batteries are zinc⁵ and aluminium⁶ based batteries. However, in order to study zinc and aluminium batteries, an alternative method should be developed to study the electroactive species using ¹H NMR signal from the electrolyte⁵.

This project focuses on using MRI techniques to determine the speciation and distribution of electroactive zinc species in novel electrolytes, such as room temperature ionic liquids (RTILs) and deep eutectic solvents (DESS). Studying the effect of Zn²⁺ on the NMR parameters, such as T_1 and T_2 relaxation times, of the electrolyte will facilitate visualization of the distribution of zinc species in RTILs or DESS based batteries.

References:

1. M. Britton, *Chem. Phys. Chem.*, 2014, 15, 1731–1736.
2. S. Chandrashekar, N. Trease, H. Chang, L. Du, C. Grey, A. Jerschow, *Nat. Mater.*, 2012, 11, 311–315
3. H. Chang, A. Ilott, N. Trease, M. Mohammadi, A. Jerschow, C. Grey, *J. Amer. Chem. Soc.*, 2015, 137 (48), 15209–15216.
4. A. Ilott, M. Mohammadi, H. Chang, C. Grey, A. Jerschow, *Proc. Nati. Acad. Sci. U.S.A.*, 2016, 113 (39), 10779–10784.
5. M. Britton, P. Bayley, P. Howlett, A. Davenport, M. Forsyth, *J. Phys. Chem. Lett.* 2013, 4, 3019-3023.
6. M. Lin, M. Gong, B. Lu, Y. Wu, D. Wang, M. Guan, M. Angell, C. Chen, J. Yang, B. Hwang, H. Dai, *Nature*, 2015, 520, 324-328.

An Electrochemical Impedance Study of the Oxygen Evolution Reaction at Nickel-Cobalt Oxides in Base

L. A. Romeral and M. E. G. Lyons

TCD Trinity Electrochemical Energy Conversion and Electrocatalysis Group, School of Chemistry and AMBER National Centre, Trinity College Dublin, Dublin 2, Ireland

Email: romerall@tcd.ie, melyons@tcd.ie

First row transition metal oxides (Co_3O_4 , NiO , Fe_2O_3 , MnO_2 ...) catalyst are promising materials for superconductors, water splitting, microelectronics and electro-sensing.¹ The singularity of transition metal oxides properties lie in the nature of the partly electron filled d-shell which produces an easy transfer electron back and forth between free oxygen and transition metal ions shell.² Although these materials have many applications, this project focuses on the oxygen evolution reaction (OER). Poor OER catalyst limits the efficiency of H_2 production from water electrolysis making the process economically unfavourable. It is widely believed that NiO along with Co_3O_4 generates a synergetic metal oxide, NiCo_2O_4 , which has been reported as a stable catalyst in alkaline media for oxygen evolution reaction.^{3,4} In this perspective, the investigation of the oxygen evolution reaction in an aqueous alkaline solution using different composition ratio of Nickel-Cobalt oxide prepared by thermal decomposition is presented. The research herein focuses on the analysis of different physical electrode properties such as film resistivity and double layer capacitance, along with the kinetics and reaction mechanism during the OER. These properties were studied using electrochemical impedance spectroscopy (EIS) and Tafel plot analysis. The oxide films were synthesised using thermal decomposition method of the precursor salt ($\text{Ni}(\text{NO}_3)_2$ and $\text{Co}(\text{NO}_3)_2$) at 400°C in air. Titanium wire (0.6 cm^2 area) was used as electrode support. All the experiments were carried out in 1M alkaline solution and iR (solution resistance) corrected.

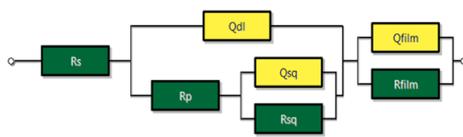


Fig 1. Equivalent circuit used in the CNLS fitting of the impedance data presented in Fig 2.

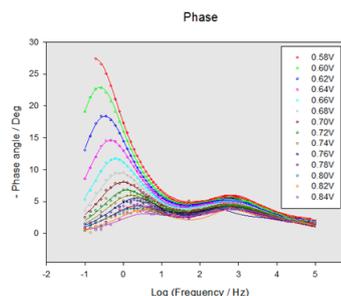


Fig 2. Electrochemical impedance spectra recorded in 1 M NaOH at a series of potentials associated with OER in Bode format.

References:

- 1.Artero, V.; Chavarot-Kerlidou, M.; Fontecave, M. Splitting Water with Cobalt. *Angewandte Chemie International Edition* 2011, 50 (32), 7238-7266.
- 2.Rao, C. N. R. Transition Metal Oxides. *Annual Review of Physical Chemistry* 1989, 40 (1), 291-326.
- 3.Wu, G.; Li, N.; Zhou, D.-R.; Mitsuo, K.; Xu, B.-Q. Anodically electrodeposited Co+Ni mixed oxide electrode: preparation and electrocatalytic activity for oxygen evolution in alkaline media. *Journal of Solid State Chemistry* 2004, 177 (10), 3682-3692.
- 4.Hu, H.; Guan, B.; Xia, B.; Lou, X. W. Designed Formation of $\text{Co}_3\text{O}_4/\text{NiCo}_2\text{O}_4$ Double-Shelled Nanocages with Enhanced Pseudocapacitive and Electrocatalytic Properties. *Journal of the American Chemical Society* 2015, 137 (16), 5590-5595.

Sensors & Analytical

Poster Abstracts

VOLTAMMETRIC ANALYSIS OF VITAMIN B₁ B₂ & B₆ USING SCREEN PRINTED CARBON ELECTRODES

K. L. Westmacott*, A. Crew, O. Doran, J. P. Hart †

Centre for Research in Biosciences, University of the West of England, Bristol

** Email: Kelly.Westmacott@uwe.ac.uk*

†Email: John.Hart@uwe.ac.uk

Vitamins are an important group of organic compounds which are essential for healthy growth and nutrition. They can be found in pharmaceutical products, foods, and drinks. Most vitamins have been reported to possess electroactive behaviours in media of a specific pH. These reports have involved various electrode materials such as platinum, mercury, and glassy carbon. Only a few reports have appeared which describe the application of unmodified screen printed carbon electrodes (SPCEs) to vitamin analysis. However such devices offer advantages such as mass production in a wide range of geometries and low cost; consequently they can be considered disposable.

Cyclic voltammetry has been used to ascertain the electrochemical behaviour of the water soluble vitamins thiamine (B1), riboflavin (B2), and pyridoxine (B6) using SPCEs with a selection of buffer solutions. All three vitamins produced well defined oxidation peaks in a phosphate buffer at pH 11. In the present investigation square wave voltammetry was employed to quantify the three vitamins simultaneously, with a single scan performed in only 8 seconds. The successful application of the rapid square wave voltammetric assay, employing SPCEs, to both a multi-vitamin supplement and a food product will be presented.

References

- [1] Qijin, W. Nianjun, Y. Haili, Z. Xinpin, Z. Bin, X. (2001) *Talanta*. 55, pp. 459-467.
- [2] Hart, J. P. Norman, M. and Tsang, S. (1995) *Analyst*. 120, pp. 1059-1064.
- [3] Hart, J. P. and Hayler, P. J. (1986) *Analytical Proceedings*. 23, pp. 439-441.

Acknowledgments

The authors would like to thank Gwent Electronic Materials Ltd (GEM) for supplying the screen printed carbon electrodes.

Development of an Assay for the Beta-Agonist Salbutamol in Serum using Voltammetry in Conjunction with a Disposable Screen-Printed Carbon Electrode

Adrian Crew^{*}, Guy Bartle, Alice Martin, Ryan Dunne and John P. Hart[†]

Centre for Research in Biosciences, University of the West of England, Bristol

** Email: Adrian.Crew@uwe.ac.uk*

†Email: John.Hart@uwe.ac.uk

Salbutamol, [1-(4-hydroxymethyl phenyl)-2-(t-butylamino) ethanol] also known as albuterol is a beta-2, non-catecholamine partial agonist, used to treat asthma and other airway diseases. Salbutamol may be exploited by healthy individuals to enhance performances in sport through its anabolic and stimulatory effects on the body. Therefore, the World Anti-Doping Agency (WADA) have drawn up strict regulations to prevent unfair, competitive advantages in sport by people using the drug above a designated therapeutic level.

The aim of the present study was to develop a simple, economic assay to determine salbutamol in serum which may have application in determining possible abuse of the drug in sport. Screen-printed carbon electrodes (SPCEs) have been attracted great interest due to the possibility of their mass production in a wide range of geometries at low cost; therefore these devices can be considered disposable. Our group have successfully developed electrochemical sensors and biosensors based on SPCEs for the determination of a wide range of biologically important compounds. Consequently we decided to explore this approach in the present investigation.

Initial studies were performed using cyclic voltammetry, with phosphate buffers over a wide pH range in order to understand the nature of the electrochemical reaction and to deduce the optimum buffer for quantitative analysis. Well-defined voltammetric peaks were obtained over the pH range studied with currents of highest magnitude being produced under alkaline conditions. Several different voltammetric waveforms were compared and square wave voltammetry was selected as it resulted in the best sensitivity and selectivity for the measurement of salbutamol. In order to evaluate the assay, known concentrations of salbutamol were spiked into serum, a simple solvent extraction step was performed and the reconstituted residue was analysed by square wave voltammetry; the results suggest that the method holds promise for screening salbutamol in serum samples.

Electrochemical Detection of Cellular Iron Reduction in Epithelial Cancer Cell Lines

Harry Sherman¹, Snow Stolnik¹, Judata Wibawa², Frankie J Rawson¹

¹University Park Campus, University of Nottingham, Nottingham, NG7 2RD

²Boots Pharmaceuticals, D19 Technical Centre, Thane Road, Nottingham, NG90 5EF

Email: Paxhs5@nottingham.ac.uk

Iron is an essential nutrient required for the functionality of many living organisms. In mammals, iron plays a key role within a variety of processes. These include the transport and storage of oxygen, as well as the catalysis of key reactions throughout the body. Extracellular iron has been shown to be reduced via transplasma membrane electron transport systems (TPMETS). We have utilised the electrochemical mediator ferricyanide as a tool to measure the reduction capacity of three epithelial cancer cell lines (A549, Calu-3 and H1299) toward iron. Linear sweep voltammetry was used to monitor the magnitude of oxidation current which could be correlated to the concentration of iron reduced. Viability studies were also carried out to ensure our iron compound, potassium ferricyanide, did not cause cytotoxicity upon incubation. The capability of both cell lines to reduce iron hints at the presence of ferrireductase enzymes present in the membrane of the cells. Our further work will seek to confirm and quantify these enzymes, with further implications for understanding the underlying biochemical modulation of iron transport via transplasma membrane electron transport systems. This work is important for the understanding TPMET systems in more detail, and in particular adsorption of ions onto membranes.

The Role of Electrochemistry in Understanding the Drugs Targeting Copper Complexation for Alzheimer`s Disease

Bongiwe Silwana^a, V. Somerset^b, R. Katakya^{a*}

a) *Department of Chemistry, Durham University, Durham, United Kingdom.*

b) *Department of Chemistry, Faculty of Applied Sciences, Cape Peninsula University of Technology, Bellville, South Africa*

Email: ritu.katakya@durham.ac.uk

Complexation of certain metals with therapeutic compound is assumed to be significant in metal dependent diseases. The medicinal uses and applications of metals and metal complexes are of increasing clinical and commercial importance. In the search for new therapeutic tools against Alzheimer`s disease, complexation of copper with ligands that target prevent aggregation of beta amyloids in presence of metal ions such as Cu^{2+} , were characterized using voltammetry and spectroscopic techniques. Chelation therapy has been scientifically proven to remove excess toxic metals before they can damage the body, but at the same time chelation is not completely risk free. Henceforth the challenge of well-designed metal-based drugs is to minimize possible toxicity. Oxygen is required for many life-sustaining metabolic reactions. Oxygen and its activated intermediates, ROS (reactive oxygen species), however, may react with cellular components with resultant degradation or inactivation of essential molecules. This work reports results on the complexation of ligands with copper (II) using glassy carbon electrode. The drugs were designed to cross the blood brain barrier (BBB). The basic aim of this study is to understand the role of drugs targeting copper complexation for Alzheimer`s disease. The binding parameter such as the binding constants was determined from voltammetry data.

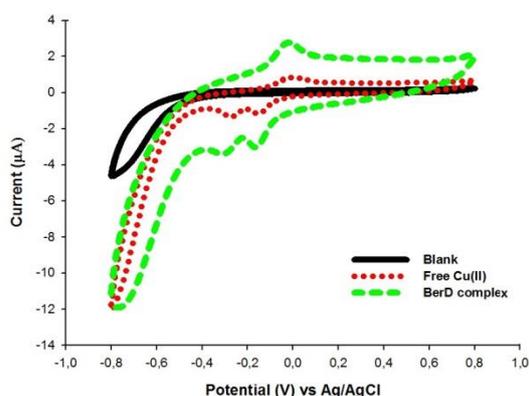


Fig. 1 Overlaid voltammogram of bare glassy carbon electrode, free copper and Cu-BerD complex.

References:

[1] Farrell, N. P. Transition Metal Complexes as Drugs and Chemotherapeutic Agents; James, B.

Detection of Biomarkers of *Pseudomonas aeruginosa* Bacteria by Electrochemistry at the Interface between Two Immiscible Electrolyte Solutions

Edward Burgoyne,^a Micheál D. Scanlon^a

a) Department of Chemical Sciences & The Bernal Institute,
University of Limerick (UL), Republic of Ireland.

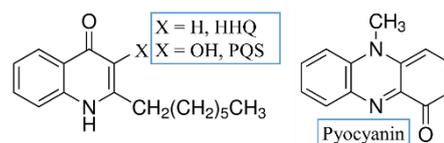
Email: micheal.scanlon@ul.ie

Chronic lung infections with *Pseudomonas aeruginosa* are directly responsible for the large majority of premature deaths in CF patients [1]. After initial colonisation, a window of opportunity exists, during which establishment of chronic infection may be prevented or delayed by aggressive antibiotic eradication therapy in the majority of patients [2]. *P. aeruginosa* bacterial populations synchronise group behaviour (such as biofilm development, swarming motility, etc.) by Quorum Sensing (QS), a chemical cell-to-cell communication process regulated by small extracellular signalling molecules [3]. Molecules used in QS, such as **2-heptyl-4(1H)-quinolone (HHQ)**, **pseudomonas quinolone signal (PQS)** and **pyocyanin**, are unique indicators of the presence of *P. aeruginosa* in clinical sputum samples (see Figure).

In this presentation innovative **electrochemical sensors** to detect *P. Aeruginosa* QS biomolecules

will be demonstrated that generate characteristic signals from their adsorption at polarised immiscible water-oil interfaces. The latter approach offers several significant advantages: (i) soft interfaces are pristine and defect-free, thus the time-consuming step of polishing electrodes between measurements is eliminated; (ii) pre-concentration steps can be implemented with stripping voltammetry to provide sub-nM limits of detection; and (iii) the hydrophilic/hydrophobic nature of the sensors completely circumvents any issues due to analyte solubility

The premise of this research is to take advantage of the inherent amphiphilic nature of QS molecules, a trait developed to facilitate their interaction with bacterial cell membranes. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) responses at *pristine* polarised water/1,2-dichloroethane interfaces give clear unambiguous signals in the presence of each QS biomolecule. Variables such as pH of the aqueous phase are investigated.



- References:**
- [1] Singh, P. K. *et al.*, *Nature*, (2000), **407**, 762.
 - [2] Frederiksen, B. *et al.*, *Pediatr. Pulmonol.* (1997), **23**, 330.
 - [3] Williams, P. *et al.*, *Philos Trans. R, Soc. Lond. B Biol.*, (2007), **362**, 1119.

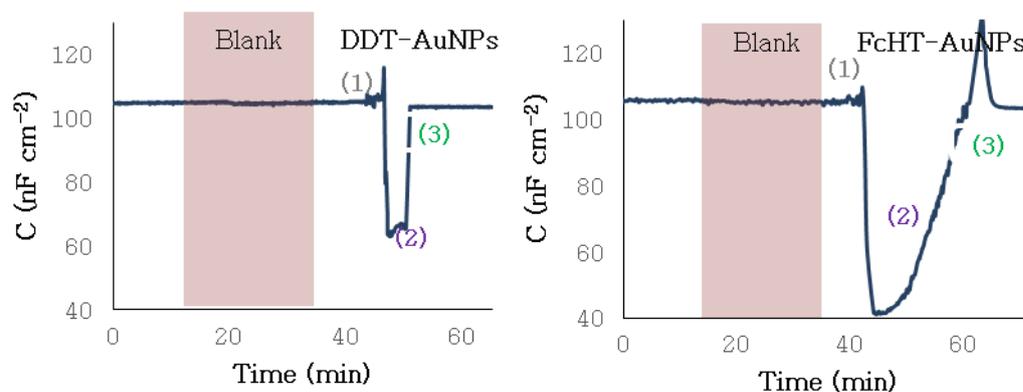
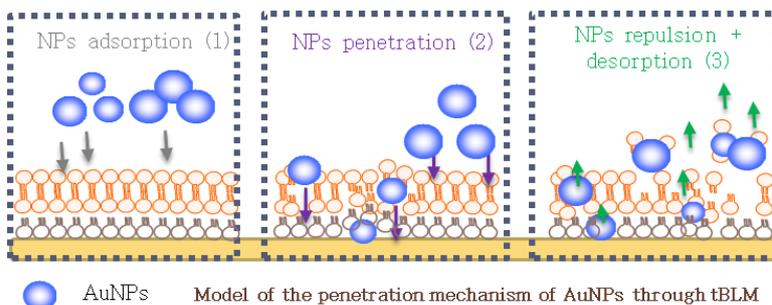
Interactions of thiolated gold nanoparticles with lipid membranes

Y. Bunga, R. Katakya

Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, UK
Email: ritu.katakya@durham.ac.uk

Gold nanoparticles (AuNPs) have shown to have very unique physicochemical properties; they are widely used as materials in the development of devices within the nanotechnology field in their use in pharmaceuticals, medical and biological applications.¹ There are many advantages to NPs in the biomedical field; these have a high surface area to volume ratio giving advantageous properties as good drug carriers, manipulation of size and charges allows the enhancement of the surface reactivity of NPs.²

The work reports the study of non-electroactive and electroactive thiol-stabilised AuNPs and their interactions with artificial cell membranes (tBLM models) using electrochemical and microscopic techniques.



CVs of the SAM-modified gold electrode in 0.1 M KNO_3 at 60, 120, 240, 360, 480 and 900 min immersion times. Scan rate: 50 mV/s.

References

- [1] M.J. Hajipour, K.M. Fromm, A. Akbar Ashkarran, D. Jimenez de Aberasturi, I.R. Larramendi, T. Rojo, V. Serpooshan, W.J. Parak, M. Mahmoudi, *Trends in Biotechnology*, 2012, **30**, 499-511
- [2] F. Caruso, *Advanced Materials*, 2001, **13**, 11-22

Cellulose in Sensors and Logic Gates: Ionic Diode Phenomena Based on Surface Charges in Reconstituted Cellulose Films

Abigail K. Thompson^{a,b}, David Wigmore^a, Barak D.B. Aaronson^a, Elena Madrid^a,
 Marcus A. Johns^{a,b}, Janet L. Scott^a, Igor Polikarpov^c, and Frank Marken^a

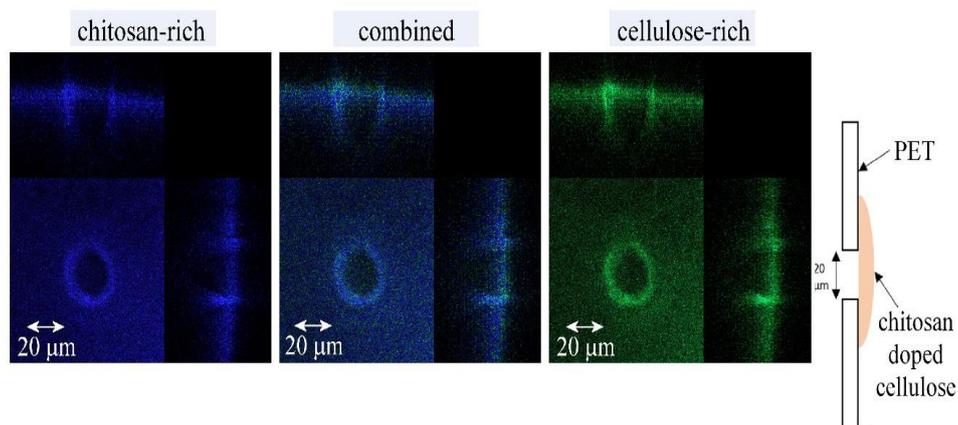
a) Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK

b) Centre for Sustainable Chemical Technologies, University of Bath, Claverton Down, Bath BA2 7AY, UK

*c) São Carlos Institute of Physics-IFSC, University of São Paulo- USP, 400 - Pq. Arnold Schmidt 13566-590
 São Carlos, SP Brazil*

Email: A.K.Thompson@bath.ac.uk

Cellulose materials provide the most abundant polymeric material on earth and there are many applications deriving from modified forms of cellulose. In particular, new fields are developing in sensing and in “paper electronics”. Here, the ion flux through reconstituted cellulose is investigated with the aim of employing ion flux in ionic diode sensors [1-3] to detect environmental pollutants, DNA, or disease bio-markers. Ion flux is measured as current through the membrane (which is deposited onto a microhole). The surface charge of cellulose (negative) and, for example, of chitosan a modified version of cellulose (positive) are employed to control the ionic current signals. Modified cellulose surfaces with switchable charge are employed in sensors.



[1] A Cationic Diode Based on Asymmetric Nafion Film Deposits. He, DP; Madrid, E; Aaronson, BDB; Fan, L; Doughty, J; Mathwig, K; Bond, AM; McKeown, NB; Marken, F *ACS Appl. Mater. Interf.* 9 (2017) 11272-11278.

[2] Ionic Diodes Based on Regenerated alpha-Cellulose Films Deposited Asymmetrically onto a Microhole. Aaronson, BDB; He, DP; Madrid, E; Johns, MA; Scott, JL; Fan, L; Doughty, J; Kadowaki, MAS; Polikarpov, I; McKeown, NB; Marken, F *ChemSelect* 2 (2017) 871-875.

[3] Metastable Ionic Diodes Derived from an Amine-Based Polymer of Intrinsic Microporosity. Madrid, E; Rong, YY; Carta, M; McKeown, NB; Malpass-Evans, R; Attard, GA; Clarke, TJ; Taylor, SH; Long, YT; Marken, F *Angew. Chem.-Internat. Ed.* 53 (2014) 10751-10754.

Simultaneous Determination of Epinephrine and Homovanilic Acid on Bromophenol Blue Modified Glassy Carbon Electrode

Ammu Rosin Jose^a and K. Girish Kumar^{a*}

^a Department of Applied Chemistry, CUSAT, Kochi – 22, Kerala, India

Email: giri@cusat.ac.in

Development of rapid methods for the determination of neurotransmitters and their metabolites is significant in clinical diagnosis. Herein, we report the development of a sensitive and reliable voltammetric technique suitable for the simultaneous determination of epinephrine (EP) and homovanilic acid (HVA) based on the electrochemical oxidation of these compounds on polybromophenol blue modified glassy carbon electrode (GCE). Bromophenol blue was electropolymerized on the GCE surface by cyclic potential scanning from -1 V to 1.8 V using a solution of 0.5mM of bromophenol blue prepared in PBS (pH=6). The modified electrode was characterized by SEM and EIS. Under optimized conditions, the oxidation peak current of EP and HVA showed a linear dynamic range from 2.0 μM to 50.0 μM for each with detection limits 0.82 μM for EP and 0.50 μM for HVA respectively. The effect of coexisting species on the electrochemical determination was also investigated. The potential of the sensor to be used for simultaneously determining these species in real samples needs to be explored further.

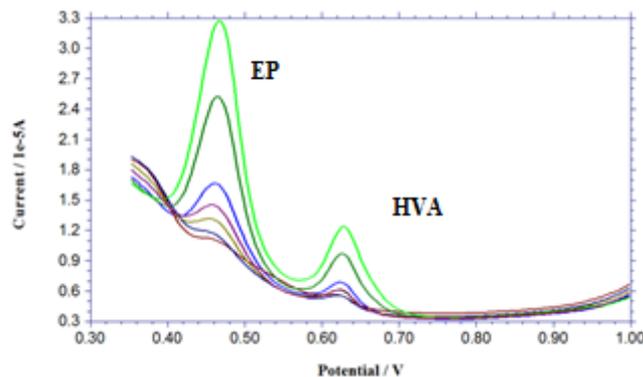


Figure 8 Simultaneous determination of EP and HVA on modified electrode

References

1. G.-J. Yang et al., Journal of Electroanalytical Chemistry 604 (2007) 48–56.

Physical & Fundamental

Poster Abstracts

Electroplating of Aluminium from Novel Ionic Liquids

Hasan AL-Esary^{a, b}, Karl S. Ryder^a, Andrew P. Abbott^a.

a) *Materials Centre, Department of Chemistry, University of Leicester, Leicester, LE1 7RH, UK*

b) *Department of Chemistry, Faculty of science, University of Kerbala, Kerbala- Iraq*

Email: hfnae1@le.ac.uk

In various applications, such for automobiles, aviation, household appliances, containers and electronic devices, aluminium is used. This due to Al having many excellent properties such as good electrical and thermal conductivities, low density, high ductility, and good corrosion resistance.¹ Electroplating of Al is normally achieved from classic ionic liquids, which are expensive, toxic and highly sensitive to air.² This work will show, for the first time, the electrodeposition of Al from novel ionic liquids, where these liquids are about ten time cheaper than traditional ionic liquids, easy to prepare, and less sensitive to moisture. The novel solvents were (1.5:1) AlCl₃:acetamide, (1.5:1) AlCl₃:N-methylacetamide and (1.5:1) AlCl₃:N,N-dimethylacetamide eutectic liquids.^{1,3} Thick and adherent pure Al coatings have been achieved on copper and mild steel substrates from these types of solvents. The electrochemical properties of the plating liquids have been studied using cyclic voltammetry, and the resultant surface morphologies and composition of the Al coating were revealed by SEM/ EDX (Fig 1). XRD was used to examine the crystal structures of the Al coatings. In addition, corrosion of the Al deposit in brine (0.1 M NaNO₃) was measured, where it was found that the Al coatings achieved from the AlCl₃:acetamide and AlCl₃:N,N-dimethylacetamide eutectic liquids had a higher resistance to corrosion compared to the Al films produced from AlCl₃:N-methylacetamide based liquid.

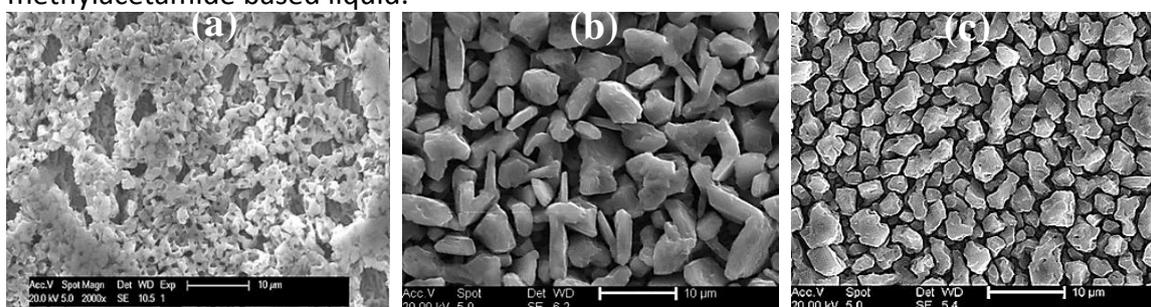


Fig 1: SEM morphology of Aluminium electrodeposition from (a) AlCl₃:acetamide, (b) AlCl₃:N-methylacetamide, and (c) AlCl₃:N,N-Dimethylacetamide-based IL.

References

1. Q. Wang, Q. Zhang, B. Chen, X. Lu and S. Zhang, *Journal of The Electrochemical Society*, 2015, **162**, D320-D324.
2. A. P. Abbott, R. C. Harris, Y.-T. Hsieh, K. S. Ryder and I.-W. Sun, *Physical Chemistry Chemical Physics*, 2014, **16**, 14675-14681.
3. H. M. Abood, A. P. Abbott, A. D. Ballantyne and K. S. Ryder, *Chemical Communications*, 2011, **47**, 3523-3525.

Development of an X-ray cell for electrochemical studies of ionic liquids on single crystal surfaces

Lisa Rhodes-Martin^a, Francesco Carla^b, Christopher Lucas^a, Yvonne Grunder^a

a) Department of Physics University of Liverpool

b) ESRF Grenoble, France

Email: lisarm@liverpool.ac.uk

Ionic liquids (IL) present an interesting alternative to traditional aqueous electrolytes for use in fuel cells and Li-ion batteries¹. IL are molten salts consisting of organic cations and organic/inorganic anions. Due to their large asymmetric shape they do not crystallize and are liquid at room temperature, their ionic nature makes them intrinsic ionic conductors. IL have several unique properties which make them promising alternate electrolytes, these properties include: large electrochemical window, high thermal stability and an extremely low vapour pressure².

The Electrochemistry of ILs on single crystal surfaces Au(111) has been investigated with the aim of elucidating the fundamental interactions at the electrode/electrolyte interface. Since the electrochemical behaviour of ILs often depends critically on the interfacial structure of the liquid adjacent to the electrode, a molecular level description is necessary to understand and improve their performance.

During this project an ionic liquid electrochemical cell has been developed which can be used in UHV and for in-situ surface X-ray diffraction experiments (SXRD). SXRD has been used to investigate structural changes at solid-electrolyte interfaces³. The final experimental design can be seen in **Error! Reference source not found.a**.

Predominantly cyclic voltammetry has been carried out. Three generations of electrochemical cell have been conceived and tested. A cyclic voltammogram from the final set up is shown in Fig 1b. First results obtained with the setup will be presented.

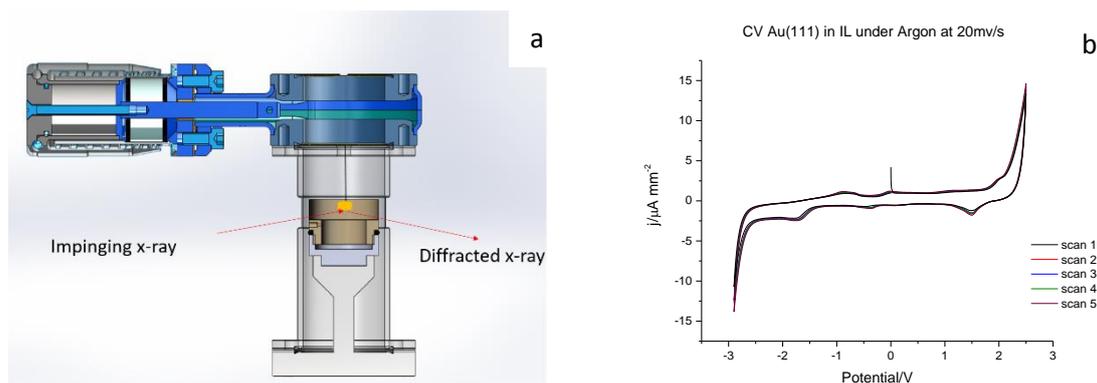


Figure 9: a) Final Experimental set up showing an electrochemical cell in vacuum in an alumina casing b) Cyclic voltammogram of ionic liquid BMPyr TFS on Au(111) recorded using experimental set up shown in b at 20mV/s

References:

1. Galiński, M., Lewandowski, A. & Stępiak, I. Ionic liquids as electrolytes. *Electrochim. Acta* **51**, 5567–5580 (2006).
2. Vranes, M., Dozic, S., Djerić, V. & Gadzuric, S. Physicochemical characterization of 1-butyl-3-methylimidazolium and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide. *J. Chem. Eng. Data* **57**, 1072–1077 (2012).
3. Lucas, C. A. Surface relaxation at the metal/electrolyte interface. *Electrochim. Acta* **47**, 3065–3074 (2002).

Phosphate-mediated electrochemical adsorption of cisplatin on gold electrodes

Adam Kolodzie^{1,2}, Marta C. Figueiredo³, Marc T. M. Koper³, Francisco Fernandez-Trillo^{1,2}, Paramaconi Rodriguez^{1,2}

¹ School of Chemistry, University of Birmingham, B15 2TT, UK

² Birmingham Centre for Strategic Elements & Critical Materials, University of Birmingham, B15 2TT, UK

³ Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

Email: axk595@bham.ac.uk

Cancers have been the biggest cause of mortality to human population over ages. Since its discovery, the use of cisplatin (CP)¹ has led to a massive improvement in cancer treatment with cure rates of certain cancers reaching over 90%. Although CP has proven to be a very effective anti-cancer drug, its associated toxicity has limited the use.² As a cytotoxic drug, it can damage both healthy and tumorous cells causing severe side effects.³

The concept of electrochemical adsorption of metalorganic drugs, such as CP, is at its very early stages but the idea behind is to create a novel system that adsorbs the CP at the electrode modified with a receptor. The system would then filter out the CP thus reducing its accompanying side effects. The electrochemical adsorption would also allow us to monitor the level of cisplatin. It has been reported that the most likely sites of cisplatin are nitrogen atoms of nucleobases and thiol-rich molecules.^{4,5} There are also some evidences that DNA's phosphate groups may interact with Pt-based drugs through hydrogen bonds.⁶

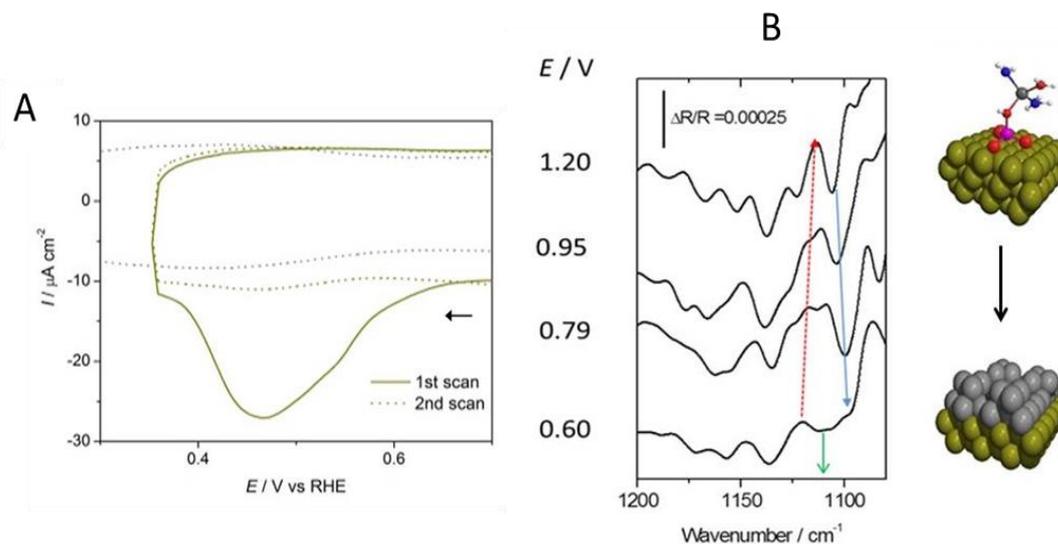


Figure 10: (A) Consecutive voltammetric profiles in a cisplatin-free DPBS solution of surface-modified Au(poly) electrode. Surface modified electrodes were obtained by immersing the electrode in 2.6 mg L⁻¹ solution of cisplatin solution during 1 min at at 0.85 V vs RHE. The scan direction is indicated by the arrow in the figure. (B) Potential-difference FTIR spectra of polycrystalline Au electrode recorded in the presence of cisplatin in DPBS accompanied with corresponding hard-sphere models.

Here we report for the first time the adsorption of cisplatin on polycrystalline gold surfaces under electrochemical control. It was found that the process is mediated by the adsorption of phosphate anions on the gold surface and that the maximum coverage of platinum adsorbed is given by the maximum coverage of phosphate

adsorbed at a given potential. The interaction of cisplatin with the phosphate groups was confirmed by in situ FTIR spectroscopy under external reflexion configuration.

References:

1. B. Rosenberg, *Cancer*, 1985, **55**, 2303-2316.
2. N. J. Wheate and J. G. Collins, *Coordination Chemistry Reviews*, 2003, **241**, 133-145.
3. J. M. Collins, *Journal of Clinical Oncology*, 1984, **2**, 498-504.
4. M.-H. Baik, R. A. Friesner and S. J. Lippard, *Journal of the American Chemical Society*, 2003, **125**, 14082-14092.
5. Y. Kasherman, S. Sturup and D. Gibson, *Journal of Medicinal Chemistry*, 2009, **52**, 4319-4328.
6. S. Komeda, T. Moulaei, K. K. Woods, M. Chikuma, N. P. Farrell and L. D. Williams, *Journal of the American Chemical Society*, 2006, **128**, 16092-16103.

Temperature dependence of Cu-UPD on Au(111) in 0.1 M sulphuric acid

Lena Reichenbach^a, Christopher A. Lucas^b, Yvonne Grunder^b

a) Stephenson Institute for Renewable Energy, Department of Physics, University of Liverpool, Liverpool L69 7ZF, UK

b) Oliver Lodge Laboratory, Department of Physics, University of Liverpool, Liverpool L69 7ZE, UK

Email: lena.reichenbach@liverpool.ac.uk

Underpotential deposition (UPD) of a metal is the deposition of a monolayer of metal on a substrate at a potential positive of the bulk deposition and it is well suited to study the influence of the substrate on the deposition process, as they are in close proximity and thus strongly interact^[1]. As most studies on the UPD process have been carried out at room temperature, and most industrial processes using metal deposition use elevated temperatures^[2], a systematic electrochemical study of the UPD process has been carried out to investigate the effect of the temperature on the UPD process. Cu-UPD on Au(111) in 0.1 M sulphuric acid has been chosen as a model system, as it is widely studied and well understood^[3,4].

Using a thermostat to regulate the temperature, cyclic voltammograms (CVs) were taken at selected temperatures (Figure 1). Both peak position and peak shapes of the CVs at different temperatures are compared. Deposition peak B sharpens and shifts towards higher potential with increased temperature. Peak A also shifts towards higher

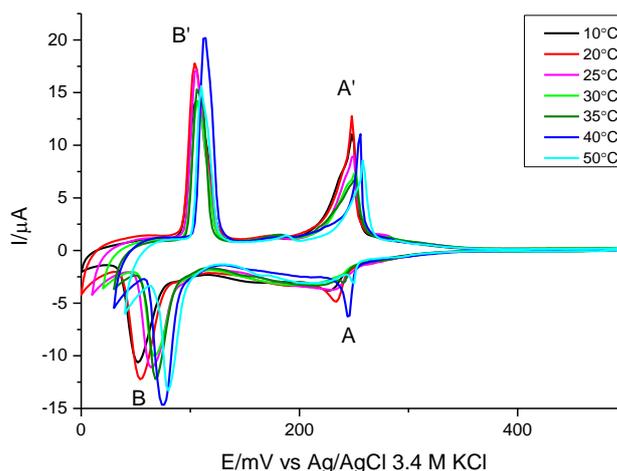


Figure 11 Temperature dependent CVs of Cu-UPD on Au(111) in 0.1 M H₂SO₄ 1 mM CuSO₄ at 5 mV/s

potential with increasing temperature, although the shift in potential does not happen as a gradual process but rather at certain threshold temperatures, in particular around 30°C and between 40°C and 50°C. A clear influence of the temperature on the UPD process can therefore be seen.

References:

- [1] Lucas, C. A. & Marković, N. M. in *Encyclopedia of Electrochemistry, Volume 2, Interfacial Kinetics and Mass Transport* (eds. Bard, A. J., Stratmann, M. & Calvo, E. J.) (WILEY-VCH, 2003).
- [2] Dini, J. W. & Snyder, D. D. in *Modern Electroplating* (eds. Schlesinger, M. & Paunovic, M.) 33–78 (John Wiley & Sons, 2010).
- [3] Herrero, E., Buller, L. J. & Abruña, H. D. Underpotential Deposition at Single Crystal Surfaces of Au, Pt, Ag and Other Materials. *Chem. Rev.* **101**, 1897–1930 (2001).
- [4] Shi, Z., Wu, S. & Lipkowski, J. Coadsorption of metal atoms and anions: Cu upd in the presence of SO₄²⁻, Cl⁻ and Br⁻. *Electrochim. Acta* **40**, 9–15 (1995).

Ionic Diode Characteristics at a Polymer of Intrinsic Microporosity (PIM) | Nafion “Heterojunction” Deposit on Microhole Poly(ethylene- terephthalate) Substrates

Budi Riza Putra¹, Elena Madrid¹, Mariolino Carta³, Richard Malpass-Evans³, Neil B. McKeown³, Frank Marken¹

¹ Department of Chemistry, University of Bath, Claverton Down, BA2 7AY, UK

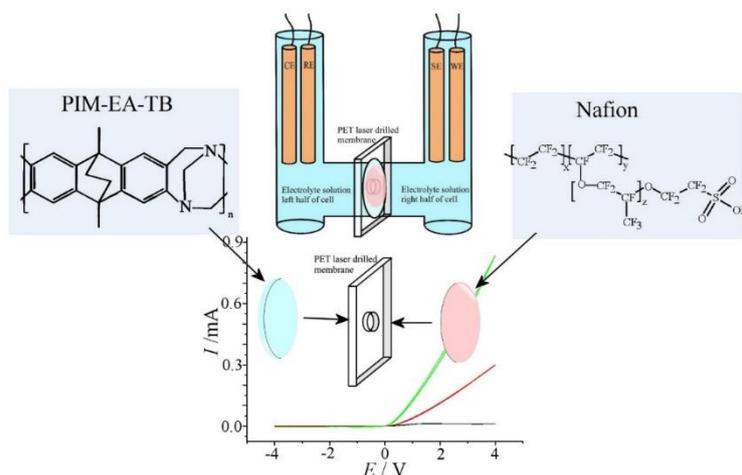
² Department of Chemistry, Faculty of Mathematics and Natural Sciences, Bogor Agricultural University, Bogor, West Jakarta, Indonesia

³ School of Chemistry, University of Edinburgh, Joseph Black Building, West Mains Road, Edinburgh, Scotland EH9 3JJ, UK

Email: brpp20@bath.ac.uk

Abstract

Ionic diode phenomena occurs at asymmetric ionomer | aqueous electrolyte microhole interfaces. Depending on the applied potential, either an “open” or a “closed” diode state is observed switching between a high ion flow rate and a low ion flow rate[1]. The phenomenon is characterized via voltammetric, chronoamperometric, and laser confocal scanning microscopy. We had explore a “heterojunction” based on an asymmetric Nafion ionomer | polymer of intrinsic microporosity (PIM) microhole interface. Improved diode characteristics and current rectification are observed in aqueous NaCl and the effect to the PIM is investigated. When it was investigated about the precipitation reaction of potassium cations with perchlorate anions to give insoluble $KClO_4$ at the microhole interface, it is shown that inversion of the rectification/diode effect occurs.



References

- [1] D. He, E. Madrid, B.D.B. Aaronson, L. Fan, J. Doughty, K. Mathwig, A.M. Bond, N. B. McKeown, F. Marken. A cationic diode based on asymmetric Nafion® film deposits. *ACS Appl. Mater. Interfaces*. 9 (12) (2017) 11272–11278, <http://dx.doi.org/10.1021/acsami.7b01774>

Microporous Heterocarbon Flakes as Catalyst for Ammonia Oxidation

Shi Xuan Leong,^{a,b} Richard Malpass-Evans,^c Mariolino Carta,^c
Neil B. McKeown,^c Frank Marken^a

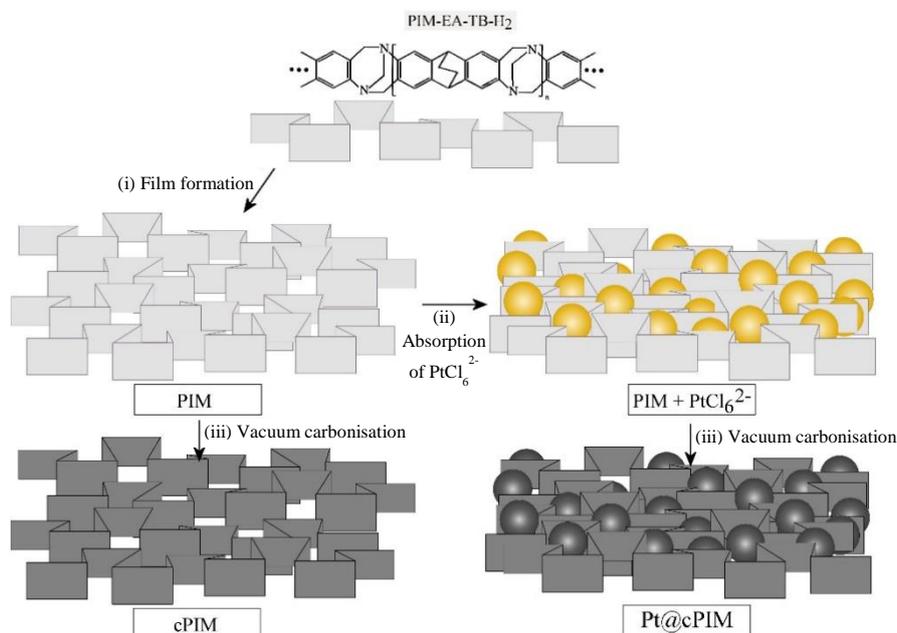
a) Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK

b) Division of Chemistry & Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

c) EastChem School of Chemistry, University of Edinburgh, David Brewster Road, Edinburgh, EH9 3FJ, UK

Email: SLEONG012@e.ntu.edu.sg

Polymers of intrinsic microporosity (PIMs¹) are developed into gas diffusion electrodes for ammonia oxidation. PIMs offer molecularly rigid structures² with the ability to carbonise into morphologically stable heterocarbon³ with micropores that can be impregnated with active nanoparticle catalysts.⁴ After carbonisation, flake-like materials are obtained and tested for catalytic activity. Pore size effects and catalyst loading effects are observed.



[1] M. Carta, R. Malpass-Evans, M. Croad, Y. Rogan, J.C. Jansen, P. Bernardo, F. Bazzarelli, N.B. McKeown, An efficient polymer molecular sieve for membrane gas separations, *Science*, 339, 2013, 303-307.

[2] D.P. He, Y.Y. Rong, M. Carta, R. Malpass-Evans, N.B. McKeown, F. Marken, Fuel cell anode catalyst performance can be stabilized with a molecularly rigid film of polymers of intrinsic microporosity (PIM), *RSC Adv.*, 6, 2016, 9315-9319.

[3] Y.Y. Rong, D.P. He, A. Sanchez-Fernandez, C. Evans, K.J. Edler, R. Malpass-Evans, M. Carta, N.B. McKeown, T.J. Clarke, S.H. Taylor, A.J. Wain, J.M. Mitchels, F. Marken, Intrinsically microporous polymer retains porosity in vacuum thermolysis to electroactive heterocarbon, *Langmuir*, 31, 2015, 12300-12306.

[4] Y.Y. Rong, D.P. He, R. Malpass-Evans, M. Carta, N.B. McKeown, M.F. Gromboni, L.H. Mascaro, G.W. Nelson, J.S. Foord, P. Holdway, S.E.C. Dale, S. Bending, F. Marken, High-utilisation nanoplatinum catalyst (Pt@cPIM) obtained via vacuum carbonisation in a molecularly rigid polymer of intrinsic microporosity, *Electrocatalysis*, 8, 2017, 132-143.

Microporous Nafion Composites in Electroanalysis

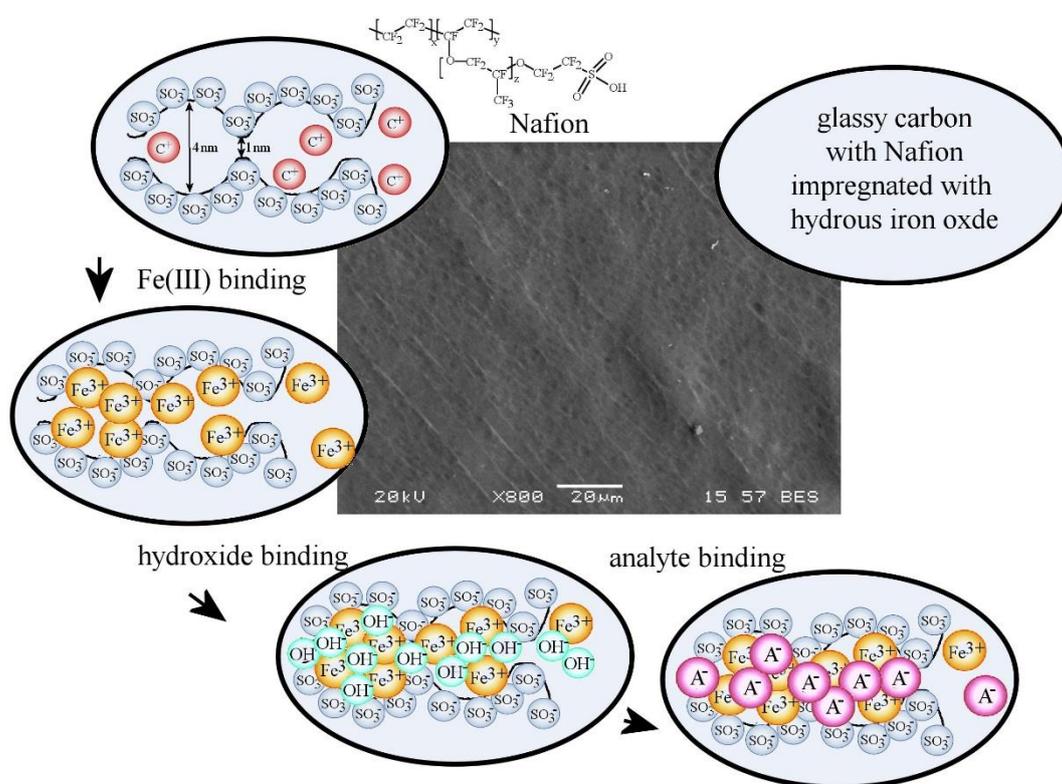
Thulase Sivasothy,^a Nche George Ndifor-Angwafor,^b and Frank Marken^a

a) Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK

b) University of Dschang, Box 814, Bamenda, North West Province, Republic of Cameroon

Email: ts819@bath.ac.uk

Nafion offers microporous channels for ion exchange and it has recently been shown that the cation exchanging properties of Nafion can be inverted¹ to anion exchange by pre-filling the hydrophilic channel structure. Here, prefilling is performed with hydrous iron oxide and sensitivity to anionic analytes is investigated. A voltammetric sensor response is obtained either indirectly (Fe(III/II)) or directly for redox active anions.



[1] U.P. Azad, D.K. Yadav, V. Ganesan, F. Marken, Hydrophobicity effects in iron polypyridyl complex electrocatalysis within Nafion thin-film electrodes, *Phys. Chem. Chem. Phys.*, 18, 2016, 23365-23373.

A Polymer of Intrinsic Microporosity (PIM-1) in Electrochemical Membranes and Diodes

Luthando Tshwenya^{a,b}, Omotayo Arotiba^b, Budi Riza Putra^a, Elena Madrid^a,
Neil B. McKeown^c, and Frank Marken^a

a) Department of Chemistry, University of Bath, Bath BA2 7AY, UK

b) Department of Applied Chemistry, University of Johannesburg, Doornfontein, 2028, South Africa

c) School of Chemistry, University of Edinburgh, Joseph Black Building, West Mains Road, Edinburgh, Scotland EH9 3JJ, UK

Email: l.tshwenya@bath.ac.uk

Polymers of intrinsic microporosity (PIMs [1]) offer rigid molecular backbone polymer structures with permanent microporosity and high processibility. Films [2,3] can be readily deposited by drop-casting. Here, the material PIM-1 is investigated for ion conductivity, membrane properties, and for diode/rectification effects when deposited asymmetrically over a microhole in a PET substrate. Reactivity changes in alkaline solution environments are highlighted and future water purification applications discussed.

[1] E. Madrid, Y.Y. Rong, M. Carta, N.B. McKeown, R. Malpass-Evans, G.A. Attard, T.J. Clarke, S.H. Taylor, Y.T. Long, F. Marken, Metastable Ionic Diodes Derived from an Amine-Based Polymer of Intrinsic Microporosity. *Angew. Chem. Int. Ed.* 2014, 53, 10751-10754.

[2] E. Madrid, P. Cottis, Y.Y. Rong, A.T. Rogers, J.M. Stone, R. Malpass-Evans, M. Carta, N.B. McKeown, F. Marken, Water Desalination Concept Using an Ionic Rectifier Based on a Polymer of Intrinsic Microporosity (PIM). *J. Mater. Chem. A* 2015, 3, 15849-15853

[3] Y.Y. Rong, Q.L. Song, K. Mathwig, E. Madrid, D.P. He, R.G. Niemann, P.J. Cameron, S.E.C. Dale, S. Bending, M. Carta, R. Malpass-Evans, N.B. McKeown, F. Marken, PH-Induced Reversal of Ionic Diode Polarity in 300 nm Thin Membranes Based on a Polymer of Intrinsic Microporosity. *Electrochem. Commun.* 2016, 69, 41-45

Corrosion

Poster Abstracts

An experimental investigation into the effects of water condensation rate and surface temperature on top of line corrosion in a CO₂ environment.

K.A. Mohammed, R. Barker, H.M.Thompson, A. Neville

*Institute of Functional Surfaces, School of Mechanical Engineering, University of Leeds
Email: ml12kam@leeds.ac.uk*

Top of Line Corrosion (TLC) is a corrosion phenomenon occurring in pipeline transportation of wet gas when there is a significant difference of temperature between the produced fluids and the surrounding environment. If the gas/liquid flow is stratified, saturated water vapour condenses on the inside walls of the pipeline and forms small water droplets which become saturated with acid gases leading to severe corrosion.

This paper provides a comprehensive experimental investigation into on the effect of condensation rate, surface temperature and iron carbonate saturation on TLC and FeCO₃ precipitation rate on carbon steel (X65) in a CO₂ environment. TLC is found to be governed by surface temperature regardless of water condensation rates (WCR) at surface temperature lower than 32°C. The results also show that WCR influences the TLC, precipitation rate and scale film formation at surface temperature higher than 32°C. On the basis of the experimental data, a new empirical model to predict the TLC rate in the absence of FeCO₃ films is described and a new kinetic constant for the calculation of FeCO₃ precipitation rate under condensing condition at the top of the line is proposed.

The Influence of Pulsed Electrical Charge on Electrochemical Remediation of Steel Reinforcement

Nikita Rathod^{a,b}, George Sergi^a, Peter Slater^b

a) Vector Corrosion Technologies

b) University of Birmingham

Email: TNR951@student.bham.ac.uk

Cathodic protection is the most common technique used to prevent/mitigate corrosion of the steel in concrete. However, many authors^{1,2}, have demonstrated that the application of a current to a steel sample produces severe side effects such as softening of the cement paste, bond strength degradation and loss of adhesion to the cement layer. Research by Koleva³ has however indicated these side effects can be reduced and controlled by applying the current in a pulse form, which proves to be less detrimental to the bulk concrete as well as the steel-cement interface.

This work investigates the effect of different pulse signatures to find the optimum pulse regime. Once the effect of pulse regime is understood, the research will look to investigate how the pulse duty cycle affects the distribution of current within a reinforced concrete specimen. The pulse technique will then be applied to a number of other electrochemical rehabilitation techniques which commonly have a constant current applied to them.

Preliminary studies for a reinforced concrete sample investigated the distance along the sample where a potential of 100mV is achieved. It can be concluded that when using a pulsed current with a square waveform and a duty cycle of 50%, a potential decay of 100mV is witnessed further along the specimen when compared to 10% and 30% duty cycles and constant current 100%. Although currently in its preliminary phase of research, once the optimum pulse regime has been determined, further experimental work will be conducted to investigate how the use of a pulse current can affect the electro migration of ions or particles through the bulk concrete to restore the passivity of the rebar or provide a protective barrier.

References:

1. Chang JJ. A study of the bond degradation of rebar due to cathodic protection current. *Cem Concr Res.* 2002;32(4):657–63.
2. Rasheeduzzafar, Ali MG, Al-Sulaimani GJ. Degradation of bond between reinforcing steel and concrete due to cathodic protection current. *ACI Mater J.* 1993;90(1):8–15.
3. Koleva D A, Guo Z, van Breugel K, de Wit JHW. Conventional and pulse cathodic protection of reinforced concrete: Electrochemical behavior of the steel reinforcement after corrosion and protection. *Mater Corros.* 2009;60:344.

We hope you enjoyed
Electrochem 2017, see
you in **Lancaster 2018**.