

RSC Electrochem 2023

University of Bristol, 10 – 12 September 2023



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RSC Electrochem 2023

University of Bristol, 10 – 12 September 2023



Dear Delegates,

On behalf of the organising committee, I would like to welcome you all to RSC Electrochem 2023 at the University of Bristol. RSC Electrochem meetings have been running for decades in different venues across the UK and Ireland. This year, the *RSC Electrochemistry Group*, the *RSC Electrochemical Sensing Group*, the *SCI Electrochemical Technology Group*, and the *Institute of Corrosion* are joined by esteem colleagues from overseas, to discuss some of the most pressing scientific challenges in our society. Indeed, from continuous health monitoring to sustainable energy conversion and storage, the role of electrochemical technologies in our lives is growing ever more prominent.

RSC Electrochem 2023 has a truly exciting technical programme spreading through five symposia:

- A. Advances in Electrochemical Energy Conversion and Storage
- B. Photoelectrochemistry and Sustainable Electrochemical Transformation
- C. Electrochemical Sensors and Electroactive Porous Materials
- D. In-Situ Spectroelectrochemistry and Interfacial Electrochemistry
- E. Corrosion Science and Technology

Symposium A has sessions dedicated to the latest advances in fuel cells, green hydrogen generation, battery science and supercapacitors. **Dr. Katherina Brinkert** (Warwick University) will initiate this symposium with her exciting studies on oxygen and fuel production under microgravity environments. **Professor Laurie Peter** (University of Bath) will kickstart *Symposium B*, describing how

dynamic photoelectrochemical responses can be used to rationalise complex multi-electron transfer reactions at illuminated semiconductor electrodes. *Symposium B* will also cover two prominent areas in sustainable electrochemical transformations: electrosynthesis and electrochemical CO₂ conversion.

We are honoured to welcome **Prof. Yitao Long** (Nanjing University), who will be awarded the distinguished *2023 RSC Faraday Medal*. Prof. Long's *Plenary Lecture* will feature some of his outstanding contributions in interfacial electrochemistry and sensing systems. These topics are at centre of *Symposia C and D*, which also feature keynote presentations by **Prof. Alvaro Colina** (Universidad de Burgos) on in-situ Raman Spectroscopy, and by **Dr. Veronica Celorrio** (Diamond Light Source) on in-situ X-ray Absorption Spectroscopy. Indeed, *in-situ* and *operando spectroelectrochemistry* is one of the hottest topics in our meeting, with contributions covering synchrotron X-Ray Absorption and Emission, EPR, Raman, and Infrared spectroscopies. Of course, two of the highlights in this topic are the *Plenary Lectures* by the *2023 RSC Parsons Medal* recipient, **Dr. Robert Weatherup** (University of Oxford), and the *2023 Fleischmann Lecture* delivered by **Prof. Andrea Russell** (University of Southampton).

It is also a privilege to welcome **Prof. Nick Birbilis** (Deakin University), the *2023 ICORR UE Evans Award* recipient, who will deliver a *Plenary Lecture* on corrosion resistance metal alloys. This is the highlight of *Symposium E*, which covers a variety of topics in corrosion science and technology, from nuclear reactors to objects of immeasurable historical value such as the SS Great Britain.

The technical programme features nearly 100 posters which will be displayed in the magnificent *Great Hall* of the Wills Memorial Building. We strongly encourage each of you to meet our company exhibitors: **Metrohm, Biologic, Alvatek, Hiden Analytical, Scimed, Equilabrium** and **Nikalyte**. We would like to express our deepest gratitude to our exhibitors and sponsoring societies for their generous contributions to this event. But most importantly, we want to thank you all for contributing and participating in RSC Electrochem 2023. We hope you enjoy every minute of the event and our City of Bristol.

Isobel Khalek

Stephen Sweeting

Alastair Lennox

David J. Fermin

RSC Faraday Medal Award

Unravelling the Nanopore Electrochemistry Landscape: My Academic Journey

Yi-Tao Long

State Key Laboratory of Analytical Chemistry for Life Science,
School of Chemistry and Chemical Engineering, Nanjing University,
Nanjing 210023, P. R. China

Yi-Tao Long yitaolong@nju.edu.cn

The development of confined electrochemistry by miniaturizing the critical sensing area is one of the great progresses in electrochemistry. Electrochemically confined measurement via confined interface offers a confined sensing area, whose dimension is comparable with single entities (e.g. single molecules, single particles, single cells) and thus could be used for ultrasensitive sensing of both electroactive and non-electroactive species.[1,2] To meet the urgent demand of sensitivity and selectivity for single molecule sensing, a single biomolecule interface is constructed in the electrochemically confined nanopore (aerolysin nanopore). Besides a narrow geometrical construction, charged amino acid residues in the inner channel of aerolysin nanopore provide the possibility to further improve the sensitivity and selectivity of nanopore sensor. We commanded individual molecules at a nano interface via site-directed mutagenesis that enables high resolution for the single biomolecule detection. The sensitivity and selectivity for various target molecules could be flexibly modulated by the choice of mutation site and amino acid residues. We also employed the aerolysin nanopore as a useful toolbox for developing the frequency-energy spectra to successfully characterize each type of non-covalent interaction between every single residue and the carriers inside membrane proteins.[3] More importantly, single molecule interface provides a confinement for the single molecule reaction which offers the possibility to study reaction kinetics in high temporal resolution. Moreover, by combining with advanced optical technology such as fluorescence or plasmonic technology, it is possible to construct an integrated single molecule interface for multi-element readouts, which is expected to further provide the rich structural information of a single analyte.[4-6]

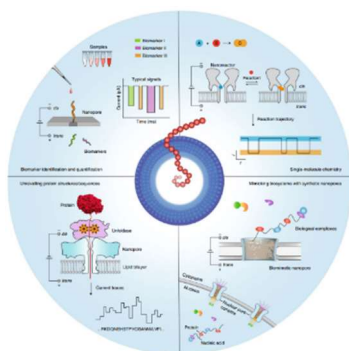
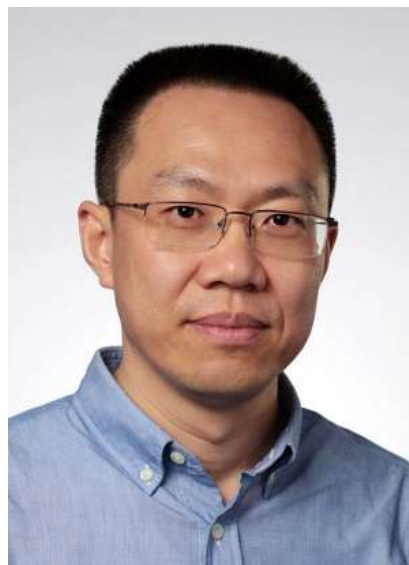


Figure 1. Nanopore electrochemistry for single entity measurements^[2]

- [1] Ying, Y.-L.; Hu, Z.-L.; Long, Y.-T., et al., *Nat. Nanotechnol.* 2022, **17**, 1136.
- [2] Lu, S.-M.; Li, M.-Y.; Long, Y.-T., *J. Phys. Chem. Lett.* 2022, **13**, 4653.
- [3] Li, M.-Y.; Ying, Y.-L.; Yu, J.; Liu, S.-C.; Wang, Y.-Q.; Li, S.; Long, Y.-T., *JACS Au* 2021, **1**, 967.
- [4] Li, X.-Y.; Ying, Y.-L.; Fu, X.-X.; Wan, Y.-J.; Long, Y.-T., *Angew. Chem. Int. Ed.* 2021, **60**, 24582.
- [5] Jiang, J.; Li, M.-Y.; Wu, X.-Y.; Ying, Y.-L.; Han, H.; Long, Y.-T., *Nat. Chem.* 2023, **15**, 578.
- [6] Xin, K.-L.; Hu, Z.-L.; Liu, S.-C.; Li, X.-Y.; Li, J.-G.; Niu, H.; Ying, Y.-L.; Long, Y.-T., *Angew. Chem. Int. Ed.* 2022, **61**, e202209970.

Yi-Tao Long is the Professor of Analytical Chemistry and Director of Molecular Sensing and Imaging Center at Nanjing University, China. He received his B.Sc. (1989) in Chemistry at Shangdong University and PhD (1998) in Bioelectrochemistry (supervisor: Professor Hong-Yuan Chen) from Nanjing University. After 2-year postdoctoral study (adviser: Professor Michael Grunze) at Heidelberg University, he worked as a Research Associate at University of Saskatchewan and University of Alberta, Canada, and the Associate Specialist at University of California, Berkeley, Then, he was appointed as a full Professor at East China University of Science and Technology in 2007 and returned to Nanjing University in 2019.



His main research focuses on the electrochemistry at nanoconfinement which involves nanopore electrochemistry for single-molecule analysis, nanospectroelectrochemistry for biointerphase and the nanoelectrochemical instruments for life science. Professor Long has published over 300 peer-reviewed scientific journal papers, 5 books/chapters and 4 PCT patents. He currently serves as Associate Editor for *Chemical Science*, and Editorial Board/Advisory Board Member of *Chemical Reviews*, *ChemElectroChem*, *Research, Theranostics*, *Microchimica Acta*, and was a founding Associate Editor for *ACS Sensors* (2015-2018). He supervised 85 graduate students, including 42 obtained PhD degrees and 29 obtained Master's degrees, and advised 15 Postdoctoral Fellows.

ICORR UE Evans Award

Towards sustainable corrosion resistant alloys

Nick Birbilis

Faculty of Science, Engineering and Built Environment. Deakin University. Australia

Metallic materials now play a key role in shaping all aspects of our way of life. Since the advent of 'stainless steels' over a century ago, the dream of having inexpensive 'stainless' commodity alloys – that also meet the physical requirements for their application – remains largely elusive. It is abundantly evident, even in the present day, that we urgently require metallic materials which can meet increasingly demanding applications, and which comply with environmental sustainability goals. This latter point includes the need for alloy production from recycled materials, with such materials requiring increased durability and lifetimes compared to existing alloys. From a corrosion engineering perspective, these are challenges that require detailed electrochemical science in order to be solved. Whilst a perspective regarding development of 'stainless' commodity alloys will be covered, an insight into the modern tools that can enable sustainable corrosion resistant alloys will also be explored, including the role of advanced manufacturing and machine learning.

Prof Nick Birbilis is the Executive Dean of the Faculty of Science, Engineering and Built Environment at Deakin University (Australia). His research is broadly in the area of materials durability and design. Metal corrosion and materials characterisation are his core research themes – with a focus on sustainable materials. Nick has made a number of major contributions in the field of corrosion; particularly in the area of localised corrosion, the role of microstructural effects on the corrosion of engineering alloys, and upon corrosion of lightweight alloys. He is a Fellow of the Electrochemical Society (ECS), a Fellow of the International Society of Electrochemistry (ISE), a Fellow of the National Association of Corrosion Engineers (NACE/AMPP) and a Fellow of ASM International. Nick has also been awarded numerous awards, including the Batterham Medal from the Australian Academy of Technological Sciences and Engineering and the HH Uhlig Award from the Electrochemical Society. He has authored over 450 publications and is the Editor-in-chief of the interdisciplinary journal *npj Materials Degradation*. and serves as a long-standing Editor for the journal *Electrochimica Acta*. He also remains a strong advocate for diversity in STEM.



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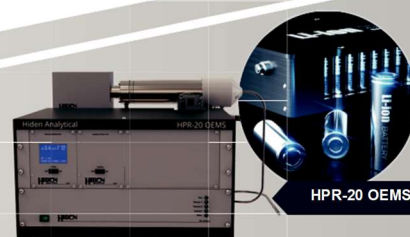
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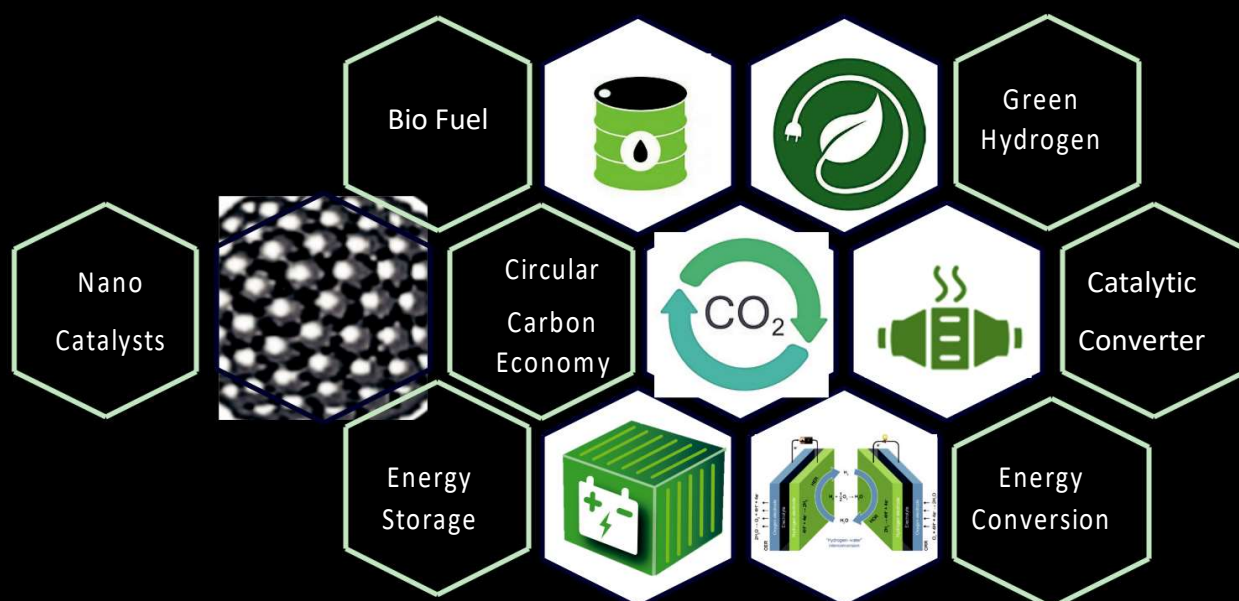
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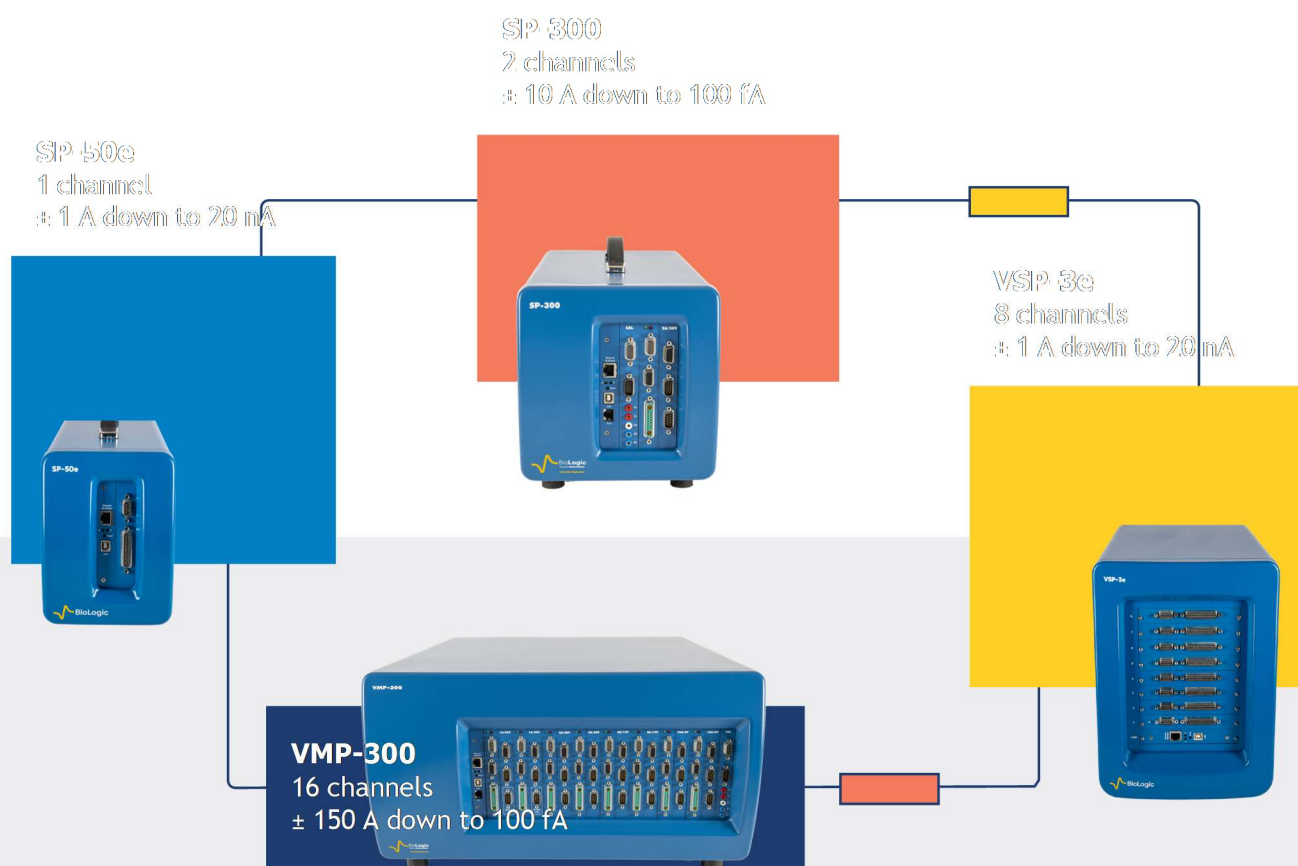
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RSC Parsons Medal Award

Revealing Reactions at Buried Electrochemical Interfaces with X-ray Spectroscopies

Robert S. Weatherup

Department of Materials, University of Oxford

The performance of materials for electrochemical energy storage and conversion depends critically on reactions taking place at the interfaces between these materials and their electrochemical environment. As the reaction conditions change so these interfaces change, with often dramatic effects on their structure and chemical state. Understanding the evolution of these interfaces under realistic conditions is critical to the selection and design of improved materials. However, it is extremely challenging to extract this information during operation, due to interference from the bulk phases either side of these buried interfaces, which disturb most interface-sensitive probes.¹

I will summarise our recent efforts to develop *operando* approaches for resolving the structural and chemical evolution of electrochemical interfaces.²⁻⁴ This includes enclosed reaction cells sealed with X-ray/electron-transparent membranes such as thin (<100 nm) silicon nitride or graphene. We have thereby used soft X-ray absorption spectroscopy (sXAS) to observe solid-electrolyte interphase (SEI) formation on Li-ion battery anodes.³ I will further discuss our recent progress in depositing thin lithium layers onto solid electrolytes, and using hard X-ray Photoelectron Spectroscopy (XPS) to study electrode-electrolyte interfaces in all-solid-state batteries.⁴ The development of these interface-sensitive *operando* approaches is expected to provide valuable tools for revealing a wide range of interfacial electrochemical reactions.

1. Wu et al. *Phys. Chem. Chem. Phys.* **2015**, *17*, 30229.
2. Velasco-Velez et al. *Angew. Chemie* **2015**, *54*, 14554.
3. Swallow et al. *Nature Commun.* **2022**, *13*, 6070
4. Gibson et al. *Faraday Discuss.*, **2022**, 236, 267; Narayanan et al. *Nature Commun.* **2022**, *13*, 7237

Bio: Rob Weatherup is Associate Professor in the Department of Materials, where he leads a group of 15 researchers working on materials for energy storage and conversion. His work aims to understand the reactions occurring at the interfaces between these materials and their operating environment in areas including Li-ion batteries, electrochemical hydrogen production, and carbon dioxide conversion. He gained his PhD from the University of Cambridge (2013) working with Professor Stephan Hofmann. He then held a research fellowship at St John's College, Cambridge (2013–2017), spending two years as a Marie Skłodowska Curie Fellow at Lawrence Berkley National Laboratory (2015–2017). After a brief return to Professor Dame Clare Grey's group in Cambridge, he started his research group as a Diamond-Manchester fellow (2018–2019) based at Diamond Light Source and took up his current position at Oxford in October 2019. He is a CAMS-UK Fellow, a Visiting Scientist at Diamond Light Source, and the Research Area Lead for Electrochemical Systems within the Royce Institute, the UK's national institute for advanced materials research and innovation. He currently holds an ERC starting grant and UKRI future leaders fellowship, through which he is developing new methods to probe electrochemical and catalytic interfaces in action using X-ray techniques.



Fleischmann Lecture

In situ to Operando: an XAS journey to understand electrocatalysts

Andrea E. Russell

School of Chemistry, University of Southampton

X-ray absorption spectroscopy (XAS) can provide insights into the structure/property relationships in electrocatalysis. The near-edge region (XANES) allows determination of the average oxidation state (edge position), coordination geometry (pre-edge features and edge structure), and in some cases the d-band occupancy. The spectra above the edge, at higher energies, (EXAFS) provides information regarding the local coordination environment (identity of neighbouring atoms and distances). Owing to the penetrative nature of X-rays these measurements can be conducted *in situ* in an electrochemical cell and if the cell approximates the true working environment of the electrocatalyst the measurements are called *operando*. However, the atom-weighted nature of the spectra needs to be carefully considered when interpreting the results as electrocatalyst particle size and dispersion, utilisation, etc. can all skew the results obtained.

I will summarise the journey of my research group, showing how we have developed electrochemical cells and electrode environments to take advantage of the information obtained via XAS studies to explore structure/property relationships for a variety of electrocatalysts. The journey begins with the study of the CO tolerance of bimetallic catalysts for PEM fuel cells, continues to the study of electrocatalysts for the oxygen reduction (ORR) and oxygen evolution (OER) reactions, and will be brought up to date with our recent studies of electrocatalysts for carbon dioxide reduction (CO₂RR). In each case the importance of *in situ* vs. *operando* conditions and careful consideration of the limitations of the measurements and requirements of the cell design will be highlighted.

Andrea Russell received her BS in 1986 from the University of Michigan and her PhD in 1989 from the University of Utah. She was a National Research Council Fellow at the US Naval Research Laboratory from 1990 – 1991 and then moved to the UK, where she started her academic career at the University of Liverpool, moved to the University of Newcastle upon Tyne in 1994, and the University of Southampton in 1997. She was promoted to Professor of Physical Electrochemistry in 2007. She is the author or co-author of > 140 refereed papers and book chapters, including invited review articles and has chaired a number of international conferences and symposia. Her research combines electrochemistry and other characterisation methods to provide additional insights, along the lines established by Martin Fleischmann.



She is currently a Vice-President of the International Society of Electrochemistry, a member of the EPSRC College, Chair of the Diamond Users Group, a member of the Diamond Scientific Advisory Committee, a member of the RSC Committee for Accreditation and Validation, and a Fellow of both the Royal Society of Chemistry and Higher Education Academy.

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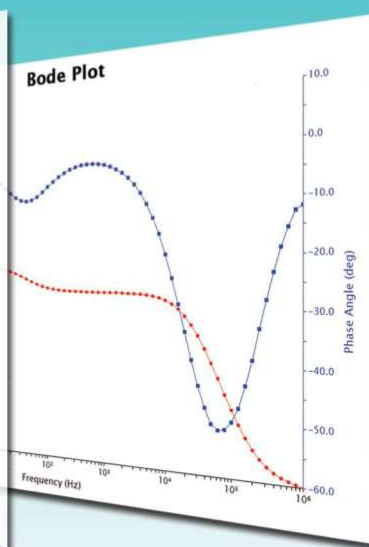
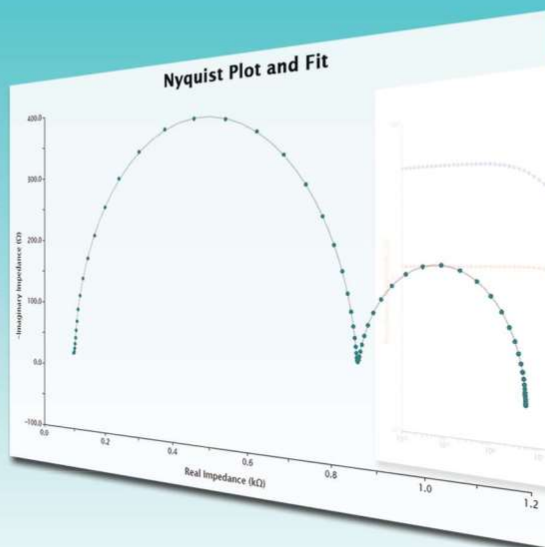
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Electrochem 2023

University of Bristol, 10th – 12th September

Programme

Sunday 10th September

Time	Event
From 17:30	Registration and Museum Access The SS Great Britain
18:00 – 20:00	Welcome Reception The SS Great Britain

Monday 11th September

Time	Symposium A Advances in Electrochemical Energy Conversion and Storage	Symposium B Photoelectrochemistry and Sustainable Electrochemical Transformation	Symposium C Electrochemical Sensors and Electroactive Porous Materials	Symposium D In-Situ Spectroelectrochemistry and Interfacial Electrochemistry	Symposium E Corrosion Science and Technology
	Reception Room	Old Council Chamber	Room 3.30	Room 3.31	Room 3.32
08:00 – 08:45	Registration Entrance Hall				
08:45 – 09:00	Opening Remarks Reception Room				

09:00 – 09:50	<p align="center"><u>RSC Faraday Medal Award</u></p> <p align="center">Unravelling the Nanopore Electrochemistry Landscape: My Academic Journey</p> <p align="center">Yitao Long</p> <p align="center">Reception Room</p> <p align="center"><i>Chairs: Sarah Horswell and David Fermin</i></p>				
09:50 – 10:10	<p align="center"><u>Presentations by Exhibitors</u></p> <p align="center">Metrohm, Biologic, Equilabrium, Alvatek</p> <p align="center">Reception Room</p>				
10:10 – 10:40	<p align="center">Refreshments, Poster Session, and Exhibitors</p> <p align="center">The Great Hall</p>				
	<p align="center">Electrolysers and Fuel Cells</p> <p align="center"><i>Chair: Mark Symes</i></p>	<p align="center">Photoelectrodes and Photoelectrochemical Reactors</p> <p align="center"><i>Chair: Anna Hankin</i></p>	<p align="center">Electrochemical Sensing I</p> <p align="center"><i>Chair: Sudipta Roy</i></p>	<p align="center">Operando Spectroelectrochemistry I</p> <p align="center"><i>Chair: Andrea Russell</i></p>	<p align="center">Corrosion Science I</p> <p align="center"><i>Chair: Thomas Martin</i></p>
10:40 – 11:10	<p>A1 – K. Brinkert</p> <p>Energy-Efficient Oxygen and Fuel Production in (Photo-)Electrochemical Devices in Microgravity Environment</p>	<p>B1 – L. Peter</p> <p>Photoelectrode Kinetics</p>	<p>C1 – A. Colina</p> <p>On the Capabilities of Electrochemical Surface Oxidation Enhanced Raman Scattering for Analysis</p>	<p>D1 – V. Celorrio</p> <p>Relationship Between Mn Oxidation State Changes and Oxygen Reduction Activity in (La,Ca)MnO₃ Probed by In-Situ XAS and XES</p>	<p>E1 – D. Kumar</p> <p>On the High Temperature Water Oxidation and Stress Corrosion Cracking of Reduced Activation Ferritic Martensitic Eurofer-97 Steel</p>
11:10 – 11:30	<p>A2 – S. Ünsal Dayanik</p> <p>Enhanced Proton Exchange Membrane Fuel Cell Performance via Graduated Catalyst Layer Ionomer Content</p>	<p>B2 – G. Creasey</p> <p>Materials and Reactor Development for Photoelectrochemical Hydrogen Production</p>	<p>C2 – F. Rawson</p> <p>Quantum Electrochemical Sensors and Actuators: Pioneering a Novel Frontier in Cancer Therapy</p>	<p>D2 – T. McIntyre</p> <p>Probing the Structure of the Electrochemical Interface Using In-Situ Surface X-Ray Diffraction Techniques</p>	<p>E2 – V. Bongiorno</p> <p>Automating Corrosion Testing for Organic Coatings: A Machine Learning Based Approach</p>
11:30 – 11:50	<p>A3 – M. Shnaiter</p> <p>The Preparation and Characterisation of</p>	<p>B3 – A. Karunakaran</p> <p>Nanophase-Photoelectrocatalysis:</p>	<p>C3 – E. Dixon</p> <p>Electrochemical Processing of</p>	<p>D3 – S. Kumar</p> <p>Development of Spectro-Electrochemical Cell for</p>	<p>E3 – Y. Liu</p> <p>Degradation of Marine Coatings</p>

	Inkjet Printed Low Iridium Loaded Anodes for PEM Water Electrolysis	Loading, Storing, and Release of H ₂ O ₂ Using a Photochemical Reaction Within Graphitic Carbon Nitride	Nanoporous Copper as a High Surface Area Enhanced Catalyst for Sensing Applications	Operando NAP-XPS/NEXAFS Investigations	During Hygrothermal Cyclic Corrosion Tests
11:50 – 12:10	A4 – D. Shinde In-situ reference electrodes for characterization of alkaline water electrolyzers	B4 – M. Colet-Lagrange Ultra-Thin Alumina Overlayer as a Protective Coating on CuWO ₄ Photoanodes	C4 – A. Etchegaray Jr A biosensor for methotrexate can be designed using dihydrofolate immobilized onto iron magnetic nanoparticles	D4 – J. J. Tully EPR Spectro-Electrochemistry as a Tool for Studying Radical Generation on Boron Doped Diamond Electrodes	E4 – L. Coghlan The Degradation Mechanism of Polyester Powder Coatings Exposed to Cyclic Corrosion Testing (CCT)
12:10 – 13:40	Lunch Refreshments, Poster Session, and Exhibitors The Great Hall SCI ECTG Committee meeting: 12.30 – 13.00 Old Council Chamber Joint RSC Electrochemistry Interest Group and SCI ECTG Committee Meeting: 13.00 - 13.30 Old Council Chamber				
13:40 – 14:30	<u>ICORR UE Evans Award</u> Towards sustainable corrosion resistant alloys Nick Birbilis Reception Room <i>Chair: Julian Wharton</i>				
14:30 – 14:50	<u>Presentations by Exhibitors</u> Scimed, Nikalys, Hiden Analytical The Great Hall				
	Electrocatalysts for Hydrogen Generation <i>Chairs: Laurie King and Katharina Brinkert</i>	Sustainable Electrochemical Transformations I <i>Chairs: Alastair Lennox and Melanie Colet-Lagrange</i>	Electrochemical Sensing II <i>Chairs: Yitao Long and Alvaro Colina</i>	Operando Spectroelectrochemistry II <i>Chairs: Robert Weatherup and Veronica Celorrio</i>	Corrosion Science II <i>Chairs: Nick Birbilis and Amber Sikes</i>
15:10 – 15:30	A5 - M. A. Buckingham	B5 – T. Liu	C5 – R. Shergill	D5 – S. Redor	E5 – R. Abou-Shakra

	Advanced Electrocatalysis from High Entropy Metal Sulphides	Redox Neutral Electrosynthesis without Added Electrolyte at Interdigitated Electrodes	Pre-printing saponification of carbon thermoplastic filaments provide ready-to-use electrochemical sensors	Using Operando Reflection Optical Microscopy to Explore the Electrochemical and Electrochromic Properties of $\text{Li}_2\text{Ni}_2\text{W}_2\text{O}_9$	Surfactant Corrosion Inhibitor Adsorption and Desorption Kinetics in Aqueous CO_2 -Containing Environments
15:30 – 15:50	A6 - T. Manyepedza	B6 – D. H. Broadhurst	C6 – C. H. Liu	D6 – L. Wichmann	E6 – H. Hilton-Tapp
	Transition Metal Dichalcogenide Heterostructures as Electrocatalysts for the Hydrogen Evolution Reaction	High Yield and Selective Electrocatalytic Reduction of Nitroarenes via Polyoxometalate Redox-Mediated Chronoamperometry	Electrochemical Aptasensor for SARS-CoV-2 Detection Based on Magnetic MOF and Screen-Printed Electrode	Correlation of Excess Lithium, 'Dead Lithium' and Functional Layers in 'Anode-Free' Lithium Metal Batteries	Production of Copper Nanocomposite Coatings Using Pulse Reverse Plating and Anionic Surfactant
15:50 – 16:20	Refreshments, Poster Session, and Exhibitors The Great Hall				
16:20 – 16:40	A7 - A. K. Samuel	B7 – N. Alhathloul	C7 – G. Smith	D7 – S. L. Horswell	E7 – T. H. E. Dobson
	Are 2D Chalcogenides Suitable for PEM Water Electrolysis: The Case Study of the Application of MoTe_2 in a Single Stack Electrolyser	Room Temperature Electro-Carboxylation of Styrene and Stilbene Derivatives: A Comparative Study	Error, Reproducibility and Uncertainty in Electrochemical Measurements	Why Do Similar Molecules Respond Differently to Electric Fields? Hydrogen Bonding Effects in Biomimetic Membranes	Effect of Biofouling on the Corrosion of Nickel Aluminium Bronze Immersed in Natural Sea Water
16:40 – 17:00	A8 - D. Belami	B8 – A. Choi	C8 – J. Lehr	D8 – F. Carla	E8 – M. Makuch
	Catalyst-Support Design for Proton Exchange Membrane Electrolysers	3D-Printing for Electrochemical Reactors and a Tool Kit for the Expansion of the ElectraSyn	Selective Detection of Protein Biomarkers via Multifunctional Molecular Layers from Electrografting Methods	In-situ and Operando Characterization of Electrochemical Interfaces by Surface X-ray Diffraction and Scattering	Phase Field Model of Accelerated Corrosion Tests and Single Crystal Polarisation Anisotropy
17:00 – 17:20	A9 – S. Yadav	B9 – F. Todman	C9 – A. M. López-Marzo	D9 – Andrew J. Wain	E9 – J. Thevakumar
	Investigating the Electrocatalytic Water	Decoupled biomass oxidation and hydrogen	Toward Completely label-Free Point-of-Care	New Cell Designs and Sample Configurations for	Casing Corrosion of Steels in Geothermal

	Splitting Efficacy During the Dimensional Transition from Single-Atom to Nanoparticles with Porous Hard-Carbon as Supports	production mediated by phosphomolybdic acid	Devices Using Bioreceptor Immobilisation by Hydrogen Bonding and Differential Pulse Voltammetry as Measurement Tool	Operando Raman Spectroscopy of Battery Electrodes	Environments Containing Sulphuric Acid
17:20 – 18:00	RSC Electrochemistry Interest Group AGM: Reception Room SCI Electrochemical Technology Group AGM: Old Council Chamber				
19:00	Banquet Bristol Museum and Art Gallery				

Tuesday 12th September

Time	Symposium A Advances in Electrochemical Energy Conversion and Storage	Symposium B Photoelectrochemistry and Sustainable Electrochemical Transformation	Symposium C Electrochemical Sensors and Electroactive Porous Materials	Symposium D In-Situ Spectroelectrochemistry and Interfacial Electrochemistry	Symposium E Corrosion Science and Technology
	Reception Room	Old Council Chamber	Room 3.30	Room 3.31	Room 3.32
08:30 – 09:00	Arrival				
09:00 – 09:50	<p align="center"><u>RSC Parsons Medal Award</u> Revealing Reactions at Buried Electrochemical Interfaces with X-ray Spectroscopies Robert S. Weatherup Reception Room <i>Chairs: Sarah Horswell and Alastair Lennox</i></p>				
09:50 – 10:10					
	Batteries and Supercapacitors I <i>Chairs: Xiaohong Li and Mark Buckingham</i>	Sustainable Electrochemical Transformations II <i>Chairs: Frank Marken and Charl Faul</i>	Electrochemical Sensing II <i>Chairs: Augusto Etchegaray and Elena Bernalte</i>	Interfacial Electrochemistry I <i>Chairs: Petra Cameron and Henry Lloyd-Laney</i>	Corrosion Science III <i>Chairs: Lawrence Coghlan and Hannah Hilton-Tapp</i>
	A10 – R. Gray	B10 – C. Sharma	C10 – S. Zhang	D10 – I. Terrero Rodríguez	E10 – P. Thomas
10:10 – 10:30	<u>RSC Regional Award</u> Alternative Architectures for Structural Batteries	Polyaniline/Polypyrrole Composites Electrodeposited from Ionic Liquids for Hydrogen Evolution Reaction	<u>S. Campbell Award</u> Biosensor for Rapid Measurement of Lactate in Exhaled Breath Condensate	The Importance of sp ² Bonded Carbon in Electrochemical Ozone Production Using Freestanding Boron-Doped Diamond Anodes	Microstructural Evolution Due to CO ₂ Oxidation and Carburisation in 9Cr-1Mo Steel
	A11 – I. J. McPherson	B11 – S. Rodriguez	C11 – T. Narayan	D11 – A. W. Black	E11 – C. Ozturk
10:30 – 10:50	Interpreting Single Particle Voltammetry of Battery Materials	Valorisation of CO ₂ and other abundant waste streams	Real-Time Electrochemical Sensor for the Detection of Endocrine Disruptors in Water Samples	Exploring Boron Doped Diamond as an Electrocatalyst Support for Alkaline Water Electrolysis	Atmospheric Corrosion of 316L Stainless Steel: The Effect of Stress and Strain

10:50 – 11:20	Refreshments, Poster Session, and Exhibitors The Great Hall				
11:20 – 11:40	A12 – G. Bree	B12 – H. Sale	C12 – C. N. Yang	D12 – H. A. Al Nasser	E12 – A. Sykes
	Calendar Aging of Commercial Cylindrical Li-Ion Batteries – Mechanisms and Mitigation Strategies	Optimising the Electrochemical Reduction of CO ₂ to Oxalic Acid in Propylene Carbonate	Observing Confined Local Oxygen-Induced Reversible Thiol/Disulfide Cycle with a Protein Nanopore	Electrochemical Assessment of a Tripodal Thiourea-Based Anion Receptor at the Liquid Liquid Interface	The Effect of CO ₂ Partial Pressure on the Formation and Protective Characteristics of Iron Carbonate Corrosion Products
11:40 – 12:00	A13 – Z. Zhu	B13 – L. Yusuf	C13 – S. O’Sullivan	D13 – J. V. Díaz-Reyes	E13 – A. Hanson
	High Sodium-Ion Battery Capacity in Sulfur-Deficient Tin(II) Sulfide Thin Films with a Microrod Morphology	Optimising Ultrasound Parameters for Efficient Sonoelectrochemical CO ₂ Reduction at Copper Electrodes	3D-Printed Microfluidics System Coupled with Electrochemical pH Control for Enhanced Chlorine Detection	Theoretic Approach to the Capacitance of Aqueous α,α,α -Trifluorotoluene Interfaces	Understanding the Effect of Strain on Corrosion of Advanced Gas-Cooled Reactor Fuel Cladding
12:00 – 12:20	A14 – J. Searle	B14 – M. S. Tovar-Oliva	C14 – F. Perez	D14 – J. W. Jordan	E14 – X. Wen
	Diketopyrrolopyrroles as Performance Enhancing Additives for Lithium-Sulfur Batteries	Optimised Electrodeposition Technique for In-Situ Fabrication of Cu-Based Catalysts on Gas Diffusion Layers for Electrochemical CO ₂ Reduction	Development of an Electrochemical Biosensing Array for Simultaneous Detection of Urinary Metabolites for Disease Profiling	Voltammetric Evidence of Proton Transport Through the Sidewalls of Single-Walled Carbon Nanotubes	Study of Carbon Steel Corrosion in Live Anaerobic Digestion Reactors
12:20 – 12:40	A15 – W. Townsend	B15 – Z. Zhu	C15 – C. Miller	D15 – S. M. Lu	E15 – J. Srivastava
	Exploring the role of redox-shuttle mediators in lithium-sulfur batteries	Carbon Nanotube Production from CO ₂ Via High Temperature Electrolysis	Evaluating the Impact of Different Electrode Surface Patterns of 3D Printed Carbon	Confinement-Controlled Nanoelectrochemistry: Study One Entity at a Time	The Influence of Grain Structure on Hydrogen-Environmentally

			Thermoplastic Electrochemical Sensors		Induced Cracking (H-EIC) Behaviour of AA7085 Alloy in Humid Air
12:40 – 14:00	Lunch, Poster Session, and Exhibitors The Great Hall				
	Batteries and Supercapacitors II <i>Chairs: Ian McPherson and Andy Wain</i>	Sustainable Electrochemical Transformations III <i>Chairs: Zeliha Ertekin and Laurie Peter</i>	Electroactive Porous Polymers <i>Chairs: Santiago Rodriguez and Loredana Vacareanu</i>	Interfacial Electrochemistry II <i>Chairs: Alison Parkin and Sara Dale</i>	Corrosion Science IV <i>Chairs: David Kumar and Tamsin Dobson</i>
14:00 – 14:20	A16 - M. Smith Investigating Degradation of 1,3-Dimethyl-2-Imidazolidinone Electrolyte in Li-S Batteries	B16 – H. L. A. Dickinson NiCuAg: An Electrochemically Synthesised Trimetallic Stack for CO ₂ Reduction	C16 – F. Marken Triphasic Electrochemical Processes Enhanced by Polymers of Intrinsic Microporosity	D16 – Z. Li Driving Electrochemical Membrane Processes with Coupled Ionic Diode	E16 – C. E. Elgar Using Ultrasound to Increase Metal Anodic Dissolution and Prevent Passivation Using Concentrated Ionic Fluids
14:20 – 14:40	A17 – M. Binari MnO ₂ Nanotube/GO Composite Anode for High Performance Lithium-Ion Capacitor	B17 – P. K. Sharma Earth Abundant CuSn Electrocatalysts for Selective Conversion of CO ₂ to CO	C17 – C. F. J. Faul Porous Organic Materials for Metal-Free CO ₂ Capture and Electrocatalytic Conversion	D17 – K. J. Levey The Importance of Considering Electrostatics When Numerically Modelling the Cyclic Voltammetric Response of an Outer-Sphere Redox Couple	E17 – A. Keogh Effect of Microstructure on Localised Corrosion and Atmospheric Stress Corrosion Cracking of 15-5 PH Stainless Steels
14:40 – 15:00	A18 – M. Hunt Few-layer Graphene as a Conductive Additive for Flexible Aqueous Supercapacitor Electrodes	B18 – L. Navarro-Tovar Electrodeposition of Cu-Based Bimetallic Catalyst Over Gas Diffusion Layer (GDL)	C18 – K. DeMonte Porphyrin-Like Designer Catalysts for Electrocatalytic H ₂ Evolution and	D18 – H. Lloyd-Laney Recovering Biological Electron-Transfer Parameters: The Perspective of Multiple Techniques	E18 – J. Rafferty Environmental Effects of a Simulated AGR Coolant on Oxidation and Carburization

		for the Electrochemical Conversion of CO ₂	Selective CO ₂ Reduction		Behaviour of Type 316H Stainless Steel
15:00 – 15:20	A19 – Z. Zhang	B19 – A. Randi	C19 – L. Vacareanu	D19 – I. Scivetti	E19 – W. Intaphan
	Electrochemical Atomic Force Microscopy in Battery Study	Atmospheric-Pressure Plasma Device for CO ₂ Conversion and Utilisation	Electrogenerated Microporous Conjugated Polymers Based on Starshaped Oligomer Derived from Triphenylamine: Exploring Structure-Properties Relationships	Stoichiometric Resolution in the Electrochemistry of Oxide Materials: Driving Computational Research with Electrochemical Quartz Crystal Microbalance	Elucidation of Charge-Transfer Mechanisms Under Paint Films by Conventional and Localised Electrochemical Impedance Spectroscopy
15:20 – 15:40	A20 – S.R. Ottakath	B20 – E. Latvyte	C20 – D. Duleba	D20 – M. E. Keal	E20 – C. Bevas
	Understanding battery health and identification of ageing history of commercial lithium-ion batteries using nonlinear frequency response analysis (NFRA)	A Low-Temperature Ammonia Electrolyser for Wastewater Treatment and Hydrogen Production	Proton Enrichment and Surface Charge Dynamics in Nanopores	Electrochemical Recycling of Ruthenium Via Nano-Impacts	The Influence of Radiation on the Corrosion of Carbon Steel for Nuclear Waste Geological Disposal
15:40 – 16:00	Refreshments, Poster Session, and Exhibitors The Great Hall				
16:00 – 16:50	<p style="text-align: center;"><i>Fleischmann Lecture</i> <i>In situ to Operando: an XAS journey to understand electrocatalysts</i> Andrea E. Russell Reception Room <i>Chairs: Sarah Horswell and David Fermin</i></p>				
16:50 – 17:00	Closing Remarks Reception Room				

Oral Abstracts

Symposium A – Advances in Electrolysers, Batteries and Supercapacitors

#	Presenting Author	Title	Affiliation
A1	Katharina Brinkert	Energy-Efficient Oxygen and Fuel Production in (Photo-)Electrochemical Devices in Microgravity Environment	University of Warwick, University of Bremen
A2	Seçil Ünsal Dayanik	Enhanced Proton Exchange Membrane Fuel Cell Performance via Graduated Catalyst Layer Ionomer Content	University College London
A3	Marwah Shnaiter	The Preparation and Characterisation of Inkjet Printed Low Iridium Loaded Anodes for PEM Water Electrolysis	Coventry University
A4	Dipak Shinde	In-situ Reference Electrodes for Characterization of Alkaline Water Electrolysers	National Physical Laboratory
A5	Mark A. Buckingham	Advanced Electrocatalysis from High Entropy Metal Sulphides	University of Manchester
A6	Tshiamo Manyepedza	Transition Metal Dichalcogenide Heterostructures as Electrocatalysts for the Hydrogen Evolution Reaction	University of Birmingham
A7	Arun Kumar Samuel	Are 2D Chalcogenides Suitable for PEM Water Electrolysis: The Case Study of the Application of MoTe ₂ in a Single Stack Electrolyser	University of Glasgow
A8	Debora Belami	Catalyst-Support Design for Proton Exchange Membrane Electrolysers	Manchester Metropolitan University
A9	Subham Yadav	Investigating the Electrocatalytic Water Splitting Efficacy During the Dimensional Transition from Single-Atom to Nanoparticles with Porous Hard-Carbon as Supports	Indian Institute of Technology
A10	Robert Gray	Alternative Architectures for Structural Batteries	University of Bath
A11	Ian J. McPherson	Interpreting Single Particle Voltammetry of Battery Materials	Loughborough University, University of Warwick
A12	Gerard Bree	Calendar Aging of Commercial Cylindrical Li-Ion Batteries – Mechanisms and Mitigation Strategies	University of Warwick

A13	Zening Zhu	High Sodium-Ion Battery Capacity in Sulfur-Deficient Tin(II) Sulfide Thin Films with a Microrod Morphology	University of Southampton
A14	Joanne Searle	Diketopyrrolopyrroles as Performance Enhancing Additives for Lithium-Sulfur Batteries	University of Nottingham
A15	William Townsend	Exploring the role of redox-shuttle mediators in lithium-sulfur batteries	University of Nottingham
A16	Margaret Smith	Investigating Degradation of 1,3-Dimethyl-2-Imidazolidinone Electrolyte in Li-S Batteries	University of Nottingham
A17	Mariam Binari	MnO ₂ Nanotube/GO Composite Anode for High Performance Lithium-Ion Capacitor	Khalifa University of Science and Technology
A18	Michael R. C. Hunt	Few-Layer Graphene as a Conductive Additive for Flexible Aqueous Supercapacitor Electrodes	Durham University
A19	Zhenyu Zhang	Electrochemical Atomic Force Microscopy in Battery Study	University of Exeter
A20	Safeer Rahman Ottakath Cholakkal	Understanding Battery Health and Identification of Ageing History of	Coventry University

Symposium B – Photoelectrochemistry and Sustainable Electrochemical Transformation

#	Presenting Author	Title	Affiliation
B1	Laurie Peter	Photoelectrode Kinetics	University of Bath
B2	George Creasey	Materials and Reactor Development for Photoelectrochemical Hydrogen Production	Imperial College London
B3	Akalya Karunakaran	Nanophase-Photoelectrocatalysis: Loading, Storing, and Release of H ₂ O ₂ Using a Photochemical Reaction Within Graphitic Carbon Nitride	University of Bath
B4	Melanie Colet-Lagrille	Ultra-Thin Alumina Overlayer as a Protective Coating on CuWO ₄ Photoanodes	Universidad de Chile
B5	Tingran Liu	Redox Neutral Electrosynthesis without Added Electrolyte at Interdigitated Electrodes	University of Bath
B6	Daniel H. Broadhurst	High Yield and Selective Electrocatalytic Reduction of Nitroarenes via Polyoxometalate Redox-Mediated Chronoamperometry	University of Glasgow
B7	Nada Alhathloul	Room Temperature Electro-Carboxylation of Styrene and Stilbene Derivatives: A Comparative Study	University of Glasgow, Jouf University
B8	Anthony Choi	3D-Printing for Electrochemical Reactors and a Tool Kit for the Expansion of the ElectraSyn	University of Bristol
B9	Fiona Todman	Decoupled Biomass Oxidation and Hydrogen Production Mediated by Phosphomolybdic Acid	University of Glasgow
B10	Chhavi Sharma	Polyaniline/Polypyrrole Composites Electrodeposited from Ionic Liquids for Hydrogen Evolution Reaction	University of Bath, IIT Roorkee
B11	Santiago Rodríguez-Jiménez	Valorisation of CO ₂ and Other Abundant Waste Streams	University of Cambridge
B12	Halilu Sale	Optimising the Electrochemical Reduction of CO ₂ to Oxalic Acid in Propylene Carbonate	University of Glasgow, Energy Commission of Nigeria
B13	Lukman Yusuf	Optimising Ultrasound Parameters for Efficient Sonoelectrochemical CO ₂ Reduction at Copper Electrodes	University of Glasgow

B14	Mayra S. Tovar-Oliva	Optimised Electrodeposition Technique for In-Situ Fabrication of Cu-Based Catalysts on Gas Diffusion Layers for Electrochemical CO ₂ Reduction	University of Edinburgh
B15	Zhixu Zhu	Carbon Nanotube Production from CO ₂ Via High Temperature Electrolysis	Imperial College London
B16	Hannah L. A. Dickinson	NiCuAg: An Electrochemically Synthesised Trimetallic Stack for CO ₂ Reduction	University of Glasgow
B17	Preetam K. Sharma	Earth Abundant CuSn Electrocatalysts for Selective Conversion of CO ₂ to CO	Loughborough University
B18	Luis G. Navarro-Tovar	Electrodeposition of Cu-Based Bimetallic Catalyst Over Gas Diffusion Layer (GDL) for the Electrochemical Conversion of CO ₂	University of Edinburgh
B19	Adriano Randi	Atmospheric-Pressure Plasma Device for CO ₂ Conversion and Utilisation	Loughborough University
B20	Egle Latvyte	A Low-Temperature Ammonia Electrolyser for Wastewater Treatment and Hydrogen Production	Coventry University

Symposium C – Electrochemical Sensors and Electroactive Porous Materials

#	Presenting Author	Title	Affiliation
C1	Alvaro Colina	On the Capabilities of Electrochemical Surface Oxidation Enhanced Raman Scattering for Analysis	Universidad de Burgos
C2	Frankie Rawson	Quantum Electrochemical Sensors and Actuators: Pioneering a Novel Frontier in Cancer Therapy	University of Nottingham
C3	Ehren Dixon	Electrochemical Processing of Nanoporous Copper as a High Surface Area Enhanced Catalyst for Sensing Applications	Tyndall National Institute, University College Cork
C4	Augusto Etchegaray	A Biosensor for Methotrexate can be Designed Using Dihydrofolate Immobilized Onto Iron Magnetic Nanoparticles	Pontifical Catholic University of Campinas
C5	Ricoveer Singh Shergill	Pre-Printing Saponification of Carbon Thermoplastic Filaments Provide Ready-to-Use Electrochemical Sensors	University of Brighton
C6	Chi-Hsien Liu	Electrochemical Aptasensor for SARS-CoV-2 Detection Based on Magnetic MOF and Screen-Printed Electrode	Chang Gung University, Chang Gung Memorial Hospital
C7	Graham Smith	Error, Reproducibility and Uncertainty in Electrochemical Measurements	National Physical Laboratory
C8	Joshua Lehr	Selective Detection of Protein Biomarkers via Multifunctional Molecular Layers from Electrografting Methods	University of Salford
C9	Adaris M. López-Marzo	Toward Completely Label-Free Point-of-Care Devices Using Bioreceptor Immobilisation by Hydrogen Bonding and Differential Pulse Voltammetry as Measurement Tool	Institute of Materials Science of Barcelona
C10	Shulin Zhang	Biosensor for Rapid Measurement of Lactate in Exhaled Breath Condensate	Imperial College London
C11	Tarun Narayan	Real-Time Electrochemical Sensor for the Detection of Endocrine Disruptors in Water Samples	Tyndall National Institute
C12	Chao-Nan Yang	Observing Confined Local Oxygen-Induced Reversible Thiol/Disulfide Cycle with a Protein Nanopore	Nanjing University

C13	Shane O'Sullivan	3D-Printed Microfluidics System Coupled with Electrochemical pH Control for Enhanced Chlorine Detection	Tyndall National Institute
C14	Fernando Perez	Development of an Electrochemical Biosensing Array for Simultaneous Detection of Urinary Metabolites for Disease Profiling	University of Brighton, Centre for Stress and Age-Related Disease
C15	Chloe Miller	Evaluating the Impact of Different Electrode Surface Patterns of 3D Printed Carbon Thermoplastic Electrochemical Sensors	University of Brighton, Centre for Stress and Age-Related Diseases
C16	Frank Marken	Triphasic Electrochemical Processes Enhanced by Polymers of Intrinsic Microporosity	University of Bath
C17	Charl F. J. Faul	Porous Organic Materials for Metal-Free CO ₂ Capture and Electrocatalytic Conversion	University of Bristol
C18	Kieran DeMonte	Porphyrin-Like Designer Catalysts for Electrocatalytic H ₂ Evolution and Selective CO ₂ Reduction	University of Otago, MacDiarmid Institute for Advanced Materials and Nanotechnology
C19	Loredana Vacareanu	Electrogenerated Microporous Conjugated Polymers Based on Starshaped Oligomer Derived from Triphenylamine: Exploring Structure-Properties Relationships	'Petru Poni' Institute of Macromolecular Chemistry
C20	Dominik Duleba	Proton Enrichment and Surface Charge Dynamics in Nanopores	University College Dublin

Symposium D – In-Situ Spectroelectrochemistry and Interfacial Electrochemistry

#	Presenting Author	Title	Affiliation
D1	Veronica Celorrio	Relationship Between Mn Oxidation State Changes and Oxygen Reduction Activity in (La,Ca)MnO ₃ Probed by In-Situ XAS and XES	Diamond Light Source
D2	Thomas McIntyre	Probing the Structure of the Electrochemical Interface Using In-Situ Surface X-Ray Diffraction Techniques	University of Liverpool
D3	Santosh Kumar	Development of Spectro-Electrochemical Cell for Operando NAP-XPS/NEXAFS Investigations	Diamond Light Source
D4	Joshua J. Tully	EPR Spectro-Electrochemistry as a Tool for Studying Radical Generation on Boron Doped Diamond Electrodes	University of Warwick
D5	Simon Redor	Using Operando Reflection Optical Microscopy to Explore the Electrochemical and Electrochromic Properties of Li ₂ Ni ₂ W ₂ O ₉	Collège de France, Sorbonne Université
D6	Lennart Wichmann	Correlation of Excess Lithium, ‘Dead Lithium’ and Functional Layers in ‘Anode-Free’ Lithium Metal Batteries	Helmholtz-Institute Münster
D7	Sarah L. Horswell	Why Do Similar Molecules Respond Differently to Electric Fields? Hydrogen Bonding Effects in Biomimetic Membranes	University of Birmingham
D8	Francesco Carlà	In-situ and Operando Characterization of Electrochemical Interfaces by Surface X-ray Diffraction and Scattering	Diamond Light Source
D9	Andrew J. Wain	New Cell Designs and Sample Configurations for Operando Raman Spectroscopy of Battery Electrodes	National Physical Laboratory
D10	Irina M. Terrero Rodríguez	The Importance of sp ² Bonded Carbon in Electrochemical Ozone Production Using Freestanding Boron-Doped Diamond Anodes	University of Warwick
D11	Alexander W. Black	Exploring Boron Doped Diamond as an Electrocatalyst Support for Alkaline Water Electrolysis	University of Bristol
D12	Hussain A. Al Nasser	Electrochemical Assessment of a Tripodal Thiourea-Based Anion Receptor at the Liquid Liquid Interface	University of Manchester
D13	Juliana V. Díaz-Reyes	Theoretic Approach to the Capacitance of Aqueous a,a,a-Trifluorotoluene Interfaces	University of Limerick

D14	Jack W. Jordan	Voltammetric Evidence of Proton Transport Through the Sidewalls of Single-Walled Carbon Nanotubes	University of Nottingham, The Faraday Institution
D15	Si-Min Lu	Confinement-Controlled Nanoelectrochemistry: Study One Entity at a Time	Nanjing University
D16	Zhongkai Li	Driving Electrochemical Membrane Processes with Coupled Ionic Diode	University of Bath
D17	Katherine J. Levey	The Importance of Considering Electrostatics When Numerically Modelling the Cyclic Voltammetric Response of an Outer-Sphere Redox Couple	University of Warwick
D18	Henry Lloyd-Laney	Recovering Biological Electron-Transfer Parameters: The Perspective of Multiple Techniques	University of York, University of Oxford
D19	Ivan Scivetti	Stoichiometric Resolution in the Electrochemistry of Oxide Materials: Driving Computational Research with Electrochemical Quartz Crystal Microbalance	The Science and Technology Facilities Council
D20	Molly E. Keal	Electrochemical Recycling of Ruthenium Via Nano-Impacts	University of Birmingham

Symposium E – Corrosion Science and Technology

#	Presenting Author	Title	Affiliation
E1	David Kumar	On the High Temperature Water Oxidation and Stress Corrosion Cracking of Reduced Activation Ferritic Martensitic Eurofer-97 Steel	National Nuclear Laboratory
E2	Vincenzo Bongiorno	Automating Corrosion Testing for Organic Coatings: A Machine Learning Based Approach	University of Manchester
E3	Yanwen Liu	Degradation of Marine Coatings During Hygrothermal Cyclic Corrosion Tests	University of Manchester
E4	Lawrence Coghlan	The Degradation Mechanism of Polyester Powder Coatings Exposed to Cyclic Corrosion Testing (CCT)	University of Manchester
E5	Ryan Abou-Shakra	Surfactant Corrosion Inhibitor Adsorption and Desorption Kinetics in Aqueous CO ₂ -Containing Environments	University of Leeds
E6	Hannah Hilton-Tapp	Production of Copper Nanocomposite Coatings Using Pulse Reverse Plating and Anionic Surfactant	University of Leicester
E7	Tamsin H. E. Dobson	Effect of Biofouling on the Corrosion of Nickel Aluminium Bronze Immersed in Natural Sea Water	University of Bristol
E8	Maciej Makuch	Phase Field Model of Accelerated Corrosion Tests and Single Crystal Polarisation Anisotropy	Imperial College London
E9	Joseph Thevakumar	Casing Corrosion of Steels in Geothermal Environments Containing Sulphuric Acid	University of Leeds
E10	Peter Thomas	Microstructural Evolution Due to CO ₂ Oxidation and Carburisation in 9Cr-1Mo Steel	University of Bristol
E11	Cemal Ozturk	Atmospheric Corrosion of 316L Stainless Steel: The Effect of Stress and Strain	University of Bristol
E12	Amber Sykes	The Effect of CO ₂ Partial Pressure on the Formation and Protective Characteristics of Iron Carbonate Corrosion Products	University of Leeds
E13	Alexander Hanson	Understanding the Effect of Strain on Corrosion of Advanced Gas-Cooled Reactor Fuel Cladding	University of Manchester

E14	Xiaoqi Wen	Study of Carbon Steel Corrosion in Live Anaerobic Digestion Reactors	University of Southampton
E15	Juhi Srivastava	The Influence of Grain Structure on Hydrogen-Environmentally Induced Cracking (H-EIC) Behaviour of AA7085 Alloy in Humid Air	University of Manchester, Indian Institute of Technology
E16	Christopher E. Elgar	Using Ultrasound to Increase Metal Anodic Dissolution and Prevent Passivation Using Concentrated Ionic Fluids	University of Leicester
E17	Alyshia Keogh	Effect of Microstructure on Localised Corrosion and Atmospheric Stress Corrosion Cracking of 15-5 PH Stainless Steels	University of Manchester
E18	James Rafferty	Environmental Effects of a Simulated AGR Coolant on Oxidation and Carburization Behaviour of Type 316H Stainless Steel	University of Manchester
E19	Woraphan Intaphan	Elucidation of Charge-Transfer Mechanisms Under Paint Films by Conventional and Localised Electrochemical Impedance Spectroscopy	University of Manchester
E20	Clayton Bevas	The Influence of Radiation on the Corrosion of Carbon Steel for Nuclear Waste Geological Disposal	Jacobs

A1: Energy-Efficient Oxygen and Fuel Production in (Photo-)Electrochemical Devices in Microgravity Environment

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Water electrolysis is not only a highly relevant process for the production of green hydrogen on Earth: it is also key for producing oxygen and hydrogen in the Environmental Control and Life Support System (ECLSS) onboard the International Space Station (ISS). One of the major challenges associated with water electrolysis in reduced gravitational environments is however the near-absence of buoyancy forces in orbit. Consequently, phase separation - such as the detachment of gas bubble from an electrode surface - is severely hindered. This causes increased reaction overpotentials, leading to a high energy inefficiency of the Oxygen Generator Assembly (OGA) on the ISS: forced water recirculation loops are perquisite to detach and collect gas bubbles. At present, the OGA requires therefore about 1.5 kW - a third of the energy consumed by the entire ECLSS [1]. This high energy demand as well as the high total mass makes the OGA unfeasible for application in future space architectures.

Here, a two-folded approach is presented for producing hydrogen and oxygen at lower energy input in space environments: firstly, the technological feasibility to utilise photoelectrochemical devices in lunar and Martian habitats is assessed in numerical simulations [2]. These devices integrate the processes of light absorption, charge separation and catalysis and present therefore weight and volume advantages in comparison to the traditionally used photovoltaic-driven electrolyser in the OGA [3,4]. Secondly, alternative phase separation methods are presented utilising magnetically-induced buoyancy and custom-tailored electrocatalyst nanostructures [5,6]. Both concepts have been tested in microgravity environment generated for 9.2 s at the Bremen Drop Tower, where (photo-) current-voltage (J-V) profiles and gas bubble trajectory analysis confirm efficient gas bubble detachment and movement in the near-absence of buoyancy as well as the production of oxygen and hydrogen close to terrestrial efficiencies.

References

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- [2] B. Ross, S. Haussener, K. Brinkert, Nat. Commun., 2023, **14** (3141).
- [3] W. H. Cheng, M. H. Richter, M. M. May, J. Ohlmann, D. Lackner, F. Dimroth, T. Hannappel, H. A. Atwater, H. J. Lewerenz, ACS Energy Lett., 2018, **3** (8) 1795-1800.
- [4] A. M. K. Fehr et al., Nat. Commun., 2023, **14** (3797).
- [5] K. Brinkert, M. H. Richter, Ö. Akay, J. Liedtke, M. Gierisig, K. T. Fountaine, Lewerenz H. J., Nat. Commun., 2018, **9** (2527).
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A2: Enhanced Proton Exchange Membrane Fuel Cell Performance via Graduated Catalyst Layer Ionomer Content

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Proton exchange membrane fuel cells (PEMFCs) could play a vital role in the future of sustainable energy, but their widespread commercialization is hindered by the high cost of cathode catalyst layers (CLs), which containing expensive Pt catalysts to help overcome the sluggish oxygen reduction reaction (ORR). To overcome this challenge and achieve high-performance, cost-effective PEMFCs, it is crucial to optimize the electrode structure to improve catalyst utilization. Recently, the idea of employing graded catalyst layers with varying Pt and/or ionomer compositions has been suggested to address the operational non-uniform current density along the CLs [1]. Typically, binary or ternary layers with differing Pt and/or ionomer compositions are combined through a spray deposition process, resulting in improved PEMFC performances over the uniformly prepared ones [2]. However, this method can lead to sharp interfaces between the layers, which may accelerate degradation due to significant fluctuations in current density. Moreover, the preparation of multiple inks with varying compositions and their individual application is not a practical and cost-effective approach, especially when considering the need for large-scale production in commercial applications.

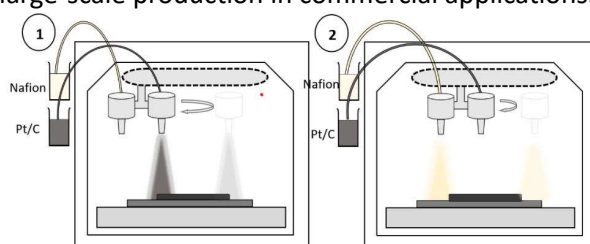


Figure 1: Graduated Catalyst Layer Preparation Schematic

In this context, we present a novel and scalable approach for designing cathode CLs with gradual ionomer content. We utilize an automated spraying system equipped with two separate nozzles, where one nozzle is used to spray the Pt catalyst dissolved in a water/isopropanol mixture, and the other nozzle is used to spray the diluted ionomer (Figure 1). The ionomer gradient along the CLs were controlled by adjusting the order and the number of layers sprayed by each nozzle until the desired catalyst loading achieved. Using this method, we fabricated CLs with increasing and decreasing ionomer content from the membrane to the gas diffusion layer (GDL), respectively, as well as one with a homogeneous ionomer content. Importantly, while preparing each electrode, it was maintained an equal total number of layers sprayed from each nozzle in order to ensure that the final ionomer and Pt content remained consistent in all samples. Those three electrodes were subjected to comprehensive electrochemical characterization in a 25 cm² single PEMFC. The results revealed 16% improvement (in H₂/Air, 60°C, 100% RH) in the peak power density of the gradual CLs where the ionomer composition progressively increases towards the membrane as compared to the ones prepared with uniform ionomer content. This improved performance is attributed to the enhanced ionic and O₂ transport in those gradual CLs. Overall, the CL manufacturing approach presented here can be extended to produce optimized CLs with gradients in the ionomer and/or Pt contents, which can counter the detrimental intrinsic operational inhomogeneity thus enhance the PEMFC performance and stability.

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A3: The Preparation and Characterisation of Inkjet Printed Low Iridium Loaded Anodes for PEM Water Electrolysis

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Hydrogen is seen as one of the potential solutions for a successful transition to a sustainable energy future. Proton exchange membrane (PEM) water electrolysis is seen as key technology for supporting a hydrogen economy but costs need to be reduced for it to be competitive with hydrogen production from fossil fuels ^{1,2}. Decreasing the amount of iridium oxide for the oxygen evolution reaction (OER) remains an important challenge that needs to be addressed ³. Hence, reducing catalyst loading at the anode is the objective of this research. Inkjet printing is a rapidly growing technology for the deposition of functional materials on various substrates. It offers cost-effective mass production of catalyst components for PEM water electrolyzers with minimal waste. This coating method has a high precision control and moreover, complex electrode patterns can be produced without the use of physical masks ⁴.

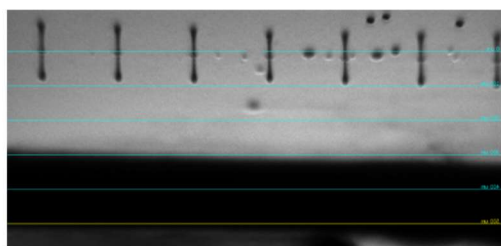


Figure 1. Captured image of ink droplets dispensed from the cartridge.

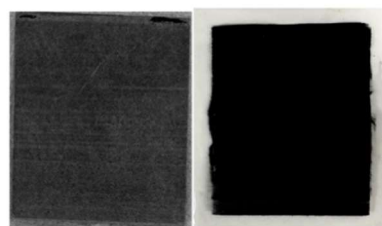


Figure 2. Inkjet printed CCS and CCM.

An iridium oxide (IrO_2) catalyst ink was formulated to create a printable ink with the desired properties. Nafion ionomer binder was added to maintain the homogeneity of the ink and minimize aggregation. A Dimatix materials printer was used to apply the ink and prepare fully covered and patterned catalyst-coated substrates (CCS) and membranes (CCM). The printer's parameters such as piezo voltage, waveform, and drop spacing were controlled to achieve short-tailed spherical droplets with similar speeds (Figure 1). By optimising the printing parameters, it was possible to produce low loadings of IrO_2 catalyst on CCS and CCMs. Dynamic light scattering measurements and shelf-life tests confirmed the stability of catalyst ink with a shelf life of one week. Examples of inkjet-printed CCS and CCM are shown in Figure 2. This work has demonstrated that it is possible to prepare low IrO_2 -loaded anodes using optimised inkjet printing parameters. The performance of 3 different loadings of CCS and CCM will be discussed and compared to a state-of-the-art PEM cell with a catalyst loading of 1.5–2 mg/cm^2 .

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A4: In-situ reference electrodes for characterization of alkaline water electrolyzers

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Water electrolysis under alkaline condition offers low-cost and scalable hydrogen production due to the use of cheaper materials as electrodes and components of electrolysis cells and stacks. However, their efficiencies are limited by the low activity of the catalysts used. There has been a tremendous amount of research devoted to developing efficient and stable electrocatalysts for the hydrogen and oxygen evolution half-reactions. However, very few of them have progressed from the lab to deployment. This is, in part, due to a lack of robust testing protocols to provide information on real-world behaviour. Currently, almost all performance and stability measurements are carried out either in a three-electrode or a two-electrode cell. The former doesn't accurately represent the actual conditions present in commercial alkaline electrolyzers, while the latter, although tested under actual conditions, makes it impossible to assign performance and processes to specific electrodes [1]. In this study, we designed a cell with an active area of 1 cm^2 , where reference electrodes are placed close to the anode and cathode using Luggin capillaries. This design allows us to separate the anode and cathode responses (see Figure 1). The cell can be used for rapid screening of anode and cathode electrocatalysts under relevant conditions. The characterization of various catalysts using the developed setup will be discussed.

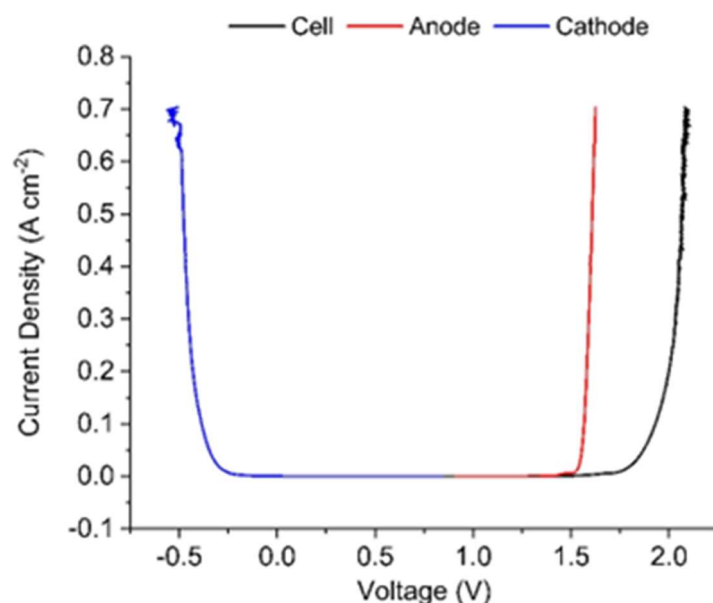


Figure 1. Representative linear sweep voltammogram of the cell with commercial Ni alloy electrodes in 1 M KOH at a flow rate of 80 ml/min. The cell voltage is corrected for 85 % of resistance obtained from impedance spectroscopy measurements.

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A5: Advanced electrocatalysis from High entropy metal sulphides

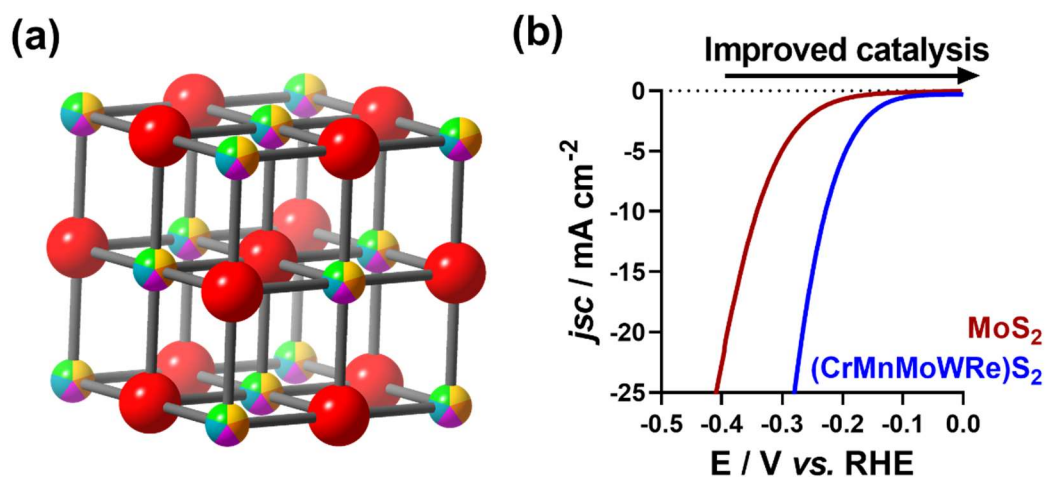
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High entropy (HE) metal sulphides are an emerging sub-class of HE materials that have shown great promise in thermoelectrics, energy storage, and electrocatalysis. HE materials are classed as such when five or more elements are present in a 5 mol% abundance or higher within a sub-lattice of a multi-lattice system (for example the metal position in a metal sulphide). The presence of multiple elements within the lattice leads to a large configurational entropy arising from the random arrangement of elements (Fig. 1(a)). [1] In order to achieve the highest entropy in these materials, disorder needs to be achieved at the atomic level. Traditional methods such as high temperature and long-time elemental annealing struggle to achieve atomic level disorder of these materials. [2]

Here we use a single source precursor approach as an atom-up synthetic strategy for HE metal sulphides. This technique has been used to synthesise a range of metal sulphides (MnCoCuZnAgGaInS), [3] and metal disulphides $(\text{CrMnMoWRe})\text{S}_2$. [4] A range of characterisation techniques have been used to assess these materials including pXRD, Raman spectroscopy, SEM and STEM combined with EDX and XPS. Both these materials were investigated for their HER catalytic ability. The $(\text{CrMnMoWRe})\text{S}_2$ is of particular interest as a HE analogue of the heavily investigated MoS_2 . We found the HER catalytic performance was significantly enhanced through LSV (Fig. 1(b)) and stable over a 20 h period using chronoamperometry. [4] Computational analysis of metal substituted MoS_2 found that the hydrogen absorption energy was significantly reduced with the substitution of Cr and Mn for Mo, indicating that a combined computational, experimental approach can be used in the future to drive the development of these emergent materials.



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A6: Transition metal dichalcogenide heterostructures as electrocatalysts for the hydrogen evolution reaction

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Transition metal dichalcogenides (TMDs) have been studied as hydrogen evolution reaction (HER) catalysts. In this study the heterostructures of different TMDs (MoS_2 , MoSe_2 and WS_2) are investigated for their HER catalytic activity. Creation of the heterostructures results in increased active sites for hydrogen adsorption as well as improving charge transportation thus improving overall catalytic activity of the material.^{1,2} Two methods of forming the heterolayers were used: heterolayer one consisting of a dropcast nanoparticle layer with an electrodeposited layer of a different TMD on top ('NP/L'), and the second was obtained by sequential electrodeposition of layers of the two different TMDs ('L/L'). Heterolayers with a film of MoS_2 displayed an improved HER ability when compared to the starting TMD materials. An earlier onset potential for HER was also observed for them. The resulting reaction kinetics due to the heterolayers was investigated and these included Tafel analysis and electrochemical rate constant calculation. WS_2/MoS_2 and $\text{MoSe}_2/\text{MoS}_2$ heterolayers registered rate constants of $(3.20 \pm 0.10) \times 10^{-4} \text{ cm s}^{-1}$ and $(1.73 \pm 0.03) \times 10^{-4} \text{ cm s}^{-1}$ respectively, which was an improvement compared to the reported rate constant of MoS_2 .³ This further showed the improved HER catalytic activity of the heterolayers and how there is still room for improvement when it comes to TMDs.

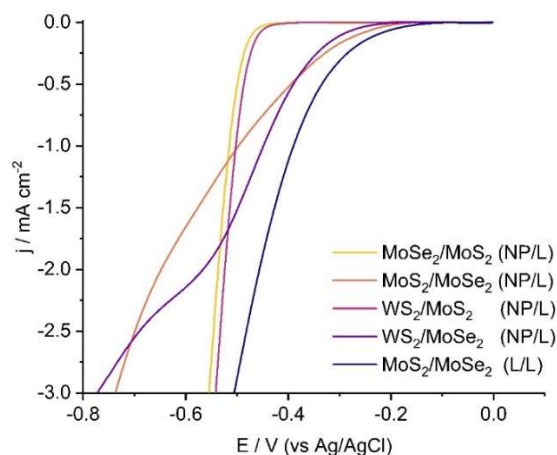


Figure 1. Overlay of the different heterolayers and how they compare to each other. All conditions were kept the same and the voltammetry was carried out in a 10 mM H_2SO_4 and 0.1 M K_2SO_4 solution.

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A7: Are 2D Chalcogenides Suitable for PEM Water Electrolysis: The Case Study of the Application of MoTe₂ in a Single Stack Electrolyser

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Hydrogen production is a crucial process for various applications, including clean energy generation and fuel cell technologies [1]. Water electrolysis, which involves splitting water molecules into hydrogen and oxygen using electricity, is a viable method for hydrogen production [1,2]. However, to enhance the efficiency of water electrolysis, an electrocatalyst is necessary. While noble metals have traditionally been used as catalysts in commercial electrolyzers, alternative materials are being explored to make the process more sustainable and cost-effective. Among these, 2D chalcogenides are promising targets, as they can be deposited as atomically thin and continuous films. The continuity allows for the maximisation of the area of the catalyst while the atomic thickness minimises the material cost. Films of 2D materials on suitable supports (such as carbon-cloth, FTO-substrate and mesh) has been shown before [2,3] however, they have never been tested in a proton exchange membrane (PEM) electrolyser to produce hydrogen at scale.

In this work, we have chosen the metallic 1T'-MoTe₂ as a model 2D material due to its previously reported ability to catalyse the hydrogen evolution reaction from water [3,4]. We achieved the film growth on a high surface area carbon cloth substrate in a custom-built CVD reactor using the route developed in our group that preferentially produces metallic 1T'-MoTe₂ films over semiconducting polymorph on Si/SiO₂ [5]. To optimize the film growth process, the parameters such as precursor choice, deposition temperature, and carrier-gas-flow rates were varied. The optimisation of the process by varying precursor, deposition temperature and carrier-gas-flow rates led to the targeted 1T'-MoTe₂ phase confirmed by XRD and Raman spectroscopy. The formation of homogenous surface coverage was also validated by SEM. Routine electrochemical testing of films allowed for the evaluation of catalytic performance for the hydrogen evolution reaction in 1M H₂SO₄. Finally, we discuss preliminary research data of testing at scale in a single-cell electrolyser that could lead to a more sustainable and cost-effective way of producing hydrogen through water electrolysis.

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A8: Catalyst-Support Design for Proton Exchange Membrane Electrolysers

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Proton exchange membrane electrolysers (PEM-ELs) require catalysts to facilitate the anodic oxygen evolution (OER) and the cathodic hydrogen evolution reactions (HER). The OER specifically requires high mass loadings of iridium ($> 2 \text{ mg/cm}^2$) to be stable and active within the PEM-EL. However, the use of Ir at such high loadings as a catalyst in PEM-ELs has been the topic of discussion for many years due to its scarcity and rising cost.

Many researchers have focused on different pathways such as electrocatalyst morphologies¹ to reduce the mass loading of iridium whilst still achieving high stability and activity. Another promising pathway towards designing improved and economic electrocatalysts is the use of catalyst-supports. Studies have shown that supports can positively affect the stability and activity of a catalyst.² However, the support must have high conductivity, high surface area, low cost and the interaction between catalyst and support needs to be beneficial to the OER half-reaction. If achieved, these factors can promote the intrinsic activity of the catalyst and reduce the mass loading of the catalyst whilst maintaining sufficient activity and stability.

We focused on synthesising transition metal oxide (Sn and Ti) based supports and used various Ir deposition techniques to achieve low iridium loadings ($< 50 \text{ wt\%}$). The catalyst-supports were evaluated for their durability and conductivity. Specifically, TiO_2 supports contained additives of Au/Pd (1 and 5 wt% Au) and SnO_2 supports contained additives (Sb, Ta, Nb and Mo) of 4 – 13 wt%. We investigated the influence of the additives on electrochemical performance. When comparing the highest performing TiO_2 and SnO_2 supported catalysts with commercial IrO_2 , the supported catalysts exhibited a 3 and 6-fold mass activity increase (respectively) in a rotating disk electrode (RDE) configuration. The implementation of the TiO_2 supported catalyst into a proton exchange membrane electrolyser, led to the same mass activity trend as RDE with the supported catalyst overperforming commercial IrO_2 . The stabilities of the supported catalysts in MEA and RDE were shown to be dependent on the composition of the support.

Our investigations indicate that factors such as Ir deposition technique and support composition must be considered when designing supported catalysts, as the composition, structure and morphology influences electrochemical performance of the electrocatalyst.

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A9: Investigating the Electrocatalytic Water Splitting Efficacy During the Dimensional Transition from Single-Atom to Nanoparticles with Porous Hard-Carbon as Supports

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Electrocatalytic water splitting has shown immense potential to deliver green hydrogen to meet the requirements of clean energy and thereby enable the transition to a hydrogen-driven economy.¹ Although, Pt-group based metals/metal oxides exhibit low adsorption enthalpies² and form the natural choice for such electrocatalysis, their low abundance and high cost propels the search for other earth-abundant, low-cost substitutes. In this direction, we describe a rational approach to fabricate a systematic dimensional series of nickel-based catalysts supported on unique porous hard-carbons as supports. The nanostructured carbon florets (NCFs) acting as supports are fabricated through a template-based chemical vapor deposition strategy and deliver high specific surface area (~893 cm²) and graded porosity (5-15 nm) for facilitating the diffusional access of reactants and products.^{3,4} Such unique floral-like morphology serves as ideal support for anchoring monodisperse nickel oxide systems, to realize NiO-NCF electrocatalysts. Importantly, the strength of this approach lies in precise dimensional control over the NiO catalysts fabricated. The entire range of dimensions starting from single-atom (SA) to nanoparticles (NP, mean diameter ~ 5 nm) are accessed through atomic layer deposition technique. An interesting non-linear dependence of the catalyst size and its efficacy (in terms of overpotential and Tafel slope) is unravelled through towards OER studies. Accordingly, while SA like NiO-NCF exhibits high overpotential owing to large charge-transfer resistance, the NP NiO-NCF system exhibits inferior kinetics due to low density of catalytically active sites. This enables on identifying a 'sweet-spot' wherein the catalysts density and size effects become prominent to drive favourable electrocatalytic kinetics at low overpotentials. A summary of these results will be discussed, along with potential directions for imbuing the magnetic properties of such catalysts towards sustainable magneto-electrocatalytic pathways.

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A10: Alternative architectures for structural batteries

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Structural batteries are energy storage materials that are additionally capable of carrying mechanical loads, with this bifunctionality allowing for mass savings on a systems level when they are used as structural components in electrified transport applications. The 3D architecture for structural batteries, which consists of a carbon fibre anode coated in a polymer separator embedded in a cathode-doped matrix [1,2], has been relatively unexplored but may have the potential to outperform current structural batteries in terms of electrochemical and mechanical performance. In this work, the individual components of the 3D architecture are characterised. Introducing 10% cathode particle content to the matrix material decreased the storage modulus from 333 MPa to 231 MPa, and free-standing films could not be formed when cathode particle content was greater than 30%. Carbon fibre anodes were found to reversibly expand during cycling by up to 3.17% and 3.55% in the radial and axial directions, respectively, which could potentially cause issues with crack formation in the polymer separator coating. This work provides useful data as inputs for modelling of the 3D architecture and highlights areas for improvement when considering producing full cells.

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A11: Interpreting Single Particle Voltammetry of Battery Materials

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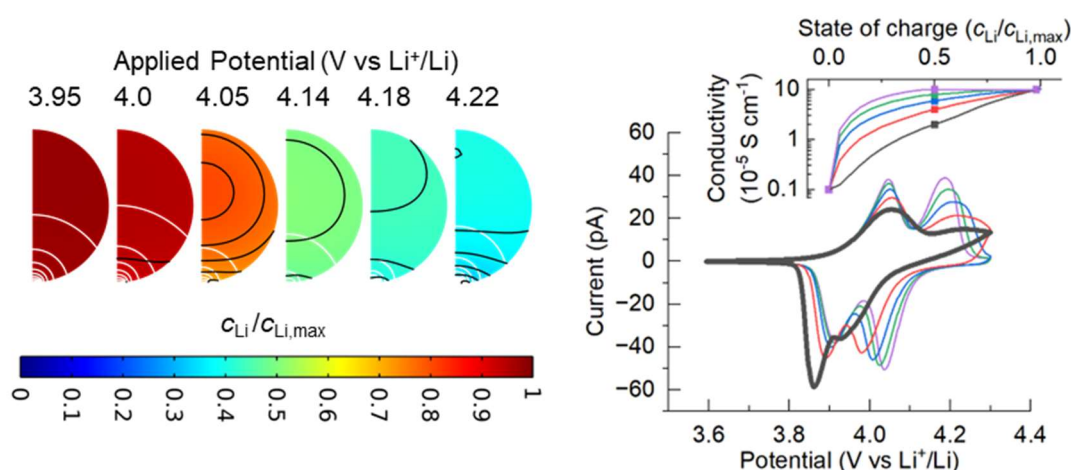
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Voltammetry is an appealing characterisation method for electrode materials as it provides a rapid overview of the redox processes occurring. However, it has long been recognised that voltammetry of composite electrodes is liable to interference from matrix effects, limiting its applicability. Recently, single particle analysis has become possible, eliminating these effects and allowing fast scan rates that extend the kinetic window accessible in these experiments. Furthermore, with the advent of scanning electrochemical cell microscopy (SECCM), particle-by-particle measurement of large arrays of particles can be automated, providing large datasets of individual particle responses. Previously it was noticed that such measurements generally reveal significant differences in voltammetry between seemingly similar particles, posing a range of questions: Does this reflect an intrinsic difference between particles, or something about their environment, or is it a measurement phenomenon? Here we compare SECCM voltammetry, recorded under a range of particle wetting and agglomeration conditions, to finite element method simulations, to investigate the origin of these inter-particle differences. The results reveal that a range of properties are probed by the SECCM experiment and can be deconvoluted with the help of simulation. This understanding opens up many avenues for future, targeted studies of battery material properties at the single particle level.



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A12: Calendar Aging of Commercial Cylindrical Li-ion Batteries – Mechanisms and Mitigation Strategies

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A solid understanding of the degradation mechanisms of Lithium-ion batteries is crucial in enabling electric vehicles (EVs) and consumer devices with long lifetime, as well as reducing material waste and energy usage. These mechanisms are highly dependent on chosen battery chemistry, and recently developed high-performance electrode materials such as high-nickel cathodes and silicon anodes undergo particularly pronounced capacity loss.^{1,2} This capacity loss is brought about during both active usage of the cell (cycling-related losses) and simple degradation over time (calendar aging).³ Cycling-related losses are widely assessed through repeated charging and discharging of the cell in quick succession, however calendar aging is far less widely studied.⁴ This is despite the fact that the battery system of an EV spends 96 % of its life at rest,⁵ and thus the degradation mechanisms related to calendar aging are crucial.

Here we report on the findings of a Faraday Institute funded project involving an industry-academic consortium in which commercial cylindrical cells (LG INR21700 M50 18.20Wh) were calendar-aged in controlled environments, during which cell capacity was monitored. Cells were stored over a range of state-of-charges (SOCs) and temperatures, providing valuable information on their influence on calendar aging. The degradation mechanisms were assessed via differential voltage analysis, as well as through cell disassembly and analysis of the individual electrodes using electrochemical and material characterisation methods.

Presented results will include: (a) influence of cell storage SOC and temperature on extent of calendar ageing, (b) XCT of cylindrical cells to examine electrode deformation, (c) neutron diffraction study tracking cathode lattice evolution (d) visual inspection of disassembled cell electrodes/separator and reconstruction of disassembled electrodes into 3-electrode cell enabling identification of limiting electrode, and (e) X-ray fluorescence of separator examining material dissolution. The presentation will conclude with an assessment of dominant degradation mechanisms, and insights on the potential mitigation strategies, encompassing material structure, cell design and usage conditions.

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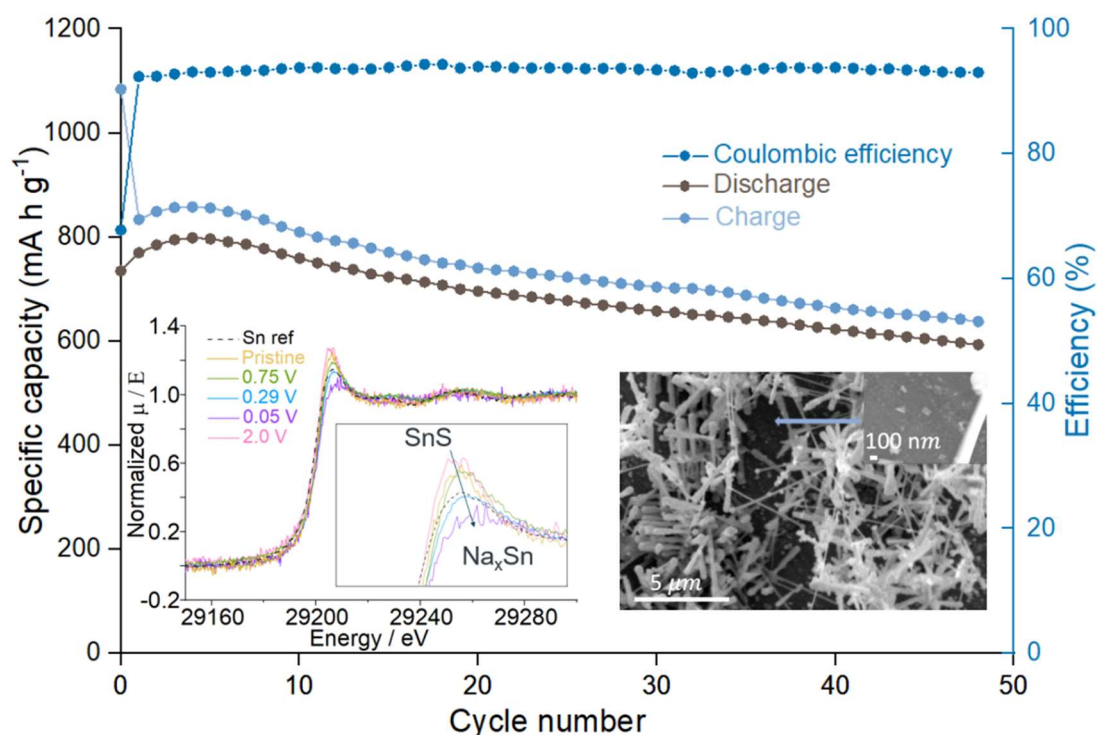
A13: High sodium-ion battery capacity in sulfur-deficient tin(II) sulfide thin films with a microrod morphology

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Sulfur-deficient SnS thin films for sodium-ion battery anode application were prepared using aerosol assisted chemical vapour deposition. Growth directly onto the metal foil current collector formed sulfur-deficient SnS rod structures via a vapour-liquid-solid growth mechanism, with 92 nm average SnS crystallite size and an 800 nm film thickness. The sulfur deficiency was demonstrated with energy dispersive X-ray analysis, powder X-ray diffraction and X-ray absorption near-edge structure analyses. This sulfur-deficient SnS material demonstrated a very high capacity in sodium half cells. The first reduction scan at a specific current of 150 mA g⁻¹ showed a capacity of 1084 mA h g⁻¹. At the 50th cycle the specific capacity was 638 mA h g⁻¹ for reduction and 593 mA h g⁻¹ for oxidation. This capacity is demonstrated for tin sulfide itself without the need for a nanostructured carbon support, unlike previous high capacity SnS anodes in the literature. Both the capacity and ex situ characterisation experiments indicate a conversion reaction producing tin, followed by alloying with sodium during reduction, and that both of these processes are reversible during oxidation.



A14: Diketopyrrolopyrroles as performance enhancing additives for lithium-sulfur batteries

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Although the lithium-ion battery (LIB) has been instrumental in global electrification, more premium applications (such as electrification of aircraft) require capacities and performance beyond the capabilities of traditional LIB chemistries.¹ Lithium-sulfur (Li-S) batteries are a front runner among next generation battery technologies thanks to their very high theoretical capacities (1675 mAh g^{-1}) and impressive gravimetric energy densities ($2,700 \text{ Wh kg}^{-1}$) [2,3]. Despite their potential, there are numerous chemical challenges (polysulfide shuttle, dendrite formation etc.) that must be overcome before widespread adoption of the technology [4]. Electrolyte additives have been explored as a means to facilitate the electron transfer reactions that occur within the cell and improve cell capacity and cyclability [5].

Diketopyrrolopyrroles (DPPs) are a class of organic p-conjugated compounds that have garnered significant interest in a variety of electrical applications, including solar cells and sensors [6]. The high electrochemical tunability, made possible through the editable organic structure, makes them suitable candidates for redox active electrolyte additives. Here, we explore DPP derivatives as a novel class of electrolyte additive for improving the cell cycling performance of Li-S batteries. A variety of electrochemical and analytical techniques have been utilised to assess the suitability of DPPs as redox active additives, building an understanding of their interactions with active materials in a Li-S cell. Galvanostatic cycling allows us to connect these electrochemical findings to cell cycling performance, where we observe a large enhancement in output capacity. We also present an alternative statistical approach to cell data analysis, providing a more concrete method to assessing cycling enhancement than that shown throughout literature.

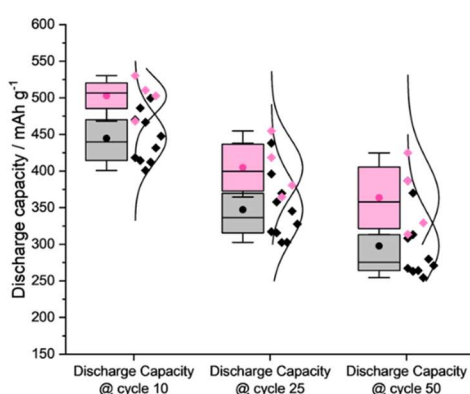


Figure 1. A blot plot displaying the discharge capacities at specific cycle numbers for standard (black) and DPP (pink) cells to provide a statistical comparison.

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A15: Exploring the role of redox-shuttle mediators in lithium-sulfur batteries

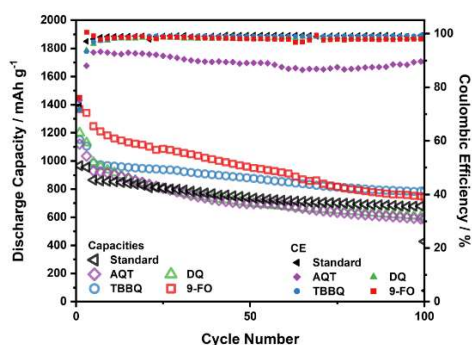
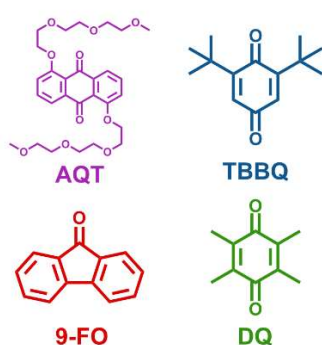
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The lithium-sulfur (Li-S) battery is one of the key contenders in replacing the lithium-ion battery. The combination of a theoretical high gravimetric energy density of $2567 \text{ W h kg}_{\text{cell}}^{-1}$, lower raw material costs and reduced environmental and sociopolitical impact make it an attractive battery technology. [1] Despite this promise, lithium-sulfur batteries still suffer from poor cycle life, rapid capacity fading and lower coulombic efficiencies largely due to the polysulfide shuttle effect. [2] Redox mediators have been proposed to mitigate these effects by delivering charge to both polysulfide intermediates in solution and insoluble sulfur/lithium sulfide during cell cycling, allowing for complete utilization of all sulfur species in the cell. [3] Currently there is a gap in the understanding of their property-performance relationship, how they affect polysulfide speciation and their compatibility with the metallic negative electrode within the cell.

Here we investigate a class of quinone-based compounds for use as molecular redox mediators in lithium sulfide cells, specifically 2,6-di-tert-butyl-1,4-benzoquinone (TBBQ), duroquinone (DQ), and 1,5-bis(2-(2-(2-methoxyethoxy) ethoxy) ethoxy) anthra-9,10-quinone (AQT) and 9-fluorenone (9-FO). [4] These were selected such that their redox potentials span the operating potential of the Li-S positive electrode ($1.8 \text{ V} - 2.6 \text{ V vs Li}^+|\text{Li}$). Interactions between the mediators and sulfur, lithium polysulfides, lithium sulfide and lithium metal were probed using chromatography, ultramicroelectrode voltammetry and cell cycling. Liquid chromatography-mass spectrometry confirmed that out of the chosen mediators, TBBQ and AQT can act effectively as both charge and discharge mediators. In real cells however, AQT showed poor coulombic efficiency as a result of shuttling, due to reaction with lithium and the high solubility of reduced AQT, as confirmed using ultra-



mediator redox chemistry, solubility, polysulfide conversion efficiency and compatibility with lithium metal when developing new mediators for Li-S batteries.

Figure 2. Structures of the redox mediators used in this study, along with cell performance, showing the maximum discharge capacity and coulombic efficiency of Li_2S coin cells with and without redox mediator, cycled at 0.1 C . Li_2S cells had a loading of 2.5 mg of Li_2S . The electrolyte comprised of 1.0 M LiTFSI , 0.5 M LiNO_3 in DOL:DME ($1:1 \text{ v/v}$) for the standard, with 50 mM of added redox mediator in mediated cells.

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A16: Investigating degradation of 1,3-dimethyl-2-imidazolidinone electrolyte in Li-S batteries

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Lithium sulfur (Li-S) batteries are promising next-generation energy storage devices due to their high theoretical energy density (2600 Wh kg^{-1}) and the natural abundance of sulfur.^[1] However, the commercial application of Li-S technology faces significant challenges. Electrolytes are integral battery components and play a significant role in determining battery performance. Recent studies have highlighted how the nature of the electrolyte can be tuned to maximize polysulfide solubility and improve sulfur utilization. Choi et al. recently proposed the high donor number solvent 1,3-dimethyl-2-imidazolidinone, (DMI), as an electrolyte that improves cell capacity by introducing a new polysulfide reaction pathway within the cell.^[2]

Here we present our ongoing study into electrolyte degradation pathways in Li-S battery systems. In particular we will report our recent studies into the stability of DMI in the cell. A series of galvanostatic cycling, electrochemical analyses and analytical chemistry techniques have been employed. ¹H nuclear magnetic resonance studies revealed changes to the structure of DMI in the presence of polysulfide. Galvanostatic cycling revealed a significant capacity fade from 500 mAh g^{-1} to $< 300 \text{ mAh g}^{-1}$ between 1.7 V and 2.7 V. The coulombic efficiency was also consistently above 100 %, also indicating possible side reactions in the cell.

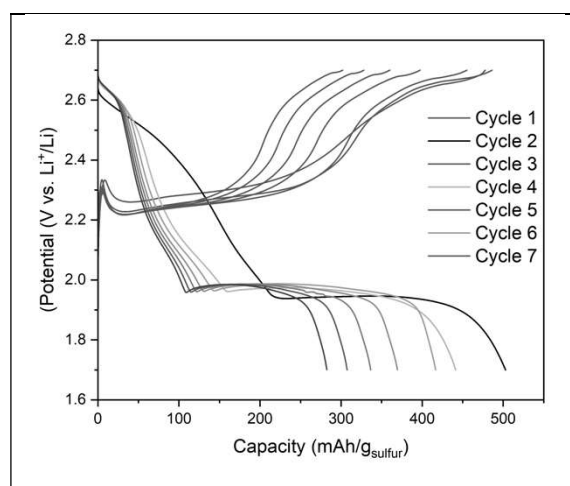


Fig. 1: Galvanostatic charge-discharge voltage profile of a Li-S coin cell, DMI, 1M LiTFSI, 0.5M LiNO₃

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A17: MnO₂ nanotube/GO composite anode for high performance lithium-ion capacitor

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Utilizing lithium-ion batteries alongside with supercapacitors gives rise to distinct properties that make lithium-ion capacitors (LICs) the perfect candidate for commercial applications. The collective properties of the battery (high-energy density) and the rapid energy delivery properties of the supercapacitor (high-power density) makes such combination significantly desirable in industry. In this research, a unique architecture of graphene oxide (GO) is encapsulated on MnO₂ nanorods which gives rise to a composite material to be utilized as the anode for LIC. The composite electrode of MnO₂/GO is fabricated with the aid of a hydrothermal process. In-depth electrochemical analysis has shown superior charge storage capability of the composite electrode. Under the half-cell configuration the composite electrode displayed significant discharge capacity of 1300 mAh/g at 0.2 C current density. A superior rate capability is obtained as the composite electrode holds a high discharge capacity of 1100, 900, 700, 300 mAh/g at the current density of 0.5, 0.7, 1, and 2 C, respectively. The fabricated LIC anode using the MnO₂/GO composite exhibited remarkable electrochemical performance.

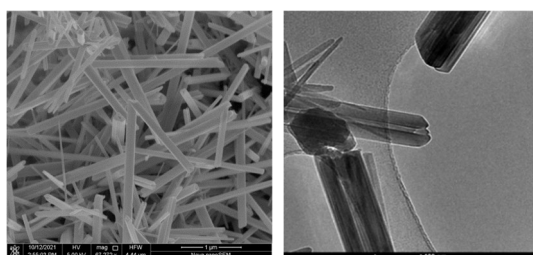


Figure 3: a) SEM imaging b) TEM imaging of MnO₂ nanotube

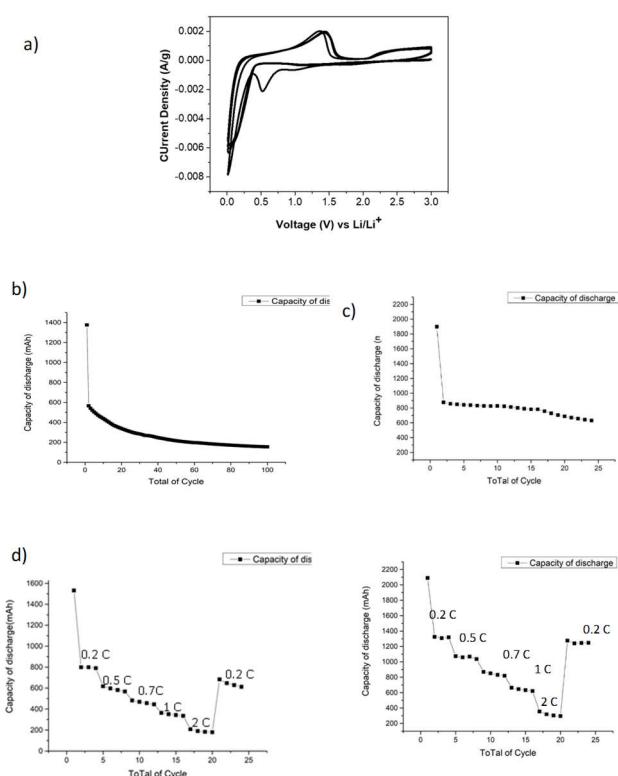


Figure 2: a) CV plot of MnO₂/GO b) Stability Plot of pristine MnO₂ c) Stability plot of MnO₂/graphene composite d) Figure 12: Rate Capacity of pristine MnO₂ e) Figure 13: Rate Capacity of MnO₂/graphene

A18: Few-layer Graphene as a Conductive Additive for Flexible Aqueous Supercapacitor Electrodes

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The intermittent nature of many renewable energy sources, coupled with fluctuations in energy demand, creates a pressing need for efficient, low-cost energy storage technologies. Supercapacitors are promising candidates to play a role in next-generation energy storage systems. They have a higher power density and better cycle life (although lower energy density) than batteries making them ideal for rapid energy storage and deployment [1]. Activated carbon is a favoured electrode material due to high surface area, although low conductivity requires use of additives (often carbon black), reducing available surface area for charge storage. In contrast, the high conductivity and specific surface area of graphene has made it promising for electrochemical double layer supercapacitors (EDLCs) [2], however, performance is limited by restacking of t graphene sheets, reducing available surface area.

In this work, few-layer graphene (FLG) is produced by high-shear exfoliation [3] into a surfactant stabilised suspension and investigated as a conductive additive in activated carbon EDLC electrodes. FLG suspensions were produced under a variety of exfoliation conditions, with platelet thickness and linear dimension determined from Raman spectroscopy using metrics developed by Backes et al. [4] and directly through scanning electron microscopy (SEM).

We demonstrate that FLG can be successfully employed as an ‘active’ conductive additive in flexible activated carbon-based aqueous EDLC electrodes if introduced by a novel ‘vacuum infiltration’ technique. The effectiveness of the FLG can be optimised by tailoring its size distribution and loading. It is found that best performance is achieved using FLG with the broadest size distribution and, moreover, that the larger size distribution is effective over the broadest range of loading.

At optimum size distribution and loading FLG is shown to outperform a commercial carbon black conductive additive (Timcal C65). Electrodes containing 10 wt% FLG have an equivalent series resistance (ESR) of 1.201 ± 0.003 W, and a specific capacitance of 140 ± 10 F g⁻¹ over a working voltage window (WVW) of 1.2 V, compared with an ESR of 1.54 ± 0.06 W and a specific capacitance of 118 ± 1 F g⁻¹ for equivalent electrodes produced with carbon black. As a result, the specific energy density of EDLCs produced with a vacuum-infused FLG additive is demonstrated to be ~15% superior to those containing carbon black at a similar power density. The FLG infused electrodes are shown to have an excellent cycle life, retaining 105% of their initial capacitance after 5000 charge/discharge cycles at a WVW of 1.2 V.

In contrast to vacuum infusion, direct mixing of surfactant-stabilised FLG suspension into the electrodes is found to be ineffective, resulting in limited improvement relative to electrodes without any conductive additive whatsoever. The detailed reasons for this behaviour are discussed.

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A19: Electrochemical Atomic Force Microscopy in Battery Study

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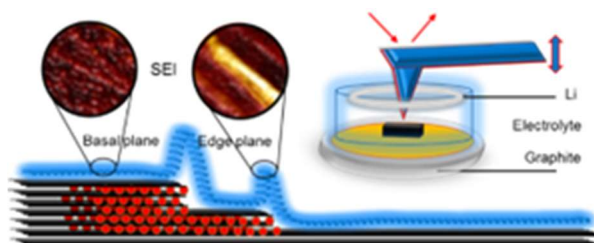
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Over the past few decades, lithium-ion batteries (LIBs) have become one of the most important electrochemical energy storage systems, utilised in applications from electric vehicles to portable devices. Yet many of the electrochemical and physical processes that underpin the operation of LIBs, and drive their degradation and failure, are not fully understood. Hence, to enhance our understanding of these electrochemical mechanisms various ex situ, in situ and operando characterisation methods are being employed to study battery degradation, enabling improved battery performance. Electrochemical atomic force microscopy (EC-AFM), and related techniques, have emerged as crucial platforms to facilitate the versatile characterisation of material surfaces and interfaces. They have revealed insights into morphological, mechanical, chemical and physical properties of LIB materials, and their evolution when under electrochemical control.

Our recent work provides a new insight into SEI formation during the first lithiation and delithiation of graphite battery anodes using operando EC-AFM. To validate these findings with respect to real-world battery electrodes, operando EC-AFM of individual graphite particles like those in commercial systems are studied. Vinylene carbonate (VC) and fluoroethylene carbonate (FEC) are shown to be effective additives to enhance SEI layer stability in 1 M LiPF₆/ethylene carbonate/ethyl methyl carbonate (EC/EMC) electrolytes, attributed to their role in improving its structure, density and mechanical strength of the SEI layer. The influence on anode SEI formation of transition metal ions such as Ni²⁺, Mn²⁺ and Co²⁺ dissolved from the cathode are also discussed. This work therefore presents an unambiguous picture of SEI formation in a real battery environment, contributes a comprehensive insight into SEI formation of electrode materials and provides a visible understanding of the influence of electrolyte additives on SEI formation.



Acknowledgements: The authors acknowledge the funding support from the Faraday Institution degradation project, and previous colleagues from electrochemical innovation lab, department of chemical engineering, UCL.

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A20: Understanding battery health and identification of ageing history of commercial lithium-ion batteries using nonlinear frequency response analysis (NFRA)

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Lithium-ion batteries undergo several aging processes during their operational life, which negatively impact their overall performance, safety and remaining useful lifetime. State-of-the-art battery management systems (BMS) typically estimate the state-of-health (SOH) of the battery in terms of its capacity vs. beginning of life but are unable to resolve the different degradation mechanisms contributing to capacity fade. Reliable and easily adaptable diagnostic methods for better understanding of the ageing pathway are required for more precise determination of remaining useful life, enabling safer operation, and evaluating suitability of used batteries for second-life applications. In this study, commercial cylindrical cells were cycled at multiple ambient temperatures and charge-discharge rates to impose different ageing conditions. At regular intervals of degradation, the cells were discontinued from cyclic ageing and were subjected to NFRA analysis at different OCVs with different amplitudes to diagnose various ageing mechanisms. A model-based assessment is also conducted to further enhance the understanding of aging mechanisms and correlation with harmonics. The NFRA results revealed that state of health of the cells significantly impacted the harmonics obtained, particularly at a lower OCV. The higher harmonics and total harmonic distortion (YTHD) of the harmonic contents obtained in NFRA has shown that different ageing mechanisms display characteristic harmonics responses in frequency range 0.1 Hz to 200 Hz.

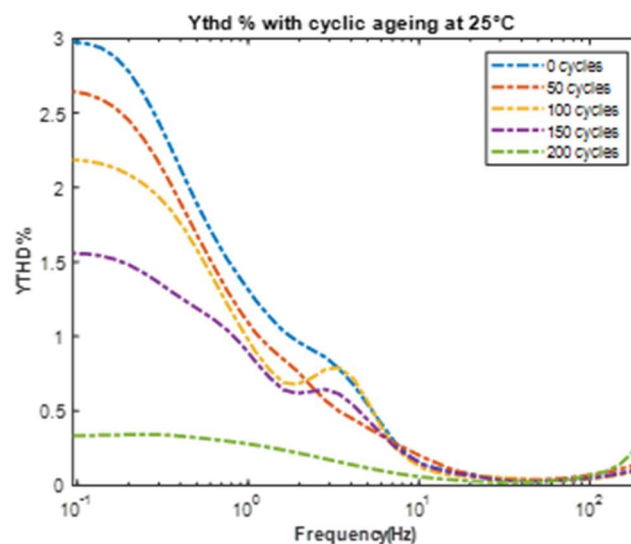


Figure 1: a) Change in YTHD % for cyclic ageing at ambient temperature of 25°C

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B1: Photoelectrode Kinetics

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The basic principles of semiconductor electrochemistry were established more than 50 years ago by Gerischer, Pleskov, Memming, Bard and others. Since then, the subject has experienced two major surges of interest, the first during the oil crisis in the 1970s and the second, more recent, in the context of solar driven water splitting and solar fuel generation as routes towards a green energy transformation. The primary research focus has been on finding appropriate photoelectrode materials that are efficient and stable, and rather less attention has been paid to the mechanisms and kinetics of the multistep electron/proton reactions involved in the generation of hydrogen and oxygen at photocathodes and photoanodes respectively. In this talk, I will highlight the differences between electrode processes occurring at metal electrodes and at illuminated semiconductor electrodes, and I will show how photoelectrode kinetics can be studied experimentally using small amplitude modulation techniques like electrochemical impedance spectroscopy [1]. My aim will be to explain how potential modulation affects the generation, transport, recombination and interfacial transfer of photogenerated electrons and holes, and to show how kinetic expressions for the photoelectrochemical impedance can be derived. I will use the photoelectrochemical oxygen evolution reaction on hematite photoanodes as an example of an analytical approach that considers the kinetics of the elementary steps involved in the overall 4-hole, 4-proton photoelectrode process and avoids approaches based on frequently (mis)used semi-empirical equivalent circuit modelling.

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B2: Materials and reactor development for photoelectrochemical hydrogen production

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While hydrogen production via photoelectrochemical water splitting has been demonstrated on a small scale, developing an industrial scale device is a challenge that brings together researchers from a range of disciplines, including engineers, material scientists and chemists. Development of photoelectrochemical water splitting devices requires an understanding of semiconductor physics, optics, (photo)electrochemistry (including catalysis and corrosion) and chemical engineering (e.g. fluid mechanics, heat and mass transport). These are all critical to the development of efficient and robust devices.

I will discuss our in-house developed photoelectrochemical (PEC) device, with a total photo-absorbing area in excess of 100 cm². The device operates with photoanodes fabricated by chemical vapour deposition, a prevalent and scalable method, of sequential layers of WO₃ nanorods and BiVO₄, to form a staggered heterojunction on FTO. The 2.4 to 2.5 eV bandgap of BiVO₄ enables light absorption up to 517 nm in wavelength and a theoretical solar-to-hydrogen efficiency (η_{STH}) of up to 9.2 %. The WO₃/BiVO₄ heterojunction system is one of the most promising in terms of performance, cost and durability. Combined with a Ni mesh cathode and an externally mounted homojunction Si PV, and operated in a pH neutral phosphate buffer solution, this creates a cost-effective and scalable photoelectrochemical-photovoltaic (PV-PEC) device with a commercially viable fabrication method. In initial experiments, we have achieved a spontaneous solar-to-hydrogen efficiency (η_{STH}) of 4.0 %.

Scale-up of PEC devices comes with numerous challenges which must be addressed by both computational and experimental approaches. I will discuss the ways in which we have combined these approaches in our research and initial progress to-date. I will also show strategies we have been developing towards mitigating performance losses within our device, including reducing severe potential and current gradients across poorly conducting photoelectrodes. I will discuss other aspects critical to the scale-up of photoelectrochemical devices, including heat and mass transfer, fluid dynamics and safety challenges associated with increasing product and precursor volumes.

Despite the urgent need for engineering progress in this area to accelerate dramatically in order for this type of solar hydrogen technology to impact on greenhouse gas emissions, there are relatively few academic publications that address this topic. With a lack of demonstration prototypes, it remains difficult to envisage what an industrial-scale installation for clean hydrogen production might look like. Ultimately, availability of green hydrogen is expected to result in the hydrogen market expansion. This research seeks to elucidate engineering challenges of developing large-scale water splitting devices, to facilitate the pathway to commercially viable photoelectrochemical hydrogen production.

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B3: Nanophase-Photoelectrocatalysis: Loading, Storing, and Release of H₂O₂ using a Photochemical Reaction within Graphitic Carbon Nitride

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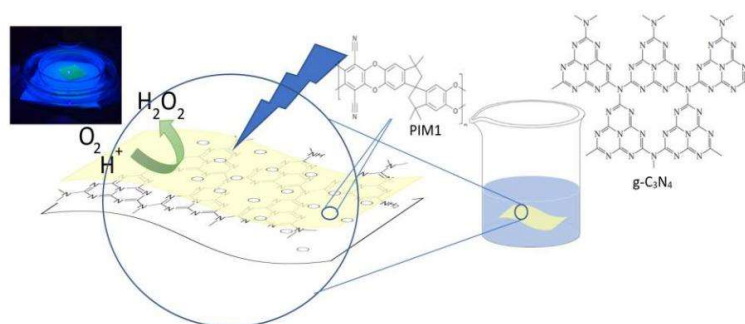
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Polymeric graphitic carbon nitride (g-C₃N₄) is a metal-free and visible light responsive photocatalyst [1]. It is a multifunctional material for light energy harvesting and environmental remediation [2]. Typically, g-C₃N₄ is employed as a liquid phase catalysis, with applications in photochemical hydrogen or hydrogen peroxide production.

Here, we explore the potential of solid g-C₃N₄ to produce, store, and release hydrogen peroxide using blue light mediated photochemical process in an ambient atmosphere and isopropanol vapour. The g-C₃N₄ photocatalyst undergoes photoexcitation, which creates an excited state and, following charge separation, a hole and electron pair. Holes interact with the isopropanol quencher. Electrons reduce oxygen to H₂O₂. In order to heterogenise g-C₃N₄, it is immobilised into a polymer of intrinsic microporosity (PIM-1 [3]). The heterogenized photocatalyst maintains photo-reactivity in the microporous matrix. PIM-1@g-C₃N₄ [4] can be recycled and reused for several cycles.



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B4: Ultra-Thin Alumina Overlayer as a Protective Coating on CuWO₄ Photoanodes

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In the last decades, the continuous industrial development has led to a heavy dependency on fossil fuels, which consumption generates serious consequences for the environment. Among the substitutes to fossil fuels, hydrogen (H₂) features as an auspicious alternative as it can be used across the energy, heating and transport industries. In this scenario, photoelectrochemical cells (PECs) for H₂ production have emerged as a promising technology since they can promote both light absorption and electrolysis reactions in one device [1].

Copper tungstate (CuWO₄) has been widely studied as a photoanode material in PECs due to its narrow bandgap energy (2.1 – 2.5 eV) and its high theoretical solar-to-hydrogen efficiency (13%) [2]. Although CuWO₄ photoelectrodes have demonstrated a high selectivity towards the oxygen evolution reaction (OER), their performance is still limited by photocorrosion and a high surface recombination rate, which has been associated with the presence of surface states acting as recombination centres at the interphase [3]. This work reports a study on the effects of an ultra-thin layer of Al₂O₃ deposited on the surface of CuWO₄ photoanodes as a protection strategy.

CuWO₄ photoelectrodes were synthesised by applying a precursor solution onto FTO-coated glass substrates by spin-coating, followed by annealing at 550°C. Afterwards, an Al₂O₃ layer was deposited onto the CuWO₄ photoelectrodes by atomic layer deposition. The fabricated photoelectrodes were characterised in terms of their optical and photoelectrochemical behaviour. The addition of the Al₂O₃ ultra-thin layer on the surface of the CuWO₄ photoanodes promoted a decrease of one order of magnitude in the charge associated with the Cu²⁺/Cu⁺ reduction peak during cyclic voltammetry experiments. Furthermore, linear sweep voltammeteries under chopped illumination (Fig. 1) showed that the addition of the Al₂O₃ protective layer results in higher photocurrents at high applied potentials, which is attributed to greater charge transfer kinetics for the OER.

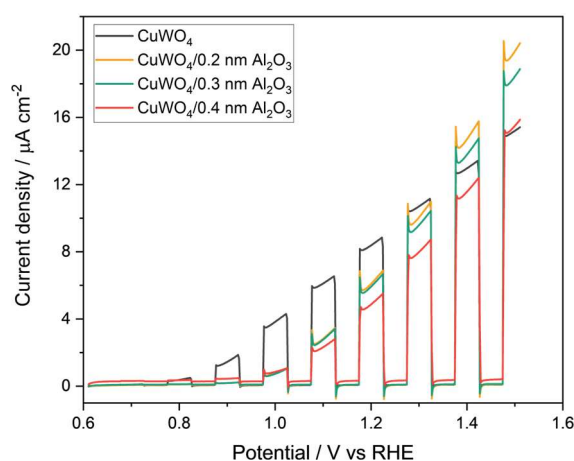


Fig 1. Linear sweep voltammograms obtained in 0.1 M Na₂SO₄ for the fabricated photoanodes under monochromatic chopped illumination (405 nm).

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B5: Redox Neutral Electrosynthesis without Added Electrolyte at Interdigitated Electrodes

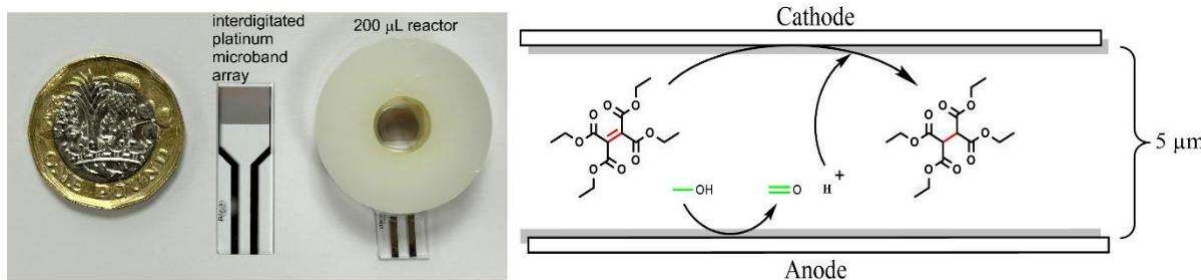
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Pioneering work by Belmont and Girault in 1994 introduced interdigitated band electrodes into electrosynthesis ^[1]. Today, interdigitated microband electrodes have been accepted as powerful tools in electrosynthesis, especially for paired and redox neutral oxidation/reduction processes ^[2,3].



Here, a microreactor based on a symmetric Pt-Pt interdigitated microband array electrode (5 mm bands with 5 mm gaps; Figure 1) is employed with typically 200 mL reaction volume. Olefin reduction is investigated in aliphatic alcohol solvents. The absence of intentionally added electrolyte has no detrimental effects on the process. Constant current mode and constant voltage mode synthesis are compared. Impedance spectroscopy is employed to investigate the reaction layer. In a typical electrolysis reaction, tetraethyl-ethylene-tetracarboxylate is reduced to tetraethyl-succinate in >95% yield. Effects of reaction time and substrate concentration are investigated.

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B6: High Yield and Selective Electrocatalytic Reduction of Nitroarenes via Polyoxometalate Redox-Mediated Chronoamperometry

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Anilines are major commodity chemicals used extensively in the production of pharmaceuticals, dyes, and polymers. However, the typical methods for synthesizing anilines suffer from poor environmental sustainability. Here, we report an electrocatalytic route for the production of anilines that works in aqueous solution at room temperature and pressure, where the electrons and protons required to reduce the nitrobenzene precursors are obtained from water. Excellent selectivities are obtained for a range of anilines, including species with ortho-iodides that are very challenging to obtain by other methods. Our approach relies on the use of a polyoxometalate redox mediator that shuts off the direct electro-reduction of the nitrobenzene at the electrode surface and thus prevents unproductive side reactions.^{1,2} Given the scale and current environmental impact of global aniline production, this electrochemical route holds promise for the development of more sustainable processes for the production of these vital chemical feedstocks.

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B7: Room Temperature Electro-carboxylation of Styrene and Stilbene Derivatives: A Comparative Study

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In recent years, significant attention has been directed toward addressing climate change and mitigating global warming by exploring avenues to convert carbon dioxide (CO₂) into valuable products. Among the promising strategies, the electrochemical reduction of CO₂ using alkene substrates has emerged as a focal point for contributing to ecological sustainability^{1,2,3}.

In this study, a highly efficient electrochemical di-carboxylation method for phenyl-substituted alkenes in the presence of atmospheric pressure of CO₂ at room temperature is investigated, eliminating the need for low-temperature or high-pressure conditions. The reaction was conducted using a Ni mesh electrode cathode and a magnesium rod anode in a dimethylformamide solution (Figure 1). The electrochemical process resulted in the formation of mono and dicarboxylic acids with satisfactory yields ranging from 44% to 78%, which were characterized through the application of various analytical techniques, including ¹H nuclear magnetic resonance (NMR), ¹³C NMR, mass spectrometry (MS), and infrared spectroscopy (IR) in detail. This eco-friendly electrochemical carboxylation method for styrene and stilbene derivatives demonstrates the potential for sustainable production of valuable compounds under mild conditions.

Keywords: Electrochemical CO₂ reduction; electrocatalysis; styrene; stilbene; carboxylation.

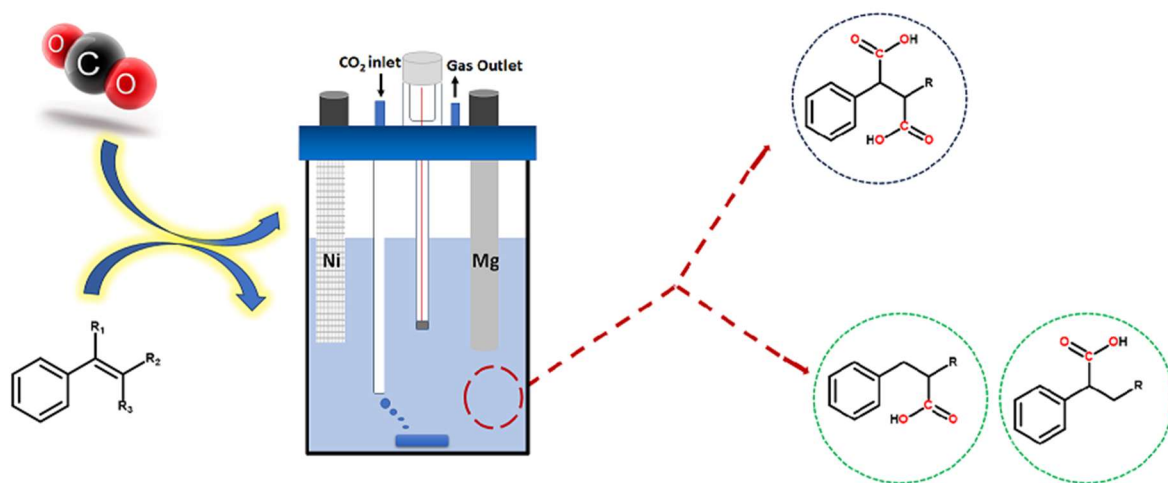


Figure 1: Electro-carboxylation of Alkenes.

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B8: 3D-Printing for Electrochemical Reactors and a Tool Kit for the Expansion of the ElectraSyn

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The use of 3D-printing within organic synthesis in recent years has found extensive applications in many fields of research from designing bespoke catalysts to the development of new flow reactors.^[1] Overall, this drive towards applying additive manufacturing technologies within organic synthesis has been enabled by the many advantages the technology has to offer, for instance the possibility to design and fabricate tailored products on demand at a low cost. An area of research we have developed within recent years is the use of 3D-printing to build electrochemical reaction platforms for use in electrosynthetic reaction discovery.^[2]

Despite the many advantages of 3D-printing the ability to apply 3D-printing technology to solve a problem within organic synthesis requires technical knowledge, such as the use of computer aided design (CAD) software. This can make the uptake of 3D-printing within organic synthesis slow and unappealing. To overcome this problem, we have developed a design tool called ERCAD to facilitate the rapid prototyping and manufacture of bespoke reactors for electrochemistry. We will demonstrate how 3D-printed reactors can be utilised to optimise reactions for organic electrosynthesis.

In addition, another common problem within organic electrochemistry is the use of bespoke reactors, which are often developed in-house for a specific purpose or are commercially available. Although this can offer high reproducibility by using standardized components. To bridge the divide between customizability and reproducibility, we have developed the Open-ESyn, a suite of 3D-printed components compatible with the popular IKA ElectraSyn. The work presented will show the development and utility of these 3D-printed components in various electrochemical reactions.



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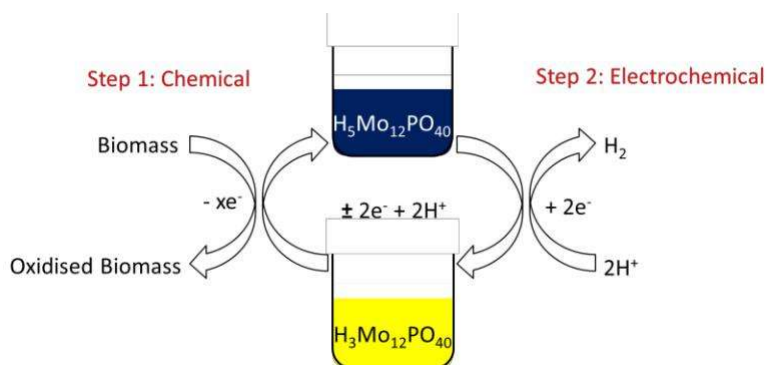
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B9: Decoupled Biomass Oxidation and Hydrogen Production Mediated by Phosphomolybdic Acid

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Hydrogen evolution via the electrolysis of water is one way to address the intermittency of renewable energy sources, and the hydrogen produced can be utilised as both a clean fuel and a feedstock for ammonia. However, improvements in electrolyser performance through further research and development are essential if hydrogen is to become a viable commercial solution for energy storage. Decoupled water electrolysis improves the flexibility and safety of traditional electrolysis by utilizing a redox mediator to separate the oxygen and hydrogen evolution reactions into two distinct steps. The polyoxometalate phosphomolybdic acid is an established redox mediator for this process.¹

Decoupled biomass oxidation and hydrogen production is a further adaptation to decoupled electrolysis, that can also be mediated by phosphomolybdic acid. In this system the first step is the spontaneous reduction of the phosphomolybdic acid mediator by a biomass material, which is itself oxidised. In the second stage the reduced mediator is electrochemically re-oxidised, forming hydrogen gas and regenerating the phosphomolybdic acid. The advantage of this approach over traditional electrolysis is that oxidation of the biomass releases additional electrons which lower the energy required to produce hydrogen. This has previously been demonstrated using waste organic materials such as lignin² and corn straw.³

Seaweed exists in abundance in the UK, so it is an excellent potential biomass source for decoupled biomass oxidation and hydrogen production. The seaweed derivatives sodium alginate and agar are widely used in the food industry, cheap, commercially available, and readily oxidisable. In this work the ability of sodium alginate and agar to reduce phosphomolybdic acid was evaluated using UV/Vis spectroscopy, and the oxidation products of the seaweed derivatives were analysed by NMR and gas chromatography.

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B10: Polyaniline/Polypyrrole Composites Electrodeposited from Ionic Liquids for Hydrogen Evolution Reaction

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Intrinsically conducting polymers (ICPs) are a class of organic materials that have electrical high conductivity like metals. When an ionic liquid is used as dopant to the ICP backbone, it results in improved conductivity and widens electrochemical potential window (1). Ionic liquids (ILs) are well-known molten salts with high thermal stability, low volatility and tunability, making them an ideal choice as electrolyte and dopant for electrodeposition (2).

In our present study, we are interested in exploring the effect of co-polymerisation of conducting polymer on the rate of hydrogen evolution reaction (HER). Hence, we investigated the electrodeposition of a Polyaniline (PANI)/polypyrrole (Ppy) composite in an ionic liquid. The electrodeposition was carried out in a solution of aniline, pyrrole, and the ionic liquid EMIM-TFSI. Electro-co-polymerization of the PANI/Ppy in ionic liquid controls film thickness, homogeneity, and morphology, which improves HER activity and has high electrical conductivity and good cyclic stability. The film has a porous morphology, which is desirable for faster interfacial kinetics of HER activity. The resulting composite film was characterized by cyclic voltammetry, impedance spectroscopy, Raman spectroscopy, X-ray diffraction spectroscopy and scanning electron microscopy.

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B11: Valorisation of CO₂ and other abundant waste streams

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The sustainable transformation of abundant waste streams such as CO₂, lignocellulosic biomass, and plastics through the utilisation of renewable energy sources represents a promising pathway towards establishing a circular economy and facilitating the generation of essential fuels and valuable chemicals. In this poster, I will detail two innovative proof-of-concept systems that our research group has developed to valorise various waste substrates.

The first system consists of a versatile photoelectrochemical platform capable of bias-free CO₂ conversion coupled with plastic reforming.¹ This system is based on a perovskite-based photocathode that enables the integration of different CO₂-reduction catalysts, such as a molecular cobalt porphyrin,² a Cu₉₁In₉ alloy³ and formate dehydrogenase enzyme,⁴ which generate CO, syngas, and formate, respectively. Additionally, a Cu₂₇Pd₇₃ alloy anode selectively transforms polyethylene terephthalate plastics into glycolate in an alkaline solution.

The second system describes the complete oxidative valorisation of lignocellulose coupled to the reduction of CO₂ employing a three-step fractionation-photocatalysis-electrolysis process. Initially, white birch lignocellulose was pre-treated using an acidic organic solution to generate predominantly cellulosic- and lignin-based fractions. The solid cellulosic-based fraction was solubilised using cellulase enzyme, followed by photocatalytic oxidation to formate with concomitant reduction of CO₂ to syngas using a phosphonate-containing cobalt(II) bis-terpyridine catalyst immobilised onto TiO₂ nanoparticles.⁵ The soluble lignin-based fraction was oxidised in an electrolyser to the value-added chemicals vanillin and syringaldehyde at the carbon-based anode, while CO₂ was converted to CO selectively at a Co(II) porphyrin catalyst modified cathode² at an applied voltage of 3 V.

These findings collectively highlight the potential of valorising solid and gaseous waste streams through diverse methods, thereby providing a pathway to obtaining valuable resources in a more environmentally sustainable way.

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B12: Optimising the Electrochemical Reduction of CO₂ to Oxalic Acid in Propylene Carbonate

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Carbon dioxide (captured from the atmosphere or obtained by other routes) constitutes a useful and widely available building block to produce numerous valuable chemicals and fuels. Electrochemical methods for carbon dioxide reduction offer advantages in terms of scalability, the prospect of coupling directly to renewable power sources and the ability to reduce carbon dioxide without the co-production of harmful by-products. Of the various possible products of carbon dioxide electroreduction, oxalate/oxalic acid is an especially attractive target because of its wide use in several chemical and pharmaceutical processes. Herein, we report the results of a study on carbon dioxide electroreduction to oxalate/oxalic acid in a propylene carbonate solvent system, catalysed by the addition of benzonitrile. Our results show that the use of benzonitrile as a homogeneous electrocatalyst improves the Faradaic and reaction yields of oxalate/oxalic acid production, as well as the area-normalised rate of formation of oxalate/oxalic acid, giving a new record rate of formation of 1.6 mM cm⁻² h⁻¹ (averaged over 1 h) or 0.9 mM cm⁻² h⁻¹ (averaged over 5 h) at a voltage of -2.7 V vs SCE (-2.46 V vs SHE). Such metrics in turn suggest that the electrochemical reduction of carbon dioxide to C₂₊ products via oxalate could be a promising avenue for further development for the sustainable production of key chemical feedstocks.

Keywords: Electrochemical carbon dioxide reduction; oxalic acid; electrocatalysis; propylene carbonate.

B13: Optimizing Ultrasound Parameters for Efficient Sonoelectrochemical CO₂ Reduction at Copper Electrodes

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Electrochemical reduction of CO₂ is a promising approach for generating hydrocarbon fuels that can be utilized without contributing to the net increase of atmospheric CO₂ [1,2]. Additionally, the combination of ultrasonic irradiation and electrochemical techniques provides significant advantages over traditional electroanalytical methods. These benefits include activation and cleaning of electrode surfaces, elimination of gas bubbles at the electrodes (reducing a possible source of overpotential), and enhanced mass transport of electroactive species facilitated by acoustic streaming, microjets and cavitation phenomena [3,4]. Despite these advantages, research on applying ultrasound during electrochemical CO₂ reduction remains uncommon. This is largely due to inadequate understanding of, and insufficient technical input into, process optimization. Herein, we present an optimization of acoustic parameters based on frequency and power for efficient sonoelectrochemical reduction of CO₂ using copper (plate and mesh) electrodes. The electrochemical reduction of CO₂ was performed for 15 minutes on copper (plate and mesh) electrodes in a CO₂ saturated 0.1 M KOH aqueous solution under varying ultrasound-assisted conditions, including frequency and power, at room temperature (~25 °C). The liquid and gas products were analyzed by ¹H NMR and gas chromatography, respectively. Our findings demonstrate that the reaction mechanism underwent a change when ultrasound was applied, as evidenced by the formation of deep reduction products with copper mesh electrodes. Analysis by Electrochemical Impedance Spectroscopy (EIS) revealed a significant decrease in charge transfer resistance under sonication, confirming the enhanced mass transportation of electroactive species associated with ultrasound. Additionally, we have established the crucial role of ultrasonic frequency and power as key acoustic parameters in optimizing the sonoelectrochemical process, as they determine the nature and type of required cavitation.

Keywords: Sonoelectrochemistry, CO₂ reduction, copper electrode, acoustic cavitation.

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B14: Optimised Electrodeposition technique for in-situ fabrication of Cu-based catalysts on Gas Diffusion Layers for electrochemical CO₂ reduction

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The development of catalysts for the electrochemical reduction of CO₂ (CO₂R) has been a topic of extensive investigation due to its critical role in sustainable CO₂ utilisation and climate change mitigation¹. Hori et al.² showed that Cu is the only transition metal catalyst with the ability to generate a wide range of hydrocarbons or alcohols, such as ethylene³ and ethanol⁴. Consequently, research has focused on improving the selectivity and activity of CO₂R toward multicarbon products by tuning the composition and morphology of Cu-based catalysts³⁻⁷. Electrodeposition is a versatile and recognised method for synthesising catalysts used in CO₂R¹. By manipulating the electrochemical parameters such as current density, deposition potential, and electrolyte composition, this technique enables precise control over the catalyst morphology, composition, and thickness, thereby enhancing the catalytic activity and selectivity towards desired CO₂R products^{1,8}. This work presents an optimised electrodeposition technique that allows the in-situ fabrication of Cu and CuAg catalysts with uniform distribution onto Gas Diffusion Layers (GDLs) to investigate the CO₂R.

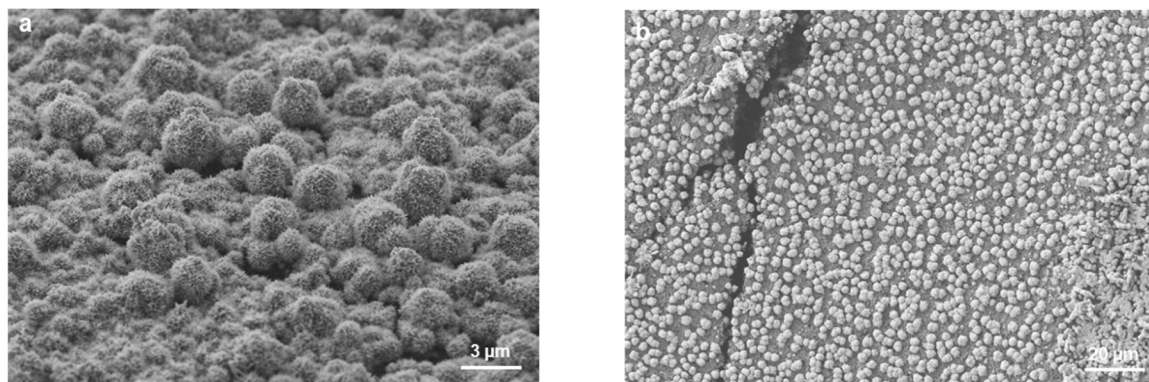


Figure 1. FIB-SEM images of the electrodeposition structure of Cu (a) and CuAg (b) using different parameters.

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B15: Carbon Nanotube Production from CO₂ via High Temperature Electrolysis

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As global warming becomes a largely accepted fact, carbon capture and utilization (CCU), along with carbon capture and sequestration (CCS), has become an important strategy for mitigating CO₂ emissions. The implementation of CCU is facing two main problems: (i) the low cost-effectiveness and (ii) the extra CO₂ emission and energy consumption during CO₂ conversion. A new CO₂ utilisation process involves its conversion into carbon nanotubes – could potentially solve these two problems – as has been reported in the literature.^{1,2}

Carbon nanotubes (CNTs) are tubular structures consisting of graphitic carbon. Their mechanical strength, electrical conductivity, and thermal conductivity accelerated their application in nanoelectronics, catalysts, lithium-ion batteries, etc. However, the high cost of CNTs (about \$114,000 per tonne) currently limits their use.³ Production of CNTs via high temperature electrolysis of CO₂ in molten carbonate salts has the potential to significantly reduce their production cost (on the order of \$660 per tonne) and with a net environmental benefit.⁴ Thermodynamic analysis predicts up to 3.65 tonnes of CO₂ consumed per tonne of CNTs produced. The method involves several key steps: (i) selective exothermic absorption of CO₂ from flue gas by a molten alkali metal oxide electrolyte (e.g., Li₂O), forming an alkali metal carbonate; (ii) electrolysis of metal carbonate, producing CNTs and oxygen gas, while regenerating the metal oxide; (iii) heat released by CO₂ absorption maintains the high temperature required for electrolysis.

In this research, carbonate ions were electrochemically reduced to carbon products including CNTs, carbon nanofibers and carbon nanoparticles on iron cathode in molten Li₂CO₃ electrolyte at 800 °C. The electrolysis current density was maintained at 200 mA/cm², with the resulting cell potential difference in the range 1.75 V – 1.92 V, substantially higher than the thermoneutral potential of 1.42 V at this temperature. The carbon products were characterised with scanning electron microscopy and transmission electron microscopy. We have been systematically investigating and relating different reaction parameters to the properties of the synthesised carbonaceous products. Electrochemical measurements were made to study the reactions taking place in the electrolytic cell, using various combinations of iron and nickel as anodes/ cathodes, and comparing results with thermodynamic predictions. Experiments are now being carried out to study the mechanism and kinetics of the CNT nucleation and growth process. Our goal is to understand the electrochemical micro-kinetics and subsequently optimise the reaction process for prototype development. We shall present our experimental setup, procedure and key findings.

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B16: NiCuAg: An Electrochemically Synthesised Trimetallic Stack for CO₂ Reduction

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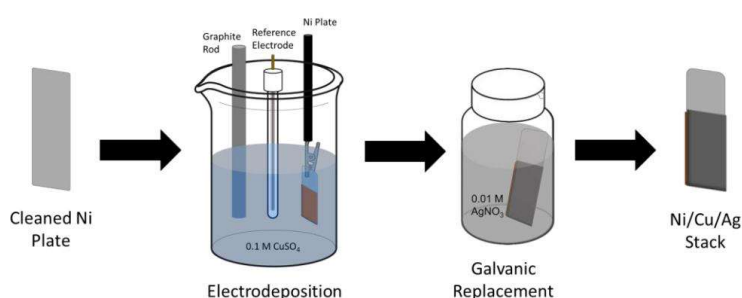
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Climate change, as a result of increased CO₂ and other greenhouse gas emissions, maintains a position, according to the United Nations as the “defining issue of our time”.¹ Thus, research efforts to close the gap in the carbon cycle and electrochemically utilise atmospheric CO₂, have increased.² Since Hori’s seminal discovery the Cu can uniquely reduce CO₂ by more than two electrons to produce hydrocarbons³, there has been significant research attention on pure metals and Cu derivatives as electrocatalysts.⁴ High overpotentials and poor selectivity remain as key challenges due to the scaling relations between the simultaneous pathways of CO₂ reduction.⁵ One approach for breaking these is alloying or the use of mixed metal phases. Bimetallic catalysts, particularly those containing Cu have gained considerable interest⁴, however, limited examples of tri-metallic catalysts have been explored.

Herein, a stacked Ni/Cu/Ag electrocatalyst has been electrochemically synthesised by copper electrodeposition on nickel, followed by galvanic replacement to produce a silver layer. The combination of Ni and Cu was proven to be promising in recent studies^{6,7} generating desirable non-CO and H₂ products such as ethanol. Ag has been shown to promote *CO intermediate production on the Cu surface⁸ thus its addition to our catalyst should further promote non-CO and H₂ products and increase their selectivities.

Linear sweep voltammetry revealed significant activity at potentials more negative than −0.8 V vs. Ag/AgCl, thus CO₂ reduction testing was completed in this region. Gaseous reduction products were analysed by gas chromatography and liquid products by NMR. The trimetallic stacks were characterised by XRD, and SEM/EDX to confirm their synthesis.



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B17: Earth Abundant CuSn Electrocatalysts for Selective Conversion of CO₂ to CO

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Electrochemical CO₂ reduction (eCO₂R) to produce chemicals and fuels can contribute towards sustainable energy. In the current work, the focus is on the selective conversion of CO₂ to CO using CuSn electrocatalysts. CO is a valuable chemical feedstock which can be converted to liquid hydrocarbons using established industrial methods like Fischer–Tropsch process¹. Copper-tin (CuSn) electrocatalysts are potential candidates for sustainable and inexpensive CO production from eCO₂R.

In this work, gas diffusion electrodes (GDEs) were prepared by painting the Cu₂O nanoparticles ink on carbon paper. The ink was prepared by mixing Cu₂O nanoparticles with Nafion ionomer in 2-propanol. The electrochemical spontaneous precipitation of Sn on Cu GDEs was performed by dipping Cu GDEs along with connected Sn foil in acidic 0.1 M SnCl₂ solution². The effect of electrochemical spontaneous precipitation time was conducted by varying deposition time in 30 s to 60 min range. Various CuSn electrodes were employed in a three-chamber GDE reactor for determining the CO₂R products. For 20 min galvanically deposited Sn, highest CO faradaic efficiency of >92% at 110 mA cm⁻² partial current density for CO was obtained. Compared to Cu₂O GDE, selectivity for CO production with CuSn GDE increased from 34% to 92% at -1.13 V vs RHE. The current density during the fixed potential measurement enhanced from 102 for Cu₂O to 120 mA cm⁻² for CuSn_{20_min}. The optimized Cu-Sn system had ca. 13% Sn coverage on the surface, as determined by XPS. The catalyst also showed stable performance and was operable for >3 h under chronoamperometric conditions. The surface of the GDE reduces from Cu₂O to Cu during the electrochemical deposition of Sn and goes further reconstruction during the eCO₂R. The encouraging results with CuSn GDEs, provide a possible route to produce CO from CO₂ using a low-cost electrocatalyst at high faradaic efficiency and high current.

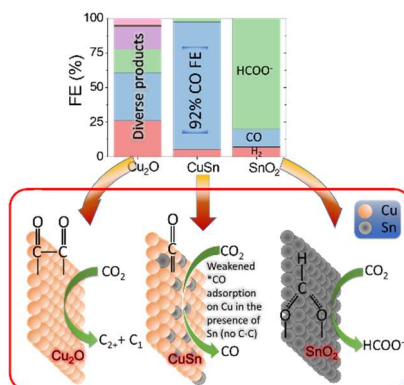


Figure 1. Comparison of Cu₂O, Cu-Sn and SnO₂ electrodes for the eCO₂R.

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B18: Electrodeposition of Cu-based bimetallic catalyst over Gas Diffusion Layer (GDL) for the electrochemical conversion of CO₂

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The Electrochemical Reduction of CO₂ (CO₂RR) is a complex multi-step process with the possibility of numerous adsorbed intermediates depending on process conditions. Developing an affordable electrocatalyst capable of reducing CO₂ in a suitable and environmentally sound electrolyte under efficient operating conditions to produce high-value carbon-based compounds selectively is essential to ensure future development. Cu is the only metal capable of reducing CO₂ to multi-carbon products. However, pure Cu selectivity cannot offer a viable path to commercial implementation. Nevertheless, Cu-bimetallic electrocatalysts provide a promising route to achieve scalability by providing a unique electronic structure and creating new active sites with enhanced characteristics for specific intermediate species that otherwise may not be accessible. [1,2,3] Bi and Sn electrocatalyst at high overpotentials and current densities (CD) presents high selectivity for formic acid. [2,4] Mixing Cu with Bi or Sn can overcome these drawbacks by regulating the bonding energy of critical. [2,4,5]

Here, we present the characterisation of CuBi and CuSn catalysts prepared with different loading ratios to validate the e3 group electrocatalyst synthesis methodology (e3ESM). An SEM analyser, coupled with energy-dispersive X-ray spectroscopy (EDx), allowed the surface and chemical characterisation of the bimetallic catalyst (Figure 1). It was necessary to develop a method to quantify the area covered over the GDL. Matlab can convert SEM images to Binary Black and White (B/W) images (figure 2) using a grey threshold and then quantify black and white pixels.

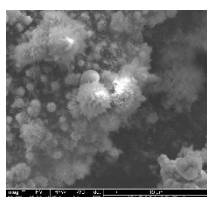


Figure 1: Cu-Bi Electrocatalyst: 100 X SEM (left) vs B/W images

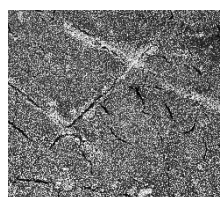
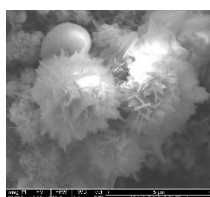


Figure 2: Cu-Sn Electrocatalyst SEM Image: 10K X (left) & 25K X (right)



e3ESM produces well-distributed nanostructures with a distinctive coverage area. However, intensive optimisation is required since electrochemical parameters significantly affect the process.

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B19: Atmospheric-Pressure Plasma Device for CO₂ Conversion and Utilization

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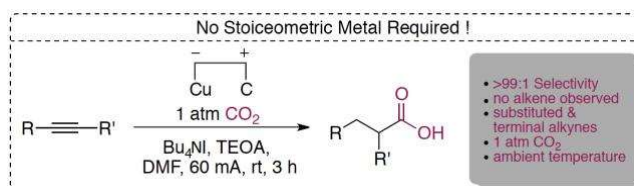
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Besides the reduction of greenhouse gases, by producing feedstocks using CO₂ will greatly reduce our dependence of fossil fuels for chemical synthesis. Our previously reported electrochemical processes have proven to be successful in terms of electron transfer between substances at room temperature and atmospheric pressure (See Scheme), in this we have explored the use of substituted acetylenes (See Scheme) to give selectively mono-carboxylated products. Atmospheric-pressure plasmas interacting with organic liquids offer a new possibility for chemical synthesis that remains largely unexplored. Here we report on the results obtained with a Jet device in which chemical reactions are triggered in an organic liquid by an atmospheric-pressure plasma.

As a proof-of-concept, we considered the incorporation of CO₂ into an alkyne to form a carboxylic acid. Here we explore plasma reduction. A CO₂ saturated solution of diphenylacetylene in Tetra-n-butylammonium iodide (Bu₄NI), Triethanolamine (TEOA) and Dimethylformamide (DMF) and Argon DC plasma is used as a gaseous cathode to provide electrons for the reduction of CO₂. Gas chromatography Mass Spectroscopy (GCMS) and Nuclear Magnetic Resonance (NMR) analysis indicate the formation of 2,3 diphenylpropanoic acid with good selectivity although further optimization is needed to increase yield and increase the current efficiency of the device.



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B20: A Low-Temperature Ammonia Electrolyser for Wastewater Treatment and Hydrogen Production

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Ammonia is a common pollutant, present in municipal wastewater streams. Stripping, recovery, and anodic oxidation of ammonia to produce hydrogen via electrolysis is gaining momentum as a technology, yet the development of an inexpensive, stable catalytic material is imperative to reduce cost. Currently, the commercialisation of the ammonia electrolyser technology is hindered by slow reactions at the anode and the cathode as well as the deactivation or degradation of the catalysts over time [1,2].

Here, we report on a new nickel-copper (NiCu) catalyst electrodeposited onto a high surface area nickel felt (NF) as an anode for ammonia electrolysis, see Figure 1. Cyclic voltammetry demonstrated that the catalyst/substrate combination reached the highest current density (200 mA cm⁻² at 20 °C) achieved for a non-noble metal catalyst. A NiCu/NF electrode-gas diffusion layer was tested in an anion exchange membrane electrolyser for 50 h; it showed good stability and high Faradaic efficiency for ammonia oxidation (88%) and hydrogen production (99%). We demonstrate that this novel electrode catalyst/substrate material combination can oxidise ammonia in a scaled system, and hydrogen can be produced as a valuable by-product at industrial-level current densities and cell voltages lower than that for water electrolysis.

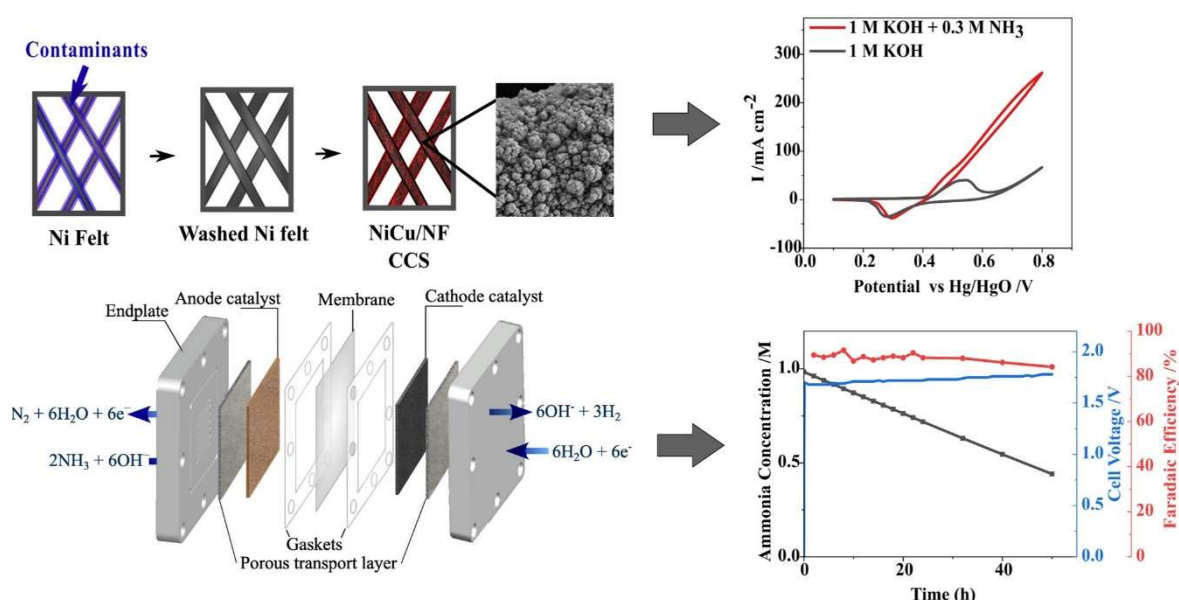


Figure 4. Overview of catalyst-coated support preparation and AEM electrolyser for anodic ammonia oxidation combined with hydrogen generation.

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C1: On the capabilities of Electrochemical Surface Oxidation Enhanced Raman Scattering for analysis

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Coupling of electrochemistry (EC) and Surface Enhanced Raman Scattering (SERS) provides a powerful tool for analytical chemistry. EC-SERS can be used to detect and quantify molecules with great sensitivity and selectivity [1]. In recent years, a number of new approaches to enhance the Raman signal have been developed. One particularly promising approach is Electrochemical Surface Oxidation Enhanced Raman scattering (EC-SOERS) [2], discovered by our research group in 2018.

EC-SOERS is based on the electrochemical oxidation of a metal electrode, allowing the design of simple potentiostatic or galvanostatic experiments to generate different Raman enhancing substrates. A new family of dielectric or semiconductor nanocrystals can be electrosynthesized and used to detect different types of molecules, enhancing the Raman signal by several orders of magnitude.

The comprehension of the fundamental origin of EC-SOERS is a key step to develop new Raman enhancing substrates, which can be activated both electrochemically or chemically. Designing new strategies to generate and activate SOERS substrates should give rise to multiple interesting applications based on these materials. EC-SOERS has a number of advantages over other analytical techniques, including high sensitivity, high reproducibility, chemical selectivity, and an intrinsic trilinear character. Moreover, the rational design of experiments based on EC-SOERS substrates that can be converted on SERS substrates opens new gates for the development of promising analytical applications.

In this presentation, the potential and key factors to consider during the synthesis of SOERS substrates based on dielectric or semiconductor materials will be discussed, which is relevant for the development of new analytical methods based on Raman spectroelectrochemistry.

Acknowledgements

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C2: Quantum Electrochemical Sensors and Actuators: Pioneering a Novel Frontier in Cancer Therapy

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The goal of this work is to develop Quantum Bioelectronics as a platform technology for bioelectronic control of quantum biology. By harnessing electromagnetic fields (EMF) to sense and regulate quantum biological electron tunnelling (QBET). Existing communication technology falls short in interfacing with cells at a level that matches native biological signalling in terms of spatial and temporal resolution. To address this challenge, we need technological innovation capable of sensing and manipulating electron tunnelling events inside of cells. Our tactic to achieve this is to build a bifunctional quantum sensor actuator to investigate quantum effects in cancer biology. Gold nanoparticle-silica core shell encapsulated nanodiamond quantum sensors (MSP-AuNP-Si-NDS) are developed. These have unique electrical and optical properties. On high EMF stimulation electron tunnelling at the gold is induced, and quantum related fluorescence is altered and can be measured at the nanodiamonds. This allows sensing and actuation of quantum mechanical effects inside cells. The AuNPs within MSP-AuNP-Si-NDS will alter cancer cell metabolism by converting electrical signals to biological sensing and actuation events through the mechanism described. This offers an exciting new therapeutic paradigm in cancer.

C3: Electrochemical processing of nanoporous copper as a high surface area enhanced catalyst for sensing applications

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Highly porous copper nanostructures have recently been shown to perform well as non-enzymatic sensors for glucose¹. The chip-based device demonstrated superior analytical performance, exhibiting excellent sensitivity, a wide linear range, and high reproducibility and reusability. In this study, we employed a silicon microelectrode array chip, as previously described², to deposit nanoporous copper (NPC). Each chip comprised 63 x 20 μm diameter disks with a spacing of 500 μm . By employing a cyclic voltammetry (CV) procedure previously reported³, the measured copper oxide peaks show the NPC exhibited an approximately 8 times larger surface area compared to planar-Cu counterparts. The scanning electron microscopy (SEM) image in Figure 1 revealed the nanoporous structure of the copper metal, and energy-dispersive X-ray spectroscopy (EDX) confirmed the absence of detectable traces of other metals in the NPC.

The oxidation of glucose at NPC was investigated under alkaline conditions using CV, which revealed that the peak oxidation of glucose occurred at -0.625V vs. Ag/AgCl. This potential was selected for chronoamperometry (CA) studies to establish a calibration curve of NPC response to varying glucose concentrations. Two distinct linear concentration-current responses were observed in the CA measurements (Figure 2), and linearity was achieved for both responses using current readings as early as two seconds. A calculated limit of detection (LOD) of approximately 4 μM was attained using the lower concentration range.

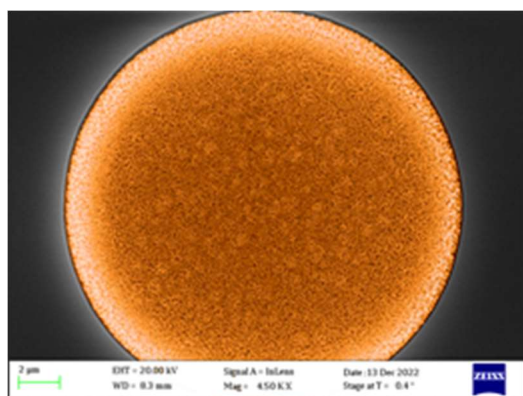


Figure 1 – SEM Image of NPC

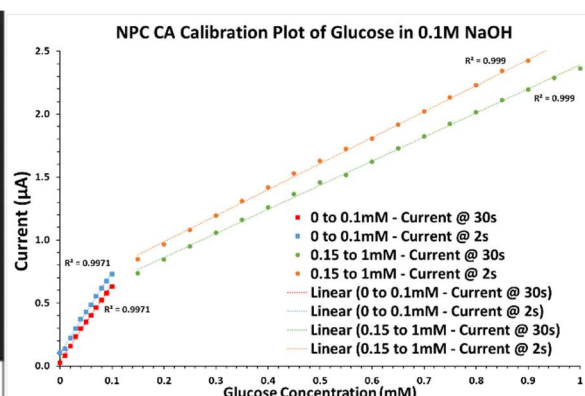


Figure 2 - NPC CA calibration for glucose in 0.1M NaOH

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C4: A biosensor for methotrexate can be designed using dihydrofolate immobilized onto iron magnetic nanoparticles

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Methotrexate (MTX) is an antitumoral agent used to treat acute lymphoblastic leukaemia (ALL) and other types of cancer [1]. High-dose MTX is used to treat children with ALL, requiring a reliable and cheap point-of-care method to allow the measurement of MTX in blood, for immediate actions, considering the side effects of medication [2]. Therefore, the aim of this work was to design a simple electrochemical device to measure MTX. The system configuration consisted of immobilized dihydrofolic acid (DHFA) onto iron magnetic nanoparticles that were adsorbed to a glassy carbon electrode, connected to an electrochemical cell, and challenged with the enzyme dihydrofolate reductase (DHFR). Figure 1 shows a scheme of the biosensor and the electrochemical impedance spectroscopy (EIS) curves obtained when the working electrode, containing modified magnetic nanoparticles, was submerged in the cell and treated with DHFR (as indicated). Curves were collected in a 12.5 mL cell in 50 mmol L⁻¹ phosphate buffer, pH 7.5, containing ferrocyanide/ ferricyanide (3 mmol L⁻¹). A sinusoidal wave with an amplitude of 10 mV and variable frequency in the 0.1 Hz to 1 MHz range was used. The pattern of enzyme binding without NADPH (blue) shows that there was an increase in charge transference resistance (CTR), which is linearly related to enzyme concentration. However, when the enzyme was added in the presence of NADPH there was a decrease in CTR (orange), possibly due to substrate desorption and consumption. Accordingly, the pattern is almost unchanged when the enzyme was previously incubated with MTX (10 mmol L⁻¹) in the presence of NADPH (grey). The different outlines in the presence and absence of MTX suggest that it would be possible to measure this compound using the electrochemical device designed here.

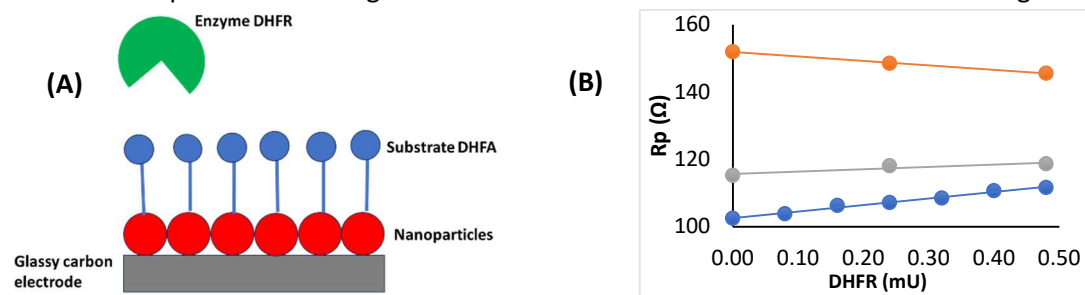


Figure 1. In (A) a schematic representation of the biosensor. In (B) The EIS curves show the results obtained when DHFR was added in the absence of NADPH (blue); DHFR was added in the presence of NADPH (orange); DHFR was previously incubated with 10 mmol L⁻¹ MTX in the presence of NADPH (grey). The difference in the initial values of polarization resistance (R_p) is due to electrode preparation and the addition of NADPH.

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C5: Pre-printing saponification of carbon thermoplastic filaments provide ready-to-use electrochemical sensors

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The fabrication of electrodes using 3D printing provides the unique ability to make sensors for varied analytical applications at mass production¹⁻³. Current available printable carbon thermoplastic filaments often make electrodes with poor electrochemical activity due to the lower amount of carbon present in the filament, this reduces the number of conductive pathways⁴⁻⁶. To overcome this various post printing treatment steps are used to enhance the electrode performance. Our study focuses on employing saponification using hydroxide, to selectively remove polylactic acid (PLA) from carbon thermoplastic filament before 3D printing. Cyclic voltammetry of varying redox probes was used to access the difference between multi-walled carbon nanotube (MWCNT)/PLA and carbon black (CB)/PLA electrodes made with native and modified filament. As the saponification process was prolonged, the resistivity decreased, and noticeable surface changes were observed in the MWCNT/PLA filaments. Electrodes made from the modified filaments (CB/PLA and MWCNT/PLA) exhibited enhanced current responses and faster electron transfer kinetics compared to electrodes made with unmodified filament. Additionally, CB/PLA electrodes produced from the modified filament demonstrated superior electrochemical performance when compared to electrochemically treated CB/PLA electrodes made with native filament. The pre-printing saponification of carbon PLA filaments provided a new approach for fabricating high performance ready-to-use 3D printed electrochemical sensors with utility in applications ranging in sensing and energy storage.

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C6: Electrochemical aptasensor for SARS-CoV-2 detection based on magnetic MOF and screen-printed electrode

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Magnetic metal-organic framework (MMOF) integrated with DNA aptamers and screen-printed electrode are applied for the electrochemical detection of SARS-CoV-2 spike protein as a point-of-care device. Aptamers offer advantages such as high affinity, specificity, chemical stability, easy modification, and cost-effectiveness. The detection mechanism and fabrication steps are demonstrated in Fig. 1. The aptamer targeting spike protein of SARS-CoV-2 is immobilized on MMOF using cross linking agents. A detection probe containing biotinylated-aptamer and streptavidin-peroxidase (SHRP), instead of two antibodies, is applied to save time and money. The H₂O₂ acts as a substrate reduced by streptavidin-peroxidase (SHRP), and hydroquinone is utilized as a mediator for electron transduction. As spike protein increases, the thickness of the immuno-complexes on MMOF also increases. These non-electroactive complexes act as a blocking layer, impeding both the mass transfer of H₂O₂ to active centers of SHRP and the transfer of the mediator hydroquinone to the electrode. An increase in the charge transfer resistance is observed after the formation of immuno-complexes on MMOF due to the increased thickness using electrochemical impedance spectroscopy. Compared with our previous study using an antibody as a detector moiety [1], this developed MMOF-based aptasensor offers a promising approach for the detection of spike protein from SARS-CoV-2, with the demonstrated detection mechanism and fabrication steps providing valuable insights into the design and optimization of such aptasensors for accurate and efficient detection of viral antigens.

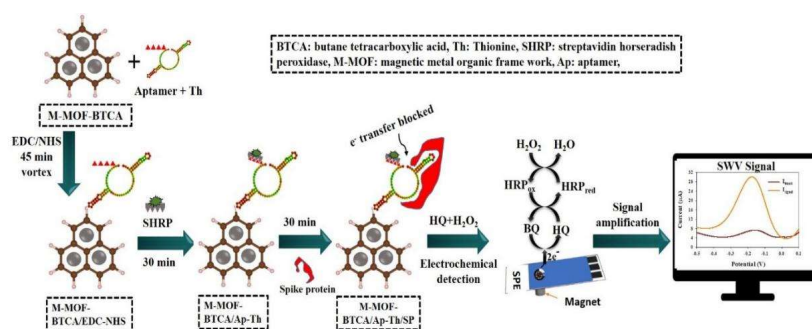


Fig. 1. Illustration of the aptamer-based electrochemical biosensor for the detection of COVID-19 spike protein

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C7: Error, Reproducibility and Uncertainty in Electrochemical Measurements

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Metrology is the science of measurement; it provides the philosophy, vocabulary and mathematical tools to express the confidence scientists have in their measurements and the comparisons made between them [1]. Metrology underpins many aspects of science and engineering in the modern world but its principles have only been haphazardly applied to electrochemical measurements.

This presentation will introduce broad metrological concepts as they relate to electrochemistry and highlight several areas of ongoing research which many researchers may find applicable to their work. Firstly, this talk will address the uncertainty associated with simple electrochemical measurements of potential, including an assessment of the uncertainty introduced by commercial potentiostats and that introduced by common reference electrodes. Secondly, the issue of uncertainty as it relates to more complex measurements such as measuring the performance of a single cell fuel cell will be discussed. Our recent analysis, using experimentally determined sensitivity factors, Figure 1, suggests that the expanded uncertainty on the cell voltage when performing such a measurement is as high as ± 27 mV ($k=2$).

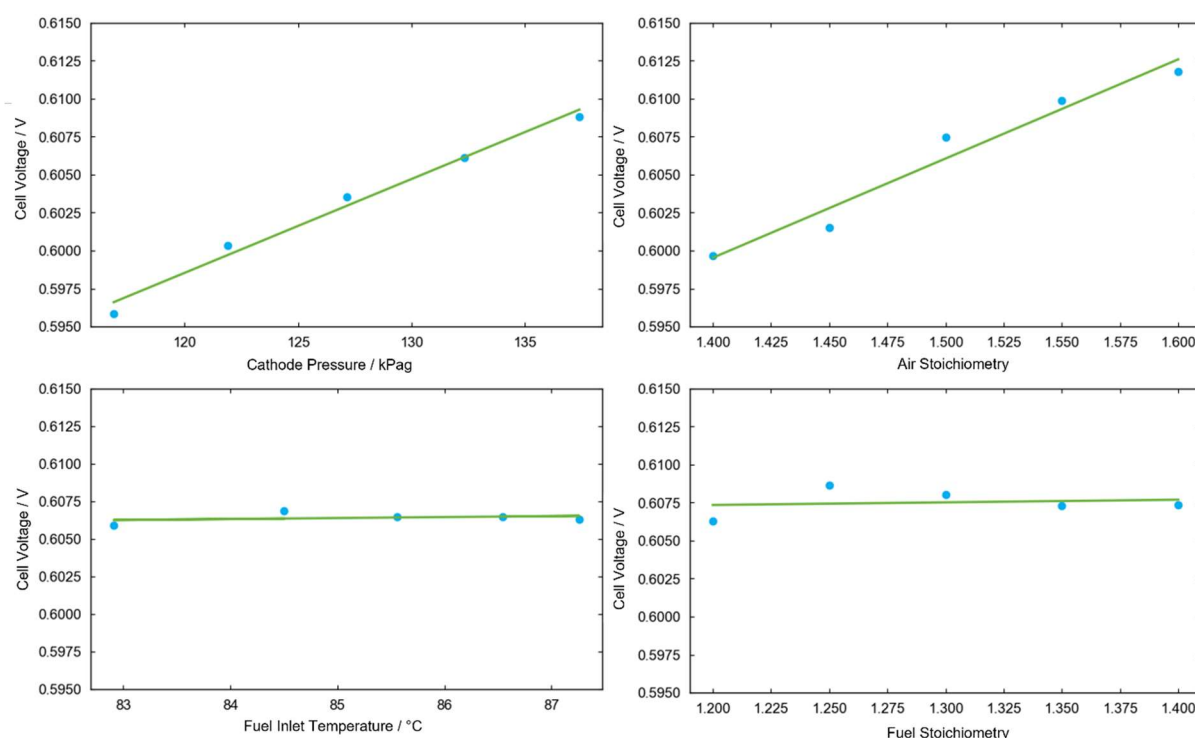


Figure 1: Sensitivity of PEMFC cell voltage at 1 A cm^{-2} to cathode pressure (top left), air stoichiometry (top right), fuel inlet temperature (bottom left) and fuel stoichiometry (bottom right). Blue points represent raw data and green line is a linear best fit.

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C8: Selective detection of protein biomarkers via multifunctional molecular layers from electrografting methods

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Electrochemical biosensors have attracted considerable attention in recent years. This has been driven by their numerous potential applications. One of the most far-reaching of these is the rapid, sensitive, selective, point-of-care detection of disease biomarkers. [1] The preparation of such systems can be achieved by the incorporation of multiple functionalities into molecular films on a sensing electrodes' interface. These functionalities include recognition sites to facilitate selective biomarker recruitment, antifouling moieties to achieve high selectivity, and redox-active species to facilitate transduction without the need to pre-treat the sampling solution with redox probes.

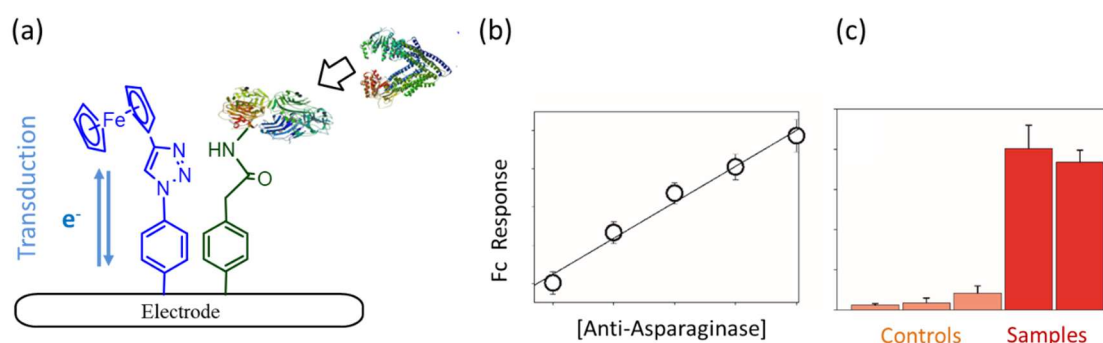


Figure 5 (a) sensing interface for detection of anti-asparaginase (b) an analytical curve showing sensor response to increasing concentration of target anti-asparaginase. (c) relative sensor response to target and controls (serum and non-specific protein).

Herein we present novel and practical strategies for the preparation of such biosensors. These systems are based on electrografting methods using diazonium cations. The performance of such systems depends on control of the precise characteristics of the sensing interface (composition, film homogeneity etc). Hence, careful consideration of grafting conditions is needed to achieve the desired film characteristics. The viability of the sensing platforms is demonstrated via detection of clinically relevant biomarkers. This includes the sensing systems for the detection on c-reactive protein, an inflammation and cardiovascular biomarker [2]; and anti-asparaginase, an important biomarker in monitoring leukaemia chemotherapy [3] (Figure 1). The resulting biosensors are capable of electrochemical detection in clinically relevant concentration ranges.

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C9: Toward completely label-free point-of-care devices using bioreceptor immobilization by hydrogen bonding and differential pulse voltammetry as measurement tool

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Electrochemistry has become an interesting and viable option to develop point-of-care devices (POCDs) for environmental and clinical applications. Electrochemical analysis as detection tool assembles multiples features suitable for the large-scale fabrication of POCDs, such as high sensitivity and precision in the analysis, low cost, feasibility to miniaturization, versatility for the design of electrodes and electrolytic cells with the availability of many printing techniques for its fabrication on low-cost materials. In addition, a wide range of recognition molecules can be implemented with electrochemical analysis, from biomolecules to synthetic organic and inorganic molecules.

The process toward the development of POCDs has been focused by the miniaturization of electrodes, potentiostats and its integration with mobile phones, in addition to the reduction of steps, reagents, and costs of the analyses. In this context, label-free electrochemical biosensors are favoured. It is because they are more economical, require less reagents, and present shorter times of analysis than the labelled ones, which enables their implementation in POCDs.

Here, four completely label-free biosensors for hepatitis B virus (HBV) detection were developed. The biosensors were fabricated on gold surfaces modified with cysteamine or cysteine linkers, immobilizing the antibody (Ab) by hydrogen bonding interactions (H-Bonding) or by covalent bonds, and measuring electrochemical spectroscopy impedance (ESI) and differential pulse voltammetry (DPV). The surface of the biosensors at each stage of the modification process was studied by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The combination of Ab immobilized by H-bonding with the DPV analysis displayed improved repeatability, lower interference to serum matrix and similar limits of detection and quantification than the traditional biosensors with Ab immobilized via covalent bonds and ESI as measurement technique. The Ab immobilization by H-bonding provided a simple and low-cost alternative to covalent bonds. Meanwhile, DPV in a completely label-free assay was faster and exhibited better performance than ESI. The Au-CysT_H-bonding biosensor showed the lowest limits of detection and quantification of 0.05 and 0.14 ng/mL, respectively, a 0-12.5 ng/mL linear analytical range and 100% of recoveries for 1/10 human serum during HBV surface antigen detection.

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C10: Biosensor for rapid measurement of lactate in exhaled breath condensate

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Lactate concentration plays an important role in disease diagnostics. Higher lactate concentrations are associated with sepsis and septic shock ², trauma ³, tissue hypoxia due to acute lung injury ⁴, and respiratory diseases ⁵. Lactate level is also widely used in monitoring athletes' training and fitness as long-term exhausting exercise leads to a rapid increase in lactate level and result in muscle weakening and fatigue ⁶. Compared with the traditional blood sample media which is invasive and capillary blood monitoring is not suitable for routine clinical use, the exhaled breath condensate (EBC) is simple and non-invasive method with no potential for adverse effects for lactate analysis.

In this presentation, a point-of-care electrochemical biosensor is introduced for the EBC lactate analysis. This disposable and low-cost sensor is aimed to be inserted in an EBC collection device developed by our team that enables real-time monitoring and rapid measurements of EBC lactate level. The sensor measurement is done directly after EBC sample collection, that minimizes the risk of sample degradation and is cheaper than the traditional laboratory techniques such as fluorometry or mass spectrometry.

The sensor is modified with poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), Prussian blue (PB) and lactate oxidase (LOD) enzyme. Lactate concentration is measured from amperometric current response generated by the redox reactions on sensor surface. The enzyme gel formulation is optimized based on rotating disk electrode (RDE) experiments and kinetics analysis, investigating the effect of LOD concentration and gel thickness, and was then applied to disposable sensors.

Finally, human EBC analysis is conducted from healthy subjects at rest and after 30 min of intense aerobic cycling exercise. Sensor's results in real EBC lactate measurements demonstrate a good correlation with fluorometry and mass spectrometry calibrations and exhibit high stability and sensitivity in both short-term and long-term use. Mass production of the sensor is done by robotic gel dispensing using a Biodot aspirate dispensing machine.

Note: This presentation is based on my recent publication 'Rapid Measurement of Lactate in the Exhaled Breath Condensate: Biosensor Optimization and In-Human Proof of Concept' in ACS Sensors (doi.10.1021/acssensors.2c01739)

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C11: Real-time electrochemical Sensor for the detection of endocrine disruptors in Water samples

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Keywords: agritech; endocrine disruptors; estrogen; electrochemical; nanomaterials; carbon; environmental monitoring

Estrogen compounds have been listed on the watch list of substances for European Union-wide monitoring in the field of water policy according to the Directive 2008/105/EC due to their endocrine disrupting properties.[1] Endocrine disrupting chemicals (EDCs) are compounds that alter the hormonal balance in an organism. This can lead to ill-health effects on the organism itself and its progeny such as cancer, neurodevelopment issues, obesity, reproductive issues and thyroid function issues[2]. There has been a steady rise in the number of EDCs, specifically estrogen endocrine disruptors found in air, water and food. Estrogen compounds can get into the water supplies via run-off from agricultural practices, pharmaceutical waste and sewage. Since pharmaceutical compounds such as estrogen cannot be effectively removed from wastewater, estrogens can end up in river waters causing detrimental harm to the local wildlife and can be reintroduced to the drinking water system. These emerging contaminants leaves a gap in the market for a real-time and reliable sensor that can detect pollutants quickly and without the need for lab analysis. The most commonly found estrogen compounds in river water is Estradiol (E2), a natural estrogen and ethinylestradiol, (EE2), a synthetic estrogen. In this study, we develop electrochemical sensor that can detect these estrogen compounds in water samples. The sensor was modified with carbon based nanomaterial which made it selective for estrogen detection. The sensor was showing good sensitivity towards the compound and will be tested for river water samples.

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C12: Observing Confined Local Oxygen-Induced Reversible Thiol/Disulfide Cycle with a Protein Nanopore

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Disulfide bonds are of significance in thiol-based redox regulation^{1,2}. However, due to the lack of analytical tools, there is still little knowledge about how local O₂ under protein confinement mediates the reversible thiol/disulfide cycle^{3,4}. Herein, a protein nanopore reactor inside a glove box was developed for acting as O₂ confinement as well as a single-molecule sensor for real-time monitoring of the reversible thiol/disulfide cycle. Results demonstrated that the presence of local O₂ molecules in protein nanopores can facilitate the redox cycle of disulfide formation and cleavage by promoting a higher fraction of effective reactant collisions due to nanoconfinement. The further kinetics calculation described that the negatively charged residues near reactive sites facilitate proton-involved oxygen-induced disulfide cleavage under protein confinement. The unexpectedly strong oxidation ability of confined local O₂ may play essential roles in cellular redox signaling and enzyme reactions.

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C13: 3D-Printed Microfluidics system coupled with electrochemical pH control for Enhanced Chlorine detection

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In this work we present the design of a novel technique for amplifying chlorine detection via a microfluidics platform for use with electrochemical sensors. This platform enables experiments to be performed in hydrodynamic conditions, utilising convection as a secondary mode of mass transport for the analyte. All experiments have also been corroborated using COMSOL Multiphysics simulations. The platform is constructed using 3-D printing, which has been used for macroscale electrode microfluidics previously [1]. However, the sensors utilised herein are of the ultramicro scale with complex geometry. This geometry allows bipotentiostatic electrochemistry to be utilised enabling localised electrochemical pH control. This effect, while studied in quiescent conditions, remains poorly understood in hydrodynamic conditions at this scale, though has been investigated at the macroscale.[2] By utilising these two phenomena in tandem, we demonstrate, both experimentally and through simulations, the feasibility of this coupling at the ultramicro scale. We report a near 30-fold enhancement of signal for a set concentration of hypochlorous acid, in water samples, when high flow is applied. Crucially, this enhancement was obtained while electrochemically regulating the local pH. Furthermore, the high linearity of the current enhancing effect of increasing flowrate is demonstrated. In boosting the signal, lower limits of detection can be obtained before signals are lost to background noise.

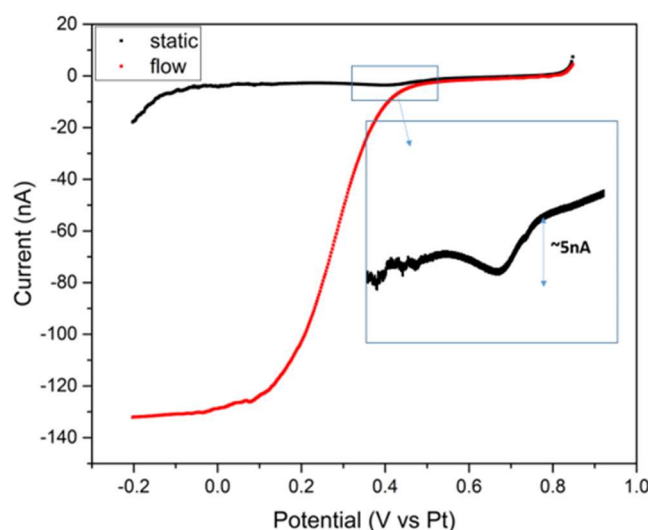


Figure 6 Hypochlorous acid detection in static and high flow conditions. Inset shows the activity of static scans in greater detail

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C14: Development of an electrochemical biosensing array for simultaneous detection of urinary metabolites for disease profiling

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Signalling molecules in the bladder urothelium have been linked to function and dysfunction in the lower urinary tract^{1–3}. These are acetylcholine, adenosine triphosphate, and nitric oxide, which regulate contraction and relaxation of bladder smooth muscle. Though these are hard to detect, their respective metabolites, choline, xanthine, and nitrite can be detected in urine. These metabolites are stable and can serve as an indirect measurement of bladder function.

Overactive bladder (OAB) is a syndrome that presents with urinary urge incontinence and increased urinary frequency⁴. It affects up to a third of adults but is underreported due to patient shame and believing it is just due to ageing⁵. It is a symptom-based diagnosis, highlighting the need for a rapid diagnostic test that can detect these signalling metabolites and relate them to bladder function.

Our biosensing multi-analyte array can be cheaply manufactured for use in clinical and non-clinical environments. The 3D printed device houses four working electrodes consisting of carbon nanotube and platinum black composite which directly detects nitrite and peroxide⁶. This allows two working electrodes to detect peroxide generated by choline oxidase and xanthine oxidase when in the presence of their respective metabolite in a urinary matrix. The null electrode is used to subtract interference from electroactive molecules as well as nitrite.

The biosensing array was evaluated on urine from an OAB rat model. The metabolites were correlated with functional data such as urinary frequency and volume per micturition to evaluate its potential as a point-of-care diagnostic.

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C15: Evaluating the impact of different electrode surface patterns of 3D printed carbon thermoplastic electrochemical sensors

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Given that all electrochemical sensing techniques are based on electrochemical processes that occur at the electrode surface, the structure of the electrode surface plays a crucial role in electrochemical sensor development. To date, most approaches to manufacturing electrodes, including 3D printing, make electrodes with flat surfaces. Given the unique capabilities of 3D printing to make complex and unique electrode surface geometries, we investigated how varied electrode geometries altered the electrochemical responses. In the proposed work, 3D printed carbon black polylactic acid electrodes with nine different surface morphologies were made where they had identical surface areas. These were compared to a flat electrode. To evaluate the performance of the electrodes, measurements were conducted in three different redox probes (ferrocene methanol, ferricyanide, and dopamine).

Our findings highlight that even though the surface area of the electrode is identical, the geometry of the electrode surface can influence the performance of the electrode. Electrodes that had a dome, and flag pattern on the electrode surface showed the highest oxidation currents and lower values for the difference between the anodic and cathodic peak current (ΔE). However, designs with rings had lower current values and higher ΔE values. These differences are most likely due to variations in the accessibility of conductive sites on the electrode surface when different patterned designs are used. Our findings highlight that when making electrodes using 3D printing, utilizing the scope to create specific patterns on the electrode surface can significantly enhance the electrochemical response and thus this aspect should be considered when manufacturing sensors.

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C16: Triphasic Electrochemical Processes Enhanced by Polymers of Intrinsic Microporosity

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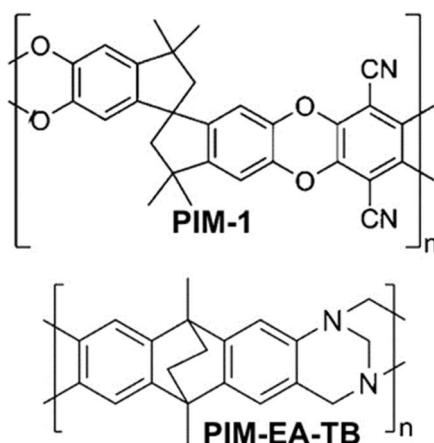
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Triphasic electrode processes require gas|liquid|solid environments, which can be stabilised by microporous materials. Polymers of intrinsic microporosity (or PIMs) are highly processable and readily applied to electrode surfaces to modify reactivity of gaseous species. Two prototypical PIMs are PIM-1 [1] and PIM-EA-TB [2] (see Figure). Both possess rigid molecular backbones and pack into porous solid films with high surface area and with typically 1 nm pore size [3].



PIMs have found their way into electrochemical applications in energy devices [3] and in sensors [4], but also provide fertile ground for fundamental study on triphasic processes. The intrinsic microporosity, for example for PIM-1, is shown to lead to binding and transport of gaseous species (hydrogen, oxygen, etc.). Concentration and activity of the gaseous species at the electrode surface can be enhanced [5].

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C17: Porous Organic Materials for Metal-Free CO₂ Capture and Electrocatalytic Conversion

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In the quest for new materials to help to solve global challenges, we have focused our efforts in recent years on the production of functional porous polymeric materials.[1a, b] The focus in this presentation will be on various strategies we are employing to tune both structure and function in these materials, and how we exploit this control to address the significant challenge posed by the high levels of CO₂.

The field of microporous conjugated polymers (CMPs), especially nitrogen-rich 3D CMP analogues of the well-known conducting polymer, poly(aniline), will be introduced.[2] Various simple design rules will be explored, showing the successful use of simple inorganic salts to carefully tune porosity, pore size distributions, as well as CO₂ uptake with high selectivity.[3a, b] The versatility of these materials will be shown in their application for gas capture, and routes to the electrocatalytic conversion and fixation of CO₂ as useful feedstock into high value chemicals will be explored.[4] Future focus areas of research will also be highlighted.

Keywords: porous organic materials, CO₂ capture, CO₂ conversion, energy storage

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C18: Porphyrin-like designer catalysts for electrocatalytic H₂ evolution and selective CO₂ reduction

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The global use of fossil fuels results in unsustainable levels of CO₂ gas being released into the atmosphere, furthering the impacts of global warming.¹ Possible capture of CO₂ from high emission processes and subsequent selective reduction (CO₂ reduction reaction, CO₂RR) to convert it into renewable fuels could move those processes towards carbon neutrality.

To move towards carbon zero, green hydrogen is a desirable alternative to fossil fuels. Hydrogen has a higher energy density and only produces water as a waste product. 'Green' hydrogen is produced from water using renewable energy (hydrogen evolution reaction, HER). Most hydrogen produced currently, for use in industry, is 'brown' hydrogen made from fossil fuels in energy intensive and carbon emitting processes, so this must also be replaced by green hydrogen.

Catalysts are needed to reduce the energy of chemical processes, such as HER and CO₂RR,² to make them more energy and cost efficient. The CO₂RR is an energy intensive process with many possible products, highlighting the need for catalysts that can not only reduce the energy required for reduction but also produce the desired useful products selectively.

We have prepared a range of porphyrin-like dimetallic macrocyclic complexes^{3,4} and these are now being tested for electrocatalytic activity for HER and CO₂RR. This testing is being carried out under both homogenous and heterogenous conditions, the latter through immobilisation of the catalysts on solid supports. This presentation will cover the synthetic steps involved in producing these macrocyclic complexes and the results of the electrochemical HER and CO₂RR testing on selected complexes.

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C19: Electrogenated Microporous Conjugated Polymers based on Star-shaped Oligomer Derived from Triphenylamine: Exploring Structure-Properties Relationships

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Electropolymerization is a valuable approach for the synthesis of polymeric electrode materials, involving the direct electrochemical deposition of insoluble polymers onto electrode surfaces through the coupling reaction of soluble monomers. This strategy holds promise for obtaining highly porous electrode materials with excellent performance in various applications. Particularly for the synthesis of conductive conjugated polymers, which are typically insoluble due to their rigid and highly conjugated network structure, electropolymerization offers a suitable method to obtain electroactive polymers onto conductive substrates, allowing precise control over their shape and dimensions while circumventing issues related to processability. Electroactive conjugated microporous polymers (CMPs) represent a distinct class of materials characterized by the combination of extended π -conjugation and a permanently microporous framework. These polymers offer notable advantages including exceptional physical and chemical stability, straightforward synthesis, high surface areas, and microporosity [1]. The desired microporous architectures are achieved through the covalent connection of rigid and contorted molecules and for this building blocks with a minimum of two polymerizable groups, are employed to facilitate the formation of highly crosslinked structures. Triphenylamine (TPA) presents an attractive option for constructing conjugated crosslinked building blocks with several beneficial properties, including a low redox potential, fast electron transfer rate, and efficient hole transport capacity. Its propeller-like structure further enables the development of cross-linked microporous polymers based on TPA, leading to enhanced capacity and superior rate performance [2]. Moreover, TPA serves as an electrochromic chromogenic group, displaying a noticeable colour contrast between its neutral and oxidized states [3].

Taking advantage of TPA's geometric features and electrochemical activity new linear and star-shaped oligomers were synthesized, incorporating TPA as both the peripheral electropolymerized units and the core unit. Thin-film polymers derived from these oligomers were prepared through electropolymerization, utilizing ITO-coated glass substrate. The electrochromic and pseudocapacitive properties of these films were examined. Remarkably, all TPA-based polymers demonstrated exceptional electrochromic properties, including high optical contrast, rapid response time, and good coloration efficiency. Moreover, considering their ability to selectively absorb light due to different colours, these polymers can be view as multifunctional electrochemical energy storage systems that hold potential for applications in smart windows, architectural glass curtain walls, and other fields, offering benefits such as privacy, energy supply, and sustainable living [4].

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C20: Proton Enrichment and Surface Charge Dynamics in Nanopores

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The acid-disassociation of surface groups on the walls of a glass nanopipette generate the surface charges that drive fundamental nanoscale transport behaviors such as ion current rectification. The disassociation of surface groups is in fact influenced by the local H^+ and OH^- concentrations, which themselves deplete or accumulate within the conical nanopore when the voltage across it is changed.[1,2] Despite this, most models of ion transport in conical nanopore systems assume a fixed surface charge and ignore localized pH changes. To study the dynamic interplay between the magnitudes and distributions of ion concentrations, pH distributions and the localized surface charge, and the overarching effect of these parameters on the ion-current rectification as a function of electrolyte concentration, a new finite element model, that dynamically calculates the surface charge based on surface-site density, surface-site acidity constants, and localized pH values, has been developed. The surface charge density is revealed to be non-linear across the nanopore and highly asymmetric at different applied potentials, as well as highly influenced by the bulk pH and electrolyte concentrations. The potential implications of our results are discussed in the context of both fundamental nanopore transport studies and charge mapping studies that use scanning ion conductance microscopy.

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D1: Relationship between Mn Oxidation State Changes and Oxygen Reduction Activity in (La,Ca)MnO₃ Probed by In-Situ XAS and XES

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The increased interest in electrochemical energy-storage/conversion systems such as metal-air batteries, fuel cells, and electrolyzers arising from the interest in electrification of energy supply and distribution has motivated many studies of oxygen reduction and evolution reaction (ORR and OER) oxide electrocatalysts. The development of more efficient and stable materials is a critical step for the final introduction of these devices in the market.

Mn-based oxides are among the most active catalysts toward the oxygen reduction reaction (ORR) in alkaline solutions. Fundamental understanding of electrocatalysis at perovskite electrodes has been dominated by the finding of activity descriptors, where the prevailing view is that a single electron occupancy of the e_g orbital of the metal at the B-site of the perovskite structure represents the optimum configuration for oxygen electrocatalysis. This trend implies that LaMnO_{3+δ} ($e_g \sim 1$) should be more active than CaMnO₃ ($e_g \sim 0$). However, numerous works have shown that the orbital occupancy on Mn states changes in the potential range relevant to the ORR. Thus, understanding the mechanism at such complex materials requires direct information regarding the changes in the orbital occupancy of the active sites that can only be achieved using operando characterization techniques.

In this talk, we will explore how X-ray based techniques such as X-ray absorption near-edge structure (XANES), extended X-ray absorption fine structure (EXAFS) and X-ray emission spectroscopy (XES) can lead the way to materials' fundamental understanding. In this work, in-situ XAS and XES are used to provide details regarding the role of the accessibility and extent of redox activity of the Mn ions in determining the ORR activity of La_xCa_{1-x}MnO₃ oxides, with XANES providing the average oxidation state, EXAFS providing the local coordination environment, and XES providing the population ratios of the Mn²⁺/Mn³⁺/Mn⁴⁺ sites as a function of the applied potential.

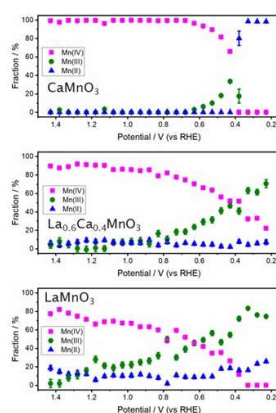


Figure 1. Percentage of the different cation species for LaMnO₃, La_{0.6}Ca_{0.4}MnO₃ and CaMnO₃ at the different potentials under study obtained by linear combination fitting of the XES data.

D2: Probing the Structure of the Electrochemical Interface using In-situ Surface X-ray Diffraction Techniques

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As the development of electrochemical surface science progresses, there is a growing need for a comprehensive understanding of the atomic structure of electrochemical interface, both of the solid electrode and in the liquid electrolyte. This is because changes in the atomic structure across the interface induced by changes in the electric field can affect the system's reactivity and stability [1]. These processes can be subtle and do not always involve the direct transfer of charge between electrode and electrolyte. Examples include metal surface relaxation and surface reconstruction, as well as charging of the double layer, which leads to rearrangement of the electrolyte side of the interface [2]. The need to understand these phenomena has necessitated the development of in-situ analysis techniques that can probe the structure of the electrochemical interface under reaction conditions. Surface x-ray diffraction (SXRD) utilizing synchrotron radiation has been prominent in the study of single crystal metal surfaces in the electrochemical environment. It offers generally non-intrusive, in-situ, 3D characterization of the interface structure, including the liquid side, in a relatively easy to control environment. To further extend the fundamental understanding of the interface structure, we have been developing resonant surface x-ray diffraction (RSXRD), a technique which combines diffraction with spectroscopy, to investigate the charge distribution in the double layer region. Combining experimental data and first-principles calculations, in-situ RSXRD was used to establish the charge distribution both at the Pt(111) electrode surface and at the Cu(001)-c(2x2)-Br electrode surface [3,4]. Both systems demonstrated the validity of the technique, and the results indicated the presence of a surface dipole within the metal electrodes and, for the Cu-Br system, the extracted electron density of the interfacial atoms suggest that the Br-adatoms couple most strongly with the subsurface Cu layer.

In this talk I will present the latest SXRD and RSXRD results from a study of the potential dependence of Pt(111) and Au(111) electrodes in 0.1 M CsOH with the aim of understanding the role that the Cs⁺ cation plays in the interface structure. In addition to standard structural measurements (CTR data), RSXRD measurements were made at the Cs L₃ adsorption edge (5012 eV) and, in the case of Pt(111) also at the Pt L₃ adsorption edge (11,564 eV). The results give unique insight into the structural and electronic properties of the electrochemical interface at negative potentials, where the surface is covered in specifically-adsorbed hydrogen, to positive potentials, where hydroxide species (OH_{ad}) are adsorbed.

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D3: Development of Spectro-electrochemical Cell for Operando NAP-XPS/NEXAFS Investigations

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To track the chemical state and structural properties of catalytically active materials under realistic reaction conditions, in order to understand charge transfer at the liquid-solid interface, CO₂ activation, and surface carbon intermediate species, reaction cells are critical for operando near ambient soft X-ray photoelectron and absorption spectroscopy (NAP-XPS/XAS) experiments. The main challenges with developing operando NAP-XPS/XAS cells for photocatalytic and electrocatalytic reactions are that these reactions are typically performed in liquid phase at the solid-liquid interface and that the catalyst must be exposed to UV-visible irradiation during reaction (and apply an external potential in both electrocatalysis and photoelectrocatalysis). The presence of the liquid phase alone poses a challenge due to the high absorbing background, but external excitation with UV-visible light or electrons imposes additional limitations on cell design. In order to address these challenges while probing catalyst surface during the reaction, we have developed back-side illuminated operando reaction cells for synchrotron-based NP-XPS and NEXAFS studies. Our design concept is based on a modular design and uses non-metal (PEEK material) body, and replaceable membranes which can be either of X-ray transparent silicon nitride or of water permeable polymer membrane materials (e.g. Nafion). These membrane materials are particularly suitable for liquid flow or electrochemical cells and enable measuring photoelectrons emitted from the membranes or from catalyst material deposited at the solid-liquid interface outside the cell. The preliminary results of in-situ NAP-XPS and NEXAFS measurements (from B07 beamline@Diamond) on electrochemical reduction with a Cu catalyst and oxidation with an IrO_x catalyst will be presented. The developed system is highly modular and can be used in the laboratory or directly at the beamline for operando XPS/XAS measurements (**Figure 1**).

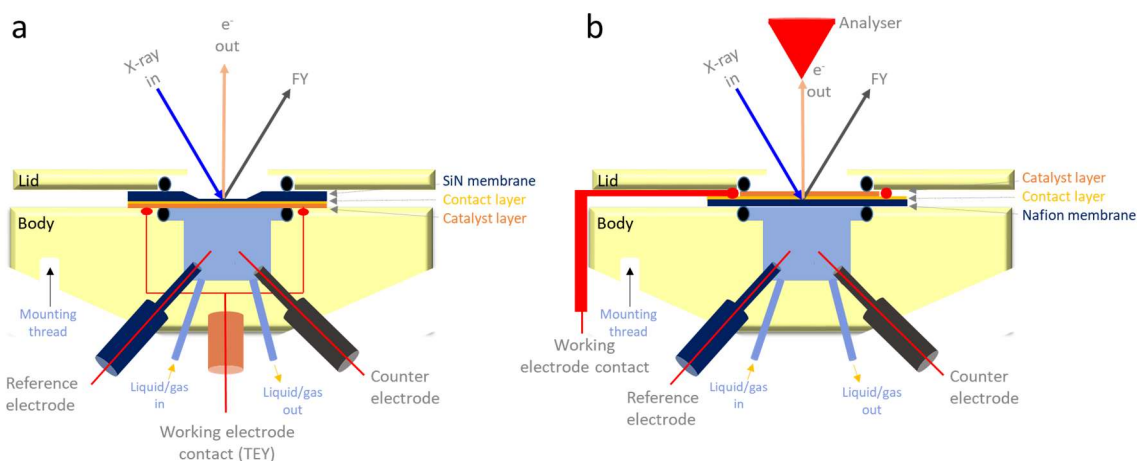


Figure 1. Schematic diagram of the elctro(photo)chemical flow cell for operando measurements: (a) NAP-XAS with silicon ninitde base working elctrode assembly and (b) NAP-XPS/XAS with permeable polymer membrane materials.

D4: EPR spectro-electrochemistry as a tool for studying radical generation on boron doped diamond electrodes.

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The ability of boron doped diamond (BDD) electrodes to generate highly oxidising free radicals is of great interest for many research applications including electrochemical synthesis and electrochemical advanced oxidation. Electron paramagnetic resonance (EPR) spectroscopy is a natural choice to study radical generation on BDD surfaces. In this talk we will present our efforts to date in using spectro-electrochemistry in our electrochemical research.

For detection of radicals with relatively long lifetimes, ex-situ EPR can be used, where the radicals are generated in solution outside the spectrometer and the solution transferred to the EPR for measurement. However, short-lived radicals (such as the highly oxidising hydroxyl radical, critical in wastewater treatment systems), require stabilisation using spin traps, such as 5,5-dimethyl-1-pyrroline N-oxide (DMPO), to generate a spin trap-adduct.¹ This spin-adduct is then detected, resulting in indirect identification of the original radical.

However, in the case of radical generation by electrochemical means, one potential pitfall which is often overlooked is what happens if the potential required to generate the radical of interest is also capable of electrochemically oxidising the spin trap. We show this is of critical importance in the case of hydroxyl radical generation, via water oxidation. In particular we focus on the common spin trap, DMPO, for hydroxyl radicals and show that the same spin trap adduct can be generated via DMPO trapping of the hydroxy radical and electrochemical oxidation of DMPO in the presence of water.² We discuss the implications of such results for EPR detection of electrochemically generated radicals.

To overcome the limitations associated with these indirect, ex-situ measurements we are now developing in-situ methods for EPR spectro-electrochemistry and present our efforts to date. The first step in this work has been to systematically study 3D printed materials which are suitable for use in the EPR cavity, in order to circumvent the limitations associated with traditional quartz cells by enabling rapid prototyping and more complex cell designs.

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D5: Using operando reflection optical microscopy to explore the electrochemical and electrochromic properties of $\text{Li}_2\text{Ni}_2\text{W}_2\text{O}_9$

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One of the challenges in the field of electrochromic devices is to find an anodic electrochromic material with good coloration efficiency, transmittance modulation, and cyclability to be used at the positive electrode.

NiO has been heavily investigated for this purpose, being doped with lithium and/or tungsten in order to improve its performances and its cyclability upon lithium (de)insertion [1,2]. The exploration of the Li_2O -NiO- WO_3 ternary diagram led us to the discovery of a new phase, $\text{Li}_2\text{Ni}_2\text{W}_2\text{O}_9$, crystallizing in the Pbcn orthorhombic space group. Its layered, corundum-like crystal structure allows this material to reversibly uptake 0.75 Li^+ equivalent ($\sim 31 \text{ mAh.g}^{-1}$) when cycled between 2.5 and 5.0 V vs Li^+/Li . Although its specific capacity is low, $\text{Li}_2\text{Ni}_2\text{W}_2\text{O}_9$ is quite remarkable for its good capacity retention, as well as its structural stability through cycling. We completed our study of $\text{Li}_2\text{Ni}_2\text{W}_2\text{O}_9$ with an operando reflection optical microscopy experiment, in order to track the optical properties of the material at the single particle scale, and at a scale of a few hundreds particles as well. From this experiment, we proved that $\text{Li}_2\text{Ni}_2\text{W}_2\text{O}_9$ is an anodic electrochromic material, and we could establish that lithium insertion in the material is kinetically limited at the single particle scale.

Overall, this study opens the way for the synthesis of new materials crystallizing in the Pbcn space group, and highlights how operando optical microscopy measurements can shed some light onto the electrochemical mechanisms of battery materials.

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D6: Correlation of excess lithium, ‘dead lithium’ and functional layers in ‘anode-free’ lithium metal batteries

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Since the deposition of lithium metal rather than lithium ion intercalation into graphite offers a tenfold increased gravimetric capacity for the negative electrode, lithium metal batteries are considered as the successor of widely commercialized lithium ion batteries, which are approaching their theoretical limits in terms of energy density ^{1–3}. While in conventional lithium metal batteries, lithium from the positive electrode is deposited on a pre-existing lithium metal electrode, ‘anode-free’ lithium metal-based batteries further maximize the energy density by abandoning excess lithium and exploiting the lithium reservoir from the positive electrode. Besides reduced volume and mass, in-situ formation of lithium metal deposits simplifies cell assembly, while mitigating safety concerns upon storage, thereby reducing costs for cell materials. This indeed renders this cell concept appealing for commercialization ^{4,5}. However, these benefits come at the expense of limited cycle life, since an excess lithium reservoir could replenish losses of active lithium upon cycling, which is not the case for limited excess electrodes. Thus, irreversible capacity losses upon cell operation limit the achievable energy density as well as cycle life of the batteries, and should be monitored carefully ⁶. Notably, mechanistic details of capacity fading in case of NMC-based ‘anode-free’ lithium metal batteries unravelled based on NMR spectroscopy revealed that this cell chemistry initially contains an apparent excess lithium reservoir that is clearly decisive for the actual extent of both capacity losses and cell longevity. Our approach of combining NMR spectroscopy to quantify and distinguish origins of capacity losses and (dynamic) impedance spectroscopy to resolve occurring phenomena at the negative electrode interfaces unambiguously demonstrates that the excess amount of lithium is created by the kinetic limitation of NMC in the initial cycle and does not only stabilize the discharge capacities by replenishing active lithium losses but also serves as ionically conductive layer to corroborate complete lithium stripping while reducing the fraction of ‘dead lithium’ formation. Once all excess lithium has been utilized for replenishing irreversible lithium losses, the absence of conducting lithium metal in the discharged state (that is, no residual lithium metal remaining on the copper current collector) yields substantially increased impedances for charge transfer at the negative electrode and thus accelerated formation of ‘dead lithium’. Nevertheless, introducing an ionically conducting functional layer that alloys with lithium alleviates the high impedances, allowing for more thorough stripping. As a consequence, less capacity is lost to electronically insulated ‘dead lithium’ fractions, thereby boosting the achievable reversibility and cycle life of ‘anode-free’ lithium metal batteries, in principle paving the way towards industrial application of high energy density cells.

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D7: Why Do Similar Molecules Respond Differently To Electric Fields? Hydrogen Bonding Effects in Biomimetic Membranes

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The biological membrane is the gateway to the cell, allowing it to communicate with other cells and to control internal composition and the ion gradients needed to drive its processes. The basis of its structure is a lipid bilayer that contains a range of functional proteins, receptors and signalling molecules [1]. Ion gradients and asymmetric distribution of lipids give rise to strong electric fields across the membrane, which can be conveniently mimicked with electrochemical experiments [2]. In situ structural techniques can then be employed to understand the effect of the field on the membrane [2]. It is now becoming accepted that the nature of the lipid components of the bilayer is as important to membrane function as the proteins. Certainly, if we are to understand the action of an electric field on membrane proteins, we must first understand how the lipid bilayer behaves.

In this study, we investigate the interactions of a common sphingolipid with an applied electric field. Sphingomyelin (SM) plays a key structural role in the plasma cell membrane and is a component of lipid rafts, in which many trans-membrane proteins are embedded [3,4]. Its structure differs from that of the other primary component of the outer membrane, phosphatidylcholine (PC), in the connection of the hydrophobic tail groups to the phosphocholine headgroup. PC chains are connected to a glycerol backbone via ester groups, while the SM backbone contains a hydroxyl group and an amide linkage. These functional groups enable strong intermolecular hydrogen bonds to form, resulting in strong mechanical properties. We show that these hydrogen bonds also result in significant differences in electrochemical phase behaviour between N-palmitoyl SM and its close structural analogue, dipalmitoyl PC (DPPC). In situ infrared spectroscopy shows that SM forms small clusters of molecules linked via amide hydrogen bonds. As the electric field is increased, these interactions are broken and replaced with interactions with water molecules entering the bilayer. This structural change is likely to be why a single change in chain tilt angle is observed for SM bilayers but not DPPC bilayers – DPPC chains return to their original tilt angle on further increasing field strength. The difference in lipid structure is subtle, yet has profound effects on electrochemical phase behaviour. Comparing these results with previous comparisons of inner membrane molecules [5] suggests that multiple types of hydrogen bonding interaction may also be responsible for the differences observed in those cases. The results are important because they show membrane polarisation can have very different effects in different regions of the cell membrane, which can strongly affect local membrane structure and tension and sphingolipid cell signalling processes.

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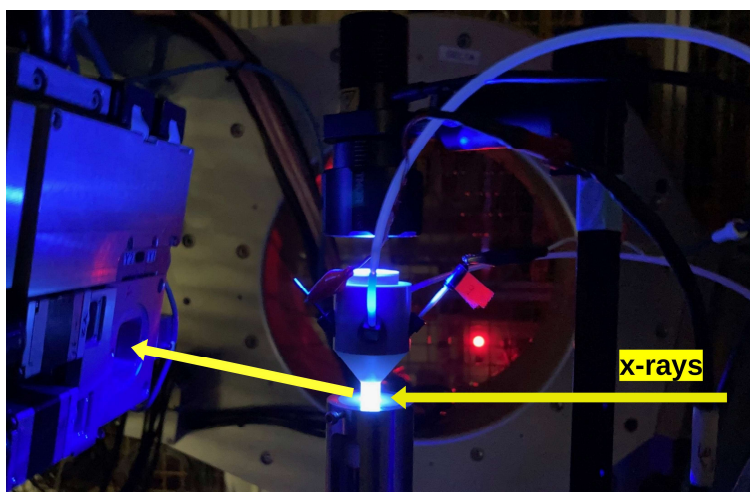
D8: In-situ and Operando Characterization of Electrochemical Interfaces by Surface X-ray Diffraction and Scattering

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The high transmission through solid and liquid materials makes high energy x-rays an incredibly versatile tools for the characterization of electrochemical surfaces and interfaces during operando and in-situ experiments. The I07 beamline at Diamond Light Source [1], is dedicated to the structural study of interfaces using surface and grazing incidence x-ray diffraction and scattering techniques. The beamline is open to external users and offers a variety of different sample environments for the investigation of chemical processes in real reaction conditions, including different cells and systems for electrochemical experiments. In this contribution the different capabilities of the beamline and the diffraction/scattering techniques will be presented, The possible applications to the characterization of surface dynamics in electrochemical systems will be also showcased using results from recent experiments in photo-electrochemistry and electrodeposition.



Flow cell for combined surface x-ray diffraction and photo-electrochemical experiments

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D9: New Cell Designs and Sample Configurations for Operando Raman Spectroscopy of Battery Electrodes

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Reliably measuring the chemical and structural properties of electrode materials is critical to the development of electrochemical energy storage technologies with improved performance, durability, safety and cost. A wide variety of techniques are available for this purpose, but the dynamic nature of the measured properties typically necessitates characterisation under operating conditions, which often leads to a compromise between the quality of the physicochemical data generated and how well the electrochemical environment reflects that of a real working device. For example, in the case of operando vibrational spectroscopy of battery materials, the need to employ optically transparent windows places constraints on electrochemical cell geometry and can introduce undesirable side-effects such as limited electrical conductivity and difficulty maintaining sustained pressure within the cell stack. Furthermore, gaining optical access to the active material or interface of interest is challenging in the case of commercially-processed electrodes, which are mounted onto opaque metal foil current collectors.[1]

Here we present our recent work in addressing these challenges for the case of operando Raman spectroscopy of electrode materials for lithium-ion batteries. We first describe different solutions to the problem of optically accessing the active material in the case of foil-backed electrodes, including a through-hole configuration and the use of ion beam milling to selectively etch the current collector foil. We also demonstrate the use of numerical modelling to guide the design of the internal cell and sample configuration. Secondly we present an alternative cell design that employs a gas-pressurised window to sustain internal stack pressure, whilst enabling in principle the coupling of operando Raman spectroscopy with X-ray absorption and emission spectroscopy. These advances are expected to pave the way toward minimally invasive spectroelectrochemistry of emerging energy materials.

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D10: The importance of sp^2 bonded carbon in electrochemical ozone production using freestanding boron-doped diamond anodes

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Dissolved ozone in water is a potent disinfectant used in many different applications due to its highly oxidizing nature. It has a half-life of ~30 mins in water, so it must be produced at the point of use [1]. Electrochemical ozone production (EOP) is a favourable method due to its scalability, simplicity and ability to generate ozone in-situ. EOP produces dissolved ozone directly through water oxidation by flowing a solution through two electrodes and applying a voltage. Boron-doped diamond (BDD) has been explored as an electrode material for EOP cells as it presents many advantages, such as mechanical robustness and chemical inertness [2-4]. In the literature there is debate concerning the role of sp^2 bonded carbon, with some papers stating the BDD should be sp^2 bonded carbon free [4] and others finding that its presence increases EOP [3].

In this work, we resolve the issue of the impact of sp^2 bonded carbon on EOP rates by controllably introducing sp^2 bonded carbon into the surface of freestanding BDD electrodes, over the range of 5-80 %, using a laser micromachining approach. An EOP cell is designed incorporating a Nafion membrane and the BDD electrodes, which can be used to generate dissolved ozone, the latter which is detected using UV-vis [5]. We find sp^2 bonded carbon has a direct impact on the rate of EOP [6]. We also find when using equivalent electrodes made all from sp^2 bonded carbon (glassy carbon) the electrodes dissolve very quickly under the same operating conditions. This has prompted us to explore in more detail the structure of the sp^2 bonded carbon on BDD before [7] and after long-term testing using transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS).

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D11: Exploring Boron Doped Diamond as an Electrocatalyst Support for Alkaline Water Electrolysis

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Green hydrogen generation, that is, hydrogen generation combined with green energy sources, is a promising approach to decarbonising the several sectors in the United Kingdom.¹ Of the methods for green hydrogen generation, electrochemical water splitting is the most mature and is receiving significant research interest. For alkaline water electrolysis, performance is limited by the activity and durability of the catalyst at the cathode.

Boron Doped Diamond (BDD) has proven to be a popular electrode material in electrochemistry. Its wide potential window, mechanical robustness, and resistance to corrosion and fouling make it useful for a variety of applications.² These are primarily for sensing or electroanalytical purposes, where typically the BDD surface is modified with metal particles (e.g. Pt, Au, Ni) to render it catalytically active towards the target molecule. There has however, been little application of BDD to electrocatalysis and energy.

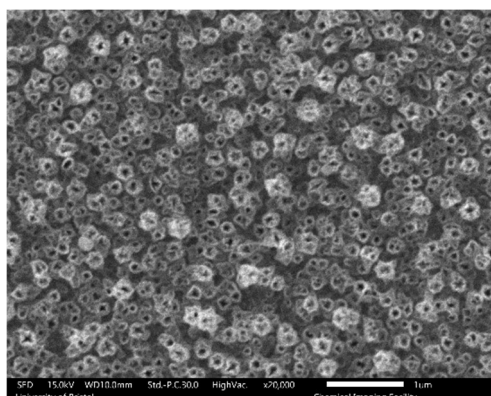


Figure 1: Representative SEM image of a porous Ni electrode prepared by electrochemical dealloying.

This work attempts to exploit the properties of diamond described above and an initial investigation into the use of BDD as a support for water splitting catalysts is presented, with a view to water electrolysis at elevated temperatures and pressures. High surface area nickel electrodes are prepared using electrochemical dealloying, whereby a Ni-Cu alloy is electrodeposited and the Cu is selectively stripped, leaving behind a porous Ni structure.³ A representative SEM image is shown in Fig. 1a. Methods to maximise the surface area of the Ni electrode are probed using measurements of the Electrochemical Surface Area (ECSA) and Hydrogen Evolution Reaction (HER) activity. Further to this, approaches to improve the intrinsic activity of the catalyst, such as surface modification with platinum by galvanic displacement, are reported. Finally, catalyst growth onto a higher surface area diamond electrode, ‘black diamond’, is attempted.

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D12: Electrochemical assessment of a tripodal thiourea-based anion receptor at the liquid|liquid interface

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Thiourea-based receptors for anions have been widely studied due to their ability to transport anions across phospholipid bilayers. The binding affinity of a tripodal thiourea-based receptor for anions was assessed at the aqueous|organic interface using electrochemical measurements. A 1 : 1 stoichiometry was determined for the complexation of most anions, with a higher stoichiometry found in the presence of excess Cl⁻ and Br⁻ anions. High stability constants were estimated for the formation of the complexes at the aqueous|1,2-dichlorobenzene (DCB) interface. When compared with an organic solvent of higher polarity, nitrobenzene (NB), the high stability constants observed in DCB are believed to be due to the less competitive environment of the less polar solvent. Protonation of the receptor at the bridgehead tertiary amine was also inferred from the potential-dependent voltammetric measurements that are not related to anion:receptor complexation.

While such an assessment is usually carried by NMR and UV-Visible titrations, the inherent advantages of the electrochemical method with the use of low polarity solvents are expected to provide new insights into the binding and transport of newly-developed neutral receptors.[1]

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D13: Theoretic Approach to the Capacitance of Aqueous | α,α,α -Trifluorotoluene Interfaces

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The classic treatment of the electrical double layer is extended to the study of the interface between two immiscible electrolyte solutions (ITIES) in the absence of specific ion absorption. The differential capacitance of the liquid|liquid interface can be analytically modelled by a circuit of three capacitors in series, as a representation of a structure conformed by two diffuse layers and an intermediate mixed layer. The model allows us to interpret trends in the capacitance curves as a function of the experimental variables of the electrochemical cells investigated: x mM electrolyte, H₂O | x mM BATB, TFT. The model adequately represents the variation of the differential capacitance with the electrolyte concentration in each phase, and the formation of a Helmholtz capacitor by accumulation of ions at the interface as a function of the interfacial Galvani potential difference.

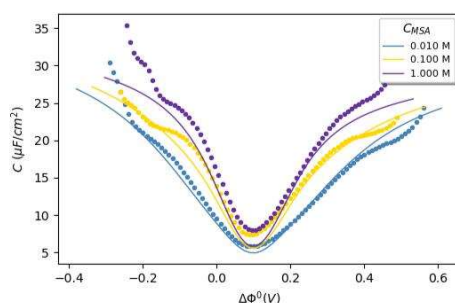


Figure 1. Effect of MSA concentration on the capacitance of the L|L interface. Differential capacitance vs. Galvani potential for the MSA, H₂O | BATB, TFT cell. MSA is methanesulfonic acid electrolyte and BATB is bis(triphenylphosphoranylidene) ammonium tetrakis(pentafluorophenyl)borate organic electrolyte. The points correspond to the experimental data and the solid line to the theoretical function. The modelling parameters are: $C_{\text{org}} = 5.0$ mM, $T = 10.0$ °C, $\epsilon_w = 78.304$, $\epsilon_{\text{TFT}} = 9.2$, $d_i = 4.9$ Å, $d_f = 5.6$ Å.

The present theoretical proposal allows us to analyse the effect of different electrolytes and parameters, such as concentration, temperature, and the size and the relative dielectric constant of the mixed layer. The solution of the capacitance function is analytical, which reduces the error due to calculation. On the other hand, this model is flexible and admits semi-empirical modifications, such as the implementation of adsorption isotherms, becoming a promising theoretical framework for the experimental interpretation of several ITIES cells.

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D14: Voltammetric Evidence of Proton Transport through the Sidewalls of Single-Walled Carbon Nanotubes

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During an electrochemical reaction, the movement of electrons is accompanied with the simultaneous flux of ions to balance the movement of charge. If there is no ion flux, charge cannot flow. This principle underpins all electrochemical reactions and is the foundation of electrocatalysis, charge storage and electrochemical sensing. Understanding ion flow in new electroactive materials is therefore required to develop new devices. In recent years, the study of ion transport across 2-dimensional (2D) materials has garnered significant interest.^{1,2} In this contribution, voltammetric methods are used to probe ion transport phenomena across a 2D, atomically thick crystal in a host-guest hybrid redox material.³ Redox-active polyoxometalates (POMs) are encapsulated within single walled carbon nanotubes (SWNTs) and act as the redox probes during analysis.^{4,5} In acidic electrolytes the encapsulated POMs are shown to undergo ideal and exhaustive electron transfer, which is rapid and reversible. By modulation of the electrolyte composition, redox is shown to be inhibited in electrolytes containing Li⁺ and Na⁺ ions. After 1000 cycles over 80% of the electrochemical activity of the material is retained in acidic electrolytes, compared to all electrochemical activity being lost in Li⁺ and Na⁺ containing electrolytes at ca. 10 cycles. By plugging the ends of the SWNTs with redox-innocent, sterically exclusive guests, ion transport to the POMs is shown to occur exclusively through the pristine graphenic lattice that makes up the SWNT sidewall.⁶ Applying Laviron analysis to the voltammograms of the material reveals that ion transport of either protons or deuterons is possible through this route and is not rate limiting during electron transfer to the guest molecules. The results demonstrate that modification of carbon coated redox materials is required for use in electrochemical devices, and show that the ion transport properties of graphene are applicable to SWNTs.²

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D15: Confinement-Controlled Nanoelectrochemistry: Study One Entity at A Time

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Do not exceed one page. Single-entity electrochemistry (SEE) provides powerful means to measure single cells, single particles, and even single molecules at the nanoscale by diverse well-defined interfaces.[1] The nanoconfined interface has significantly enhanced structural, electrical, and compositional characteristics that have great effects on the assay limitation and selectivity of single-entity measurement.[2] Mass transport and electron transfer are the two main processes at the electrochemically confined interface that underpin the most transient electrochemical responses resulting from the stochastic and discrete behaviors of single entities at the microscopic scale. Herein, we demonstrate how to achieve controllable nanoelectrochemistry by micro/nanointerface and nanopore interface.[3] We then present a fundamental understanding of how dynamic interactions control the features of the electrode interface and thus the stochastic and discrete electrochemical responses of single entities under nanoconfinement. Both stochastic single-entity collision electrochemistry and nanopore electrochemistry as examples in this presentation explore how these interactions alter the transient charge transfer and mass transport.[4] Finally, we discuss the further challenges and opportunities in SEE, from the design of sensing interfaces to hybrid spectro-electrochemical methods, theoretical models, and advanced data processing.

Figure 1. Single entity electrochemistry based on confined interface

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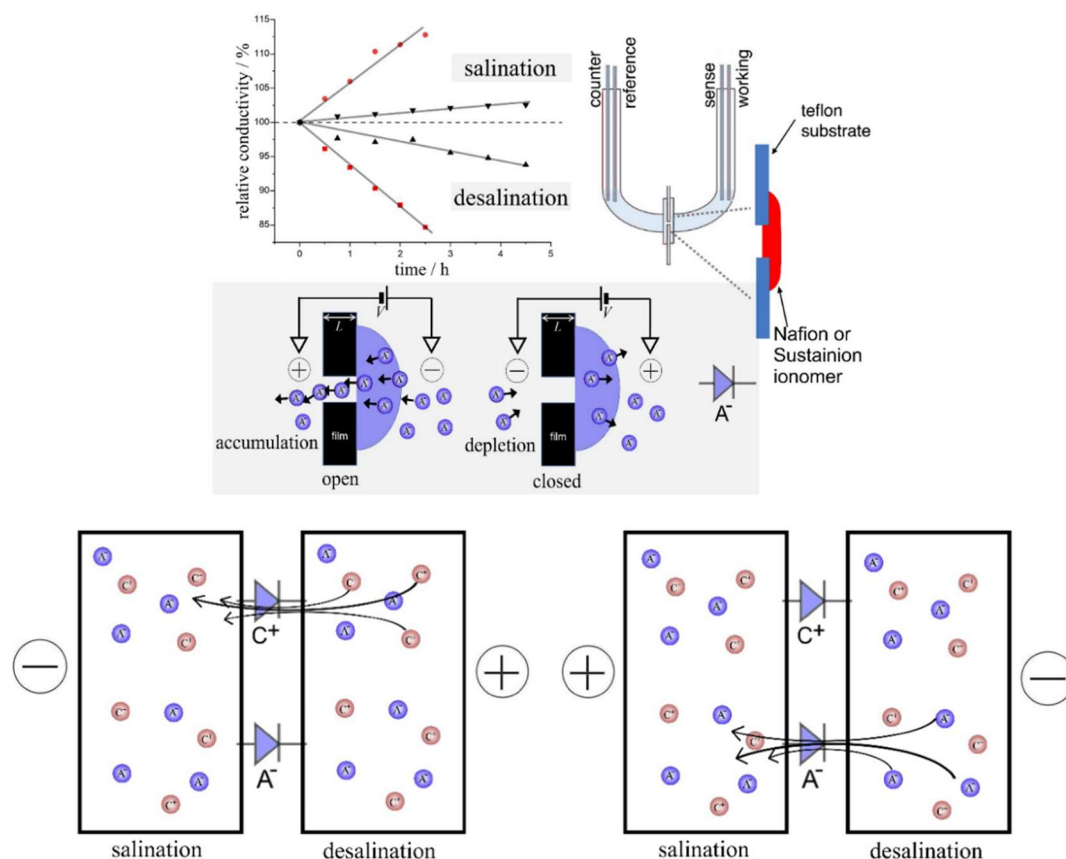
D16: Driving Electrochemical Membrane Processes with Coupled Ionic Diode

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Integrating ion-permselective membranes into asymmetric devices produces ionic diodes. Switching between closed and open states produces irreversibility which can be exploited in AC-current driven membrane processes based on two coupled ionic diodes: (i) unidirectional transport of salts for desalination, (ii) transport of solvents such as water, or (iii) transport of other small molecules [1].



The figure shows an example of 2-chamber desalination system based on coupled ionic diodes of cationic Nafion™ polymer and anionic Sustainion™ polymer [2]. Rectified transport of cation/anion in the same direction results in net salination/desalination when an AC voltage/current is applied. Recent study also suggests a coupled system with two anionic diodes can be utilised to achieve net zero ion transport and unidirectional water transport, with potential applications such as water harvesting and drug releasing. Future work on ionic diode materials and mechanisms, through both experimentation and theory, can help overcome current limitations. Improvements to the rectification ratio and the time constant for diode switching can be made, for example by employing smaller diameter ionic diodes linked to faster switching time constants.

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D17: The importance of considering electrostatics when numerically modelling the cyclic voltammetric response of an outer-sphere redox couple

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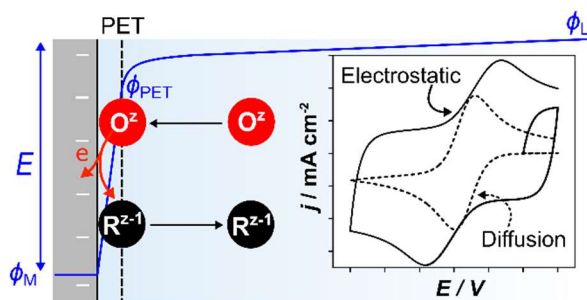
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Cyclic voltammetry (CV) is the most used technique in modern electrochemistry, offering insights into both faradaic and non-faradaic electrochemical processes. To simplify electrochemical systems assumptions are often made such as diffusion being the sole mode of mass transport and the electric double layer (EDL) does not affect the faradaic response. Making these assumptions ignores electrostatic phenomena including ohmic potential drop, ion migration, and the potential dependence of the EDL. The impact of these phenomena on the faradaic response are not widely discussed for common macroscale systems. Whilst these issues have been addressed for a range of nanoscale electrochemical systems,^{1–3} this work presents the first model to extensively treat large (> mm) electrodes, which are commonly used in different electrochemical experiments in the community.

In this work, we present a general finite-element model for examining the interactions between electrostatic phenomena, electron transfer, and mass transport by coupling the Nernst Planck Poisson equations to Butler-Volmer kinetics for a 1D macroscale system.⁴ The model presented offers insight into the electric potential and concentrations distributions across the entire electrochemical cell, enabling ohmic potential drop to be properly accounted for as well as providing information on the local concentration of charged species at the electrode/electrolyte interface. Additionally, we discuss how ohmic potential drop compensation, a feedback mechanism employed by many potentiostats, can be simulated and provide insight as to why the EDL has a negligible effect on the CV response of reversible redox systems. The numerical simulations significantly extend previous theoretical predictions by including both the effects of slow electron transfer and the finite conductivity of the bulk electrolyte solution. The model also importantly allows researchers to understand how properties such as the charge of the redox couple species, electron transfer kinetics and cell design impact their CV results and enables correct values for kinetic rate constants to be extracted from experimental CVs.



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D18: Recovering biological electron-transfer parameters: the perspective of multiple techniques

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Protein film voltammetry (PFV) is a powerful technique whereby a redox active protein is attached as a film to the surface of the electrode and interrogated with a potential. The resulting current contains information about the thermodynamics and kinetics of the electronic transfer reaction. Much PFV analysis is phenomenological --- for example intuiting reaction mechanisms from observations of changes in the current obtained after mutations to the active site of the protein. However, it is possible to obtain more information about the system than a simple acknowledgement of change. Our work is focussed on developing tools to obtain this information.

Our primary tool, allowing for the mitigation of low Faradaic-to-background current ratios, is FT voltammetry --- by using a large amplitude sinusoid as part of the potential input, the inherent non-linearity of the electron-hopping Faradaic current response is exposed, and can be analysed separately from background currents by the means of filtering in the Fourier domain, allowing for unparalleled insight into the details of the Faradaic process.

Additionally, a key benefit of electrochemistry is that multiple techniques can be used to investigate the same system and consequently yield similar parameter estimates. By only accepting parameters that can predict the experimental data from multiple experiments performed on the same film we can increase our confidence that these parameters truly describe the system under investigation. Key to this is Bayesian inference, which allows for the comparison of the degree of confidence and parameter correlation between the different techniques. Using this multiple-comparison approach allows for the skirting of the many pitfalls associated with quantitative, model-based analysis of electrochemistry data.

Our current focus is now on expanding this toolbox to another frequency domain technique --- electrochemical impedance spectroscopy. More analytical methods will allow for the analysis of progressively more complex enzymes, towards the ultimate target of multi-electron catalytic systems such as hydrogenases and nitrogenases.

D19: Stoichiometric resolution in the electrochemistry of oxide materials: driving computational research with Electrochemical Quartz Crystal Microbalance

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To date, there is no experimental technique that can provide direct, simultaneous time and spatial resolution of quantitative stoichiometry changes during electrochemical cycling. This limitation hinders atomistic interpretation of experiments and obstructs the development of improved electrochemical solutions. Although simulations based on Density Functional Theory (DFT) offer a computational tool to derive fundamental insight, it is not straightforward to build models with stoichiometries that are compatible with electrochemical experiments.

To overcome these limitations, we present a strategy using Electrochemical Quartz Crystal Microbalance (EQCM) experiments, which has been implemented in our recently developed, open-access, ALC_EQCM software [1]. EQCM allows to simultaneously measure charge and mass changes of electroactive materials. Such information is coupled with the stoichiometric changes of the participating species through the (two) charge and mass balance equations [1,2]. For complex reactions that involve more than two species, ALC_EQCM conveniently selects stoichiometric compositions among the set of possible solutions and generates atomistic models automatically. Through extra, user-defined directives, ALC_EQCM also provides input files to execute DFT simulations of the generated models using high-performance computing facilities. The possibility of linking EQCM data with DFT computational research offers a novel strategy to screen and sample, on a DFT-energy basis, only those configurations compatible with EQCM experiments, leading to DFT-assisted, quantitative resolution of stoichiometric changes during electrochemical cycling.

The capability of ALC_EQCM to derive quantitative stoichiometric resolution is demonstrated for the intercalation process of alkali metals in Ni(OH)₂, an oxide material used for energy storage and electrocatalysis (and photo-electro-catalysis) applications [2].

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D20: Electrochemical recycling of ruthenium via nano-impacts

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Platinum group metals (PGMs) play a pivotal role in modern society for use in catalysts for industrial and automotive applications as well as providing sustainable solutions to energy production (e.g., hydrogen fuel cells). Electrochemical methods for PGM recovery have become increasingly attractive¹ due to reduced solvent and energy consumption when compared to current pyro- and hydrometallurgical methods². However, a high aqueous metal ion concentration is required at the industrial scale which is not often the case in waste effluent streams where there are trace concentrations of heavy metals. Nano-impact electrochemistry has recently emerged as a promising technique to recover such low concentration metal species from solution³⁻⁵. It has numerous advantages compared to other electrochemical methods, in that it has a high rate of mass transport to the nanoparticles and lessens the fouling of a single electrode by providing high numbers of particles onto which the target metal can be electroreduced.

In this work, the recovery of ruthenium from low-concentration waste mimic ruthenium chloride solution is demonstrated through electrodeposition onto carbon black nanoparticles via impact electrochemistry. Transient reductive impact signals were observed and analysed at potentials negative of -0.50 (vs SCE) corresponding to the onset of ruthenium deposition as seen in cyclic voltammetry. Direct evidence of Ru deposition was obtained through scanning electron microscopy/energy dispersive spectroscopy and x-ray photoelectron spectroscopy. Finally, its use as an electrocatalyst for methanol oxidation is demonstrated thus showing the potential recycling applications of these carbon supported ruthenium materials.

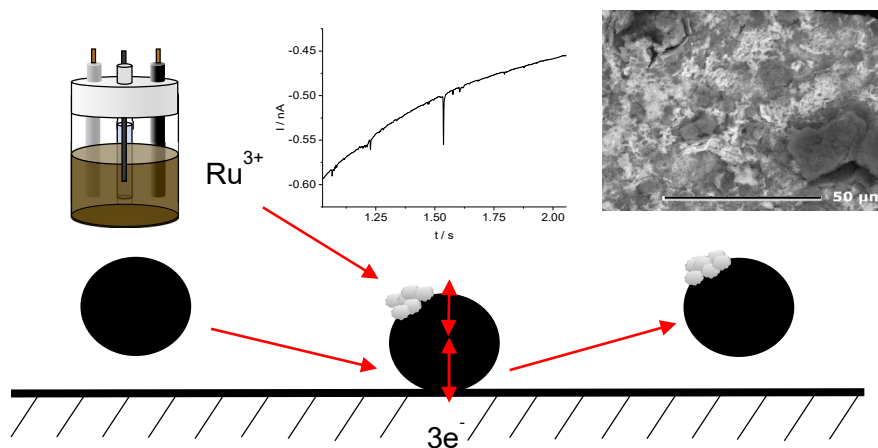


Figure 1: Schematic of nano-impact electrochemistry process with insets of a representative chronoamperogram at -0.5 V vs SCE showing impacts with the addition of carbon black nanoparticles and an SEM image of Ru modified carbon black.

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E1: On the High Temperature Water Oxidation and Stress Corrosion Cracking of Reduced Activation Ferritic Martensitic Eurofer-97 Steel

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The UK National Nuclear Laboratory has been working in collaboration with the University of Bristol to develop high-temperature water corrosion capabilities. These capabilities have been used to study the aqueous corrosion of Eurofer-97 in conditions relevant to the water-cooled lithium-lead breeder blanket designs. Eurofer-97 is a reduced-activation ferritic-martensitic steel and is Europe's candidate structural material for the European DEMO fusion reactor [1].

Results are presented on high-temperature oxidation of Eurofer-97 in pure water conditions and with zinc addition as a corrosion mitigation additive. In addition to high-temperature, high-pressure autoclave testing, a bespoke microchannel assembly was developed in order to conduct in-situ electrochemical measurements of samples exposed to autoclave experiment conditions. For fusion reactors, a high 4–10 T magnetic field will be present over the blanket components [2]. By using a modified Halbach array component alongside the autoclave flow loop, it has been possible to conduct investigations into magnetic field effects on the aqueous corrosion of Eurofer-97.

This work is to continue through a collaboration between NNL, the UK Atomic Energy Authority (UKAEA), and Lucideon Ltd. Plans for this work will involve investigating Eurofer-97 in different controlled and monitored chemistries. This will investigate the effect of different pH from 7.0–8.4 as well as the usage of KOH vs LiOH as a pH control. Comparisons will be made through characterisation of samples post-oxidation. As well as this, a compact tension specimen will be used and conditions varied during experiment to attain values of crack growth rate for differing pH control.

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E2: Automating corrosion testing for organic coatings: a Machine Learning-based approach

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Protective organic coatings are used to extend the service life of metal components and structures. Technological tests allow to assess the performance qualitatively, but Electrochemical Impedance Spectroscopy (EIS) can provide numerical values, often correlated to the coatings conditions. However, EIS interpretation is complex and it involves choosing an equivalent electric circuit and finding the numerical values of its components [1, 2]. This requires specific knowledge and time. Machine Learning (ML) models can perform a task after being trained with previously interpreted data. Therefore they could be potentially used to automate the EIS interpretation [3]. In this work, the corrosion behaviour of a wide set of organic coatings applied on cold rolled mild steel and AA2023-T3, with varying protective performance, was assessed by EIS in selected aggressive environments to obtain a large dataset for ML studies. The ML was then trained to discriminate between intact and failing coatings, identify a suitable equivalent circuit and provide estimation of the equivalent circuit component values. The results obtained show that ML has the potential to be employed to automate corrosion testing.

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E3: Degradation of marine coatings during hygrothermal cyclic corrosion tests

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Degradation of barrier type organic coatings pigmented with flaky aluminium pigments and mineral oxide extender pigments under hygrothermal cyclic corrosion tests were investigated by scanning/transmission electron microscopies and nanoscale X-ray tomography. By comparing physical and chemical status of individual coating elements before and after hygrothermal cyclic corrosion tests, it was found that coating degradation can be indicated by three critical factors. These factors included the glass transition temperatures (T_g) of the coatings, stability of aluminium pigments, and the degree of solubility and structural weakness of extender pigments. It is demonstrated that differences in these factors can have significant impact on the coating integrity and subsequent corrosion protection attributes.

Keywords: Organic coating degradation, Pigments, Aluminium pigment, Hygrothermal corrosion test

E4: The Degradation Mechanism of Polyester Powder Coatings Exposed to Cyclic Corrosion Testing (CCT)

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Crack initiation and propagation within coatings has been identified as one of the main causes for significant deterioration of organic coatings. This can lead to failure of the coating and even the complete delamination. The exposure of the coatings to the environment is widely known to reduce the coatings impedance over time, a clear sign of coating degradation [1,2]. However, this measurement gives quite a general result and does not give any insight into how the corrosion processes are taking place at a microstructural level.

Any changes to the chemical nature, average particle size and the crystal form of the fillers within the coating will affect the corrosion resistance of the coating [3], highlighting the complex interactions taking place when a coating system is exposed to the environment. The condition, composition and structure of the coating will develop during exposure to the environment and these changes can lead to defects forming, for example within the pigments, the polymer, or at the interfaces between pigment/polymer/substrate. With continued exposure these defects can transition into cracking, with the propagation of these cracks being influenced by the coating microstructure. With continued exposure these defects and cracks can lead to the failure of the coating system.

To better understand the mechanism of crack initiation and subsequent degradation of coatings, powder coated samples have been exposed to cyclic corrosion testing experiments of various lengths to characterize the formation and subsequent development of defects within the coating. These defects, and how they develop into cracks, will be linked with microstructural features within the coating and the substrate surface to better understand the mechanism of initiation and propagation.

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E5: Surfactant corrosion inhibitor adsorption and desorption kinetics in aqueous CO₂-containing environments

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Corrosion inhibitors are commonly employed to protect carbon steel infrastructures in aqueous carbon dioxide (CO₂)-saturated environments, such as those encountered in oil and gas production and geothermal operation. However, unexpected events can occur that lead to periods where corrosion inhibitor addition ceases completely, or the quantity of inhibitor added falls short of the typical concentration required for the desired level of corrosion mitigation. In these instances, there is a limited understanding of how the system responds to such variations in corrosion inhibitor dosing and the subsequent effects on the corrosion rate of carbon steel.

This study evaluates how the combination of the adsorption time, surface condition and inhibitor concentration influence the persistency of a benzyldimethyl-tetradecylammonium chloride corrosion inhibitor through a series of rotating cylinder electrode laboratory experiments. The work also examines the potential of numerical models and the application of the quartz crystal microbalance to provide insight into the adsorption-desorption characteristics.

E6: Production of Copper Nanocomposite Coatings using Pulse Reverse Plating and Anionic Surfactant

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The development of the process to produce Metal Matrix Nanocomposite (MMNC) coatings can provide opportunity for the enhancement of mechanical and electrical properties. As the mechanical, electrical and thermal demand of materials increases, the properties of these materials must progress with them. Equally, if the properties of materials improve, technology is able to progress quicker. Copper is of particular importance in industry due to its high thermal and electrical conductivity at room temperature, however it is a relatively soft, malleable metal. Incorporating nanoparticles, such as SiC, into the copper matrix can improve the hardness and wear resistance of the coatings, without significantly diminishing the other properties. The utilisation of Pulse Reverse Plating (PRP) in the production of MMNCs has been explored over the years but only recently have the anodic pulse and anionic surfactant been taken advantage of to increase particle content. [2,3] This work focuses on applying this to the production of Cu-SiC nanocomposite coatings. Anionic surfactant concentration within the plating bath against a constant concentration of SiC and plating parameters were varied; the composition and mechanical properties of the resulting coatings were determined and compared.

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E7: Effect of Biofouling on the Corrosion of Nickel Aluminium Bronze Immersed in Natural Sea Water

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Nickel Aluminium Bronze (NAB) is used extensively in the marine environment due to its good corrosion resistance and physical properties. As such it is often used for components where failure would cause a risk to life, vessel and environment.

It is generally accepted (e.g. [1-4]) that the corrosion of NAB in seawater is caused by anodic dissolution of metals and the hydrolysis of metallic chlorides. It is also well documented that NAB can experience selective phase corrosion (SPC) when exposed to natural seawater. This is classically reported as the accelerated dissolution of the Copper-rich α -phase within the $\alpha+\kappa_{III}$ eutectoid, due to the more negative electrode potential of the α -phase compared to the κ_{III} -phase [5]. However, where this SPC has been examined in more detail, it has been shown that, whilst the Copper rich α -phase will preferentially corrode at pH>4.0, the Iron, Nickel and Aluminium rich κ -phases will preferentially corrode at pH<4.0, due to the inversion of the anodic-cathodic phase behaviour of NAB [6]. In addition, under these acidic environments, the corrosion rates can be increased up to ten times with the lamellar κ_{III} -phase being the most vulnerable phase for dissolution [7].

NAB samples were immersed in natural seawater for 12 months where marine organisms were allowed to naturally attach themselves to the samples (known as biofouling). Corrosion pits were shown to develop underneath the large biofouling organisms (such as sea squirts) and underneath corrosion product deposits. The corrosion mechanism was shown to be through the dissolution of the lamellar κ_{III} -phase resulting in accelerated corrosion rates and deep corrosion pits.

Fatigue experiments showed that fatigue crack propagation also followed that path of the κ_{III} -phase meaning that corrosion pits could act as pre-initiated fatigue crack sites in NAB exposed to natural seawater. This could lead to premature failure of NAB components in the marine industry resulting in loss of vessel or life.

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E8: Phase field model of accelerated corrosion tests and single crystal polarisation anisotropy

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Accelerated corrosion tests are a fast and thus inexpensive method, which can provide a current density response for the whole test duration – something that is impossible for natural corrosion tests. This trait makes them especially attractive for numerical modelling validation. However, computational models of corrosion in any industrially appreciable scale (mesoscale and above) are incapable of modelling the transient behaviour of the electrode surface, evident in the time response of the current density [1]. This obstacle is due to the difference in spatial resolution of the surface effects and the resulting geometry change. However, introducing an equivalent circuit response into the model allows for overcoming a drawback associated with different spatial scales. Equivalent circuits are a common tool in analysing electrochemical impedance tests, as they allow for identifying time constants associated with surface effects [2]. By incorporating this method into a phase field model, it is possible to indirectly treat the double layer build-up in the initial stages of accelerated corrosion tests, thus greatly improving the accuracy of the models in this region of transient current density response. A further extension of the model by directional polarisation allows one to observe a spatial anisotropy to single crystal dissolution under activation control.

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E9: Casing corrosion of steels in geothermal environments containing sulphuric acid

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Geothermal pipelines as part of production or injection wells can undergo corrosion due to interactions with high-temperature/low-pH geothermal fluids. Areas in Taiwan and Indonesia are known to have low-pH geothermal fluids containing sulphuric acid (H₂SO₄) stemming from the mixture of underground waters and magmatic gases. However, there is limited knowledge about the corrosion behaviour of carbon steel within H₂SO₄ waters within the pH range of 2-4. This work is conducted with the aim of gathering insight into steel corrosion concerning geothermal conditions, especially focusing around fluids containing H₂SO₄. A tantalum-lined autoclave was used to perform static corrosion tests with N80 carbon steel submerged in acidic solutions (pH 2-4) and temperatures up to 150°C. Real-time in-situ electrochemical measurements of linear polarisation resistance and electrochemical impedance spectroscopy were recorded as means of relating corrosion rates and reaction mechanisms for the tested material. Surfaces of the corroded steel were analysed with scanning electron microscopy and white light interferometry to visualise the physical impacts of corrosion. The N80 carbon steel was seen to encounter high corrosion rates (>90 mm/year) along with severe signs of localised corrosion when exposed to the pH 2 test solution tested at 150°C. Additionally, the corrosion behaviour of alternative corrosion resistant alloys is explored to provide material selection options for demanding geothermal environments.

E10: Microstructural evolution due to CO₂ Oxidation and Carburisation in 9Cr-1Mo Steel

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Figure 1: Optical micrograph of a finned 9Cr-1Mo steel sample after 15,000 hours of CO₂ exposure. After breakaway of the fins, oxidation degradation of the tube wall is in a state of arrest.

The degradation mechanisms of CO₂ oxidation and carburisation present significant challenges to the integrity of 9Cr-1Mo steels used in advanced gas-cooled reactors (AGRs). This study investigates the changes in the microstructure of these steels when exposed to high-temperature CO₂ environments for extended periods. Specifically, we examine the oxidation/carburisation front and the subsequent breakaway oxidation behaviour of finned tubes in boiler circuits [1,2].

In this presentation, we provide a comprehensive overview of experimental studies on oxidation and carburisation using representative steels. We present results from long-term exposure tests conducted in both reactor and autoclave simulated conditions. Optical, electron microscopy, and focused ion beam techniques were employed to observe the morphological changes, carbide precipitation, elemental segregation, and growth rates of oxide scales as the exposure time increased.

Furthermore, based on our microstructural observations, we propose mechanisms that drive the multi-stage CO₂ oxidation and carburisation process in 9Cr-1Mo steels. We also discuss preliminary research findings that introduce a potentially new stage in the oxidation regime sequence. This finding is based on the observation of "tube wall delay" specimens, where the oxidation and carburisation process exhibits an arresting or slowing effect.

By presenting these comprehensive findings, our aim is to contribute to the understanding of the complex behaviour of 9Cr-1Mo steels under CO₂ oxidation and carburisation conditions. This knowledge will be instrumental in developing effective mitigation strategies and enhancing the structural integrity of AGR components.

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E11: Atmospheric Corrosion of 316L Stainless Steel: The Effect of Stress and Strain

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Austenitic stainless steels are widely used in the nuclear industry as a container material due to their corrosion resistance, but they can be susceptible to stress corrosion cracking (SCC) in the presence of halide ions, particularly chlorine [1]. In addition to welding residual stresses from manufacturing [2,3], the presence of decaying nuclear waste leading to temperature increases and the generation of corrosion products leading to the expansion of the container materials contribute to this susceptibility by increasing stresses and strains on the canister surface.

The effect of stress corrosion cracking (SCC) on type 316L stainless steel was investigated in this study. Sensitized and non-sensitized samples with different notch sizes were subjected to four-point bending loading in a modified chamber for 870 hours. Artificial seawater droplets were applied to the surface of the samples, and the temperature and relative humidity were controlled. Corrosion features were analyzed using optical micrography, SEM, and optical confocal microscopy techniques. The results showed that the growth of pits was severely influenced by the rolling direction of the sample and the stress and strain distribution at the notch tip. The pits were larger in the transverse direction (TD) than in the rolling direction (RD). The pits were also larger in the samples with larger notches. The findings of this study have implications for the safe storage of nuclear waste.

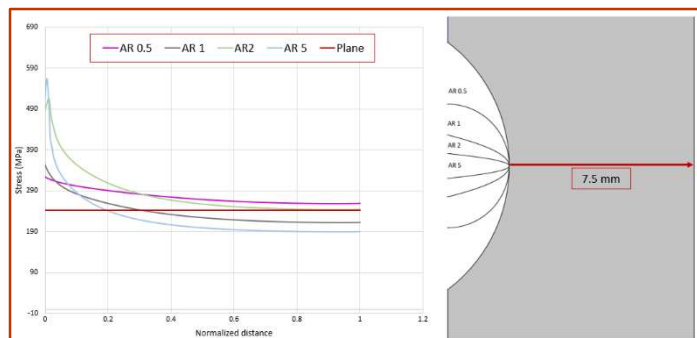


Fig. 1. Different geometries of notches and the stress and strain distribution stemming from them.

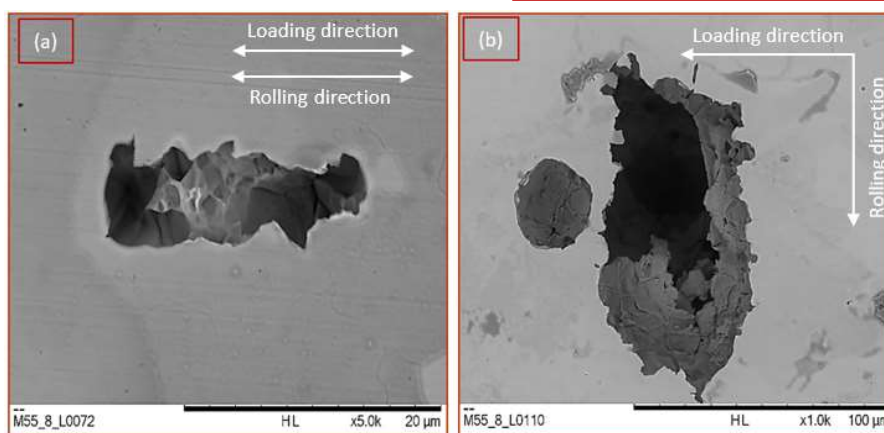


Fig. 2. The samples were subjected to a displacement of 1 mm using a 4-point bending (4-PB) rig at 50 °C and 60% RH. This resulted in a maximum principal stress of 486 and 476 MPa at the notch tip, which is approximately 1.5 times the yield stress of the material. (a) load applied in the same direction with rolling direction of the sample, (b) perpendicular to rolling direction.

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E12: The effect of CO₂ partial pressure on the formation and protective characteristics of iron carbonate corrosion products

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The presence of dissolved carbon dioxide (CO₂) in geothermal energy facilities acidifies the aqueous environment and accelerates the corrosion of carbon steel pipes. Under certain conditions, the precipitation of iron carbonate (FeCO₃) corrosion products onto pipe walls can form a dense layer that protects the underlying metal surface from further corrosion. However, the level of protection offered by the corrosion product layer is highly sensitive to changes in environmental conditions.

This study investigates how CO₂ partial pressure affects the formation and characteristics of FeCO₃ layers that form on X65 carbon steel. Autoclave corrosion testing is performed using CO₂-saturated, 3wt.% sodium chloride solution at an operating temperature of 80°C and partial pressures ranging from 5.5 to 15.5 bar. In-situ linear polarisation resistance analysis reveals the distinct stages of FeCO₃ layer development and demonstrates how operating pressure influences the rate of FeCO₃ formation. Electrochemical Impedance Spectroscopy (EIS) provides an insight into the mechanism by which the FeCO₃ layer protects the metal substrate. This was found to transition from initially blocking steel active sites, to providing additional corrosion suppression by limiting the diffusion of electrochemically active ions. The formation of an effective diffusion barrier is accelerated at high CO₂ partial pressures.

E13: Understanding the Effect of Strain on Corrosion of Advanced Gas-cooled Reactor Fuel Cladding

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Advanced gas-cooled reactor (AGR) nuclear fuel is contained within 20%Cr/25%Ni/Nb stainless steel cladding, acting as a corrosion resistant barrier to fission product release in storage. A small fraction of fuel pins could be sensitised in service, leading to possible intergranular corrosion susceptibility in absence of storage pond pH-control. This provides potential for stress corrosion cracking at cladding locations previously strained during fabrication or service, however limited research is available on this behaviour.

This study aims to investigate how changes in strain on AGR fuel cladding can impact microstructure, localised corrosion and consequently stress corrosion behaviour. An experimental method is in development applying digital image correlation (DIC) for monitoring specimens exposed to storage relevant environments, loaded in a micro-tensile stage with electrochemical control. This allows observation of local strains on the specimen surface, and potential crack formation under applied stress, whilst electrochemical measurements are taken to understand corrosion performance. The goal is to determine where cracks may initiate, and if they can be inhibited, to understand if changes in local microstructure strains play a key role in spent AGR fuel failure.

E14: Study of carbon steel corrosion in live anaerobic digestion reactors

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Anaerobic digestion (AD) is one of well-established sectors in biotechnologies. It can recover energy from biogas by-products and simultaneously convert nutrients into digestate, making it an efficient alternative to treat waste within a circular resource economy. Traditional AD is typically processed in reactors made from either enamel or epoxy coated carbon steel or concrete, separating into the liquid/slurry phase and the gas phase. The liquid conditions in AD are generally mild with neutral pH, low redox potential, typically in a range of -100 mV to -300 mV [1], and without elevated temperatures, but contains chemicals and microorganisms involving in the digestion process. The gas condition could be aggressive with the presence of carbon dioxide. Carbon steel corrosion has been widely studied in the simple test media or with specific bacteria/archaea incubated, but rarely studied in a biotic AD reactor. As a result, what still needs to be studied is the interaction among the physical, biochemical conditions, and material property changes. Combining electrochemical methods and immersion tests in the live AD reactors, this work aims to explore the corrosion performance of carbon steel in the live AD reactors.

S235 carbon steel samples were located in both the gas phase (predominately CO₂ and CH₄) and sludge phase in four continuous stirred tank reactors for three months. Two digesters were fed with food waste (FW) and maintained at 35°C and 55°C, respectively. The other two digesters were fed with municipal solid waste (MSW) and operated at 35°C and 55°C, respectively. X-ray diffraction was used to identify the corrosion products. Ex situ electrochemistry measurements combined with cross-sectional analysis were conducted to identify corrosion kinetics and rust film formation. Corrosion rates were calculated according to the weight loss. Siderite (FeCO₃) was found as the key corrosion products within the gas phase, with a corrosion rate of 0.01 mm/y. The rust film formed in the FW-fed reactors was more protective than the films formed in the MSW-fed reactors. However, the operating temperature does not appear to significantly influence the corrosion rate. Samples from the liquid phase had greater weight loss than the samples from the gas phase. The higher liquid temperature led to the higher corrosion rate. Vivianite (Fe₃(PO₄)₂(H₂O)₈) was found on the rust film on the samples removed from the FW-fed reactors. Whereas, ankerite (Ca_{1.01} Mg_{0.45} Fe_{0.54} (CO₃)₂) was found on the rust film in the samples removed from the MSW-fed reactors.

S235 carbon steel electrochemical performance in the centrifuged supernatant and the whole sludge of digestate retrieved from the live anaerobic reactors above was investigated at room temperature, 35°C and 55°C, with a low dissolved oxygen level (<0.1 mg/L). Both electrochemical impedance spectroscopy and potentiodynamic polarisations were utilised to explore the corrosion kinetics of S235 carbon steel in both the supernatant and whole sludge media.

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E15: The Influence of Grain Structure on Hydrogen-Environmentally Induced Cracking (H-EIC) Behavior of AA7085 Alloy in Humid Air

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This study investigates the role of grain structure on the Hydrogen-Environmentally Induced Cracking (H-EIC) behaviour of the new generation AA7085 aluminium alloy. Commercially available thick plate material was re-processed followed by hot rolling within the temperature range of 350–470 °C to study generate different levels of recrystallization, followed by T7651 aging. The material was then prepared into constant displacement (four-point bend) tests in humid conditions (50% RH & 70 °C) with the loading applied in the Short Transverse direction. High-resolution in-situ optical monitoring was employed to monitor H-EIC initiation and crack propagation behaviour. The crack growth rate was lower for samples with a higher fraction of recrystallization compared to the other samples. A higher fraction recrystallized grains leads to a more tortuous crack path, which subsequently reduce the crack propagation velocity. These findings reinforce the significant influence of grain structure on the H-EIC behaviour of the AA7085 Alloy.

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E16: Using ultrasound to increase metal anodic dissolution and prevent passivation using concentrated ionic fluids

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Deep Eutectic Solvents (DES) such as Ethaline – a 1:2 molar combination of choline chloride (ChCl) and ethylene glycol (EG) - provide a wider electrochemical window for metal dissolution than that of an aqueous environment; however, surface passivation and high viscosity limit the rate of mass transport and thus the rate of dissolution. [1] Forced convection from ultrasound provides three separate mechanisms for increasing mass transport: cavitation collapse, micro-jetting and acoustic streaming. [2] The use of ultrasound to increase the mass transport during anodic dissolution of copper and nickel has been investigated in this work. Ultrasonics prevent the formation of a passivating layers, allowing the current density observed to increase significantly compared with silent anodic dissolution.

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E17: Effect of Microstructure on Localised Corrosion and Atmospheric Stress Corrosion Cracking of 15-5 PH Stainless Steels

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This work aims to enhance mechanistic understanding of pitting and Atmospheric Cl⁻-Induced Stress Corrosion Cracking (AISCC) in 15-5 Precipitation Hardened (PH) Stainless Steels (SS) by establishing links between microstructural features effected by varying ageing temperature (here, 450 °C, 540 °C and 650 °C) and susceptibility to such phenomena. The microstructural evolution as a function of ageing temperature was investigated via scanning TEM energy dispersive X-ray spectroscopy (STEM EDS), whilst differences in environmental behaviours were assessed using both electrochemical and environmental testing under controlled conditions of temperature and Relative Humidity (RH).

Statistical scatter in pitting potential (E_{pit}) determined via potentiodynamic polarization was too high to determine any trend in localised corrosion resistance with confidence. However, useful information was, obtained via Double Loop Electrochemical Potentiokinetic Reactivation (DL-EPR) and Electrochemical Noise (EN) measurements. DL-EPR revealed a linear trend between the degree of reactivation (DOR) and ageing temperature which correlated with an increase in number density of Cr carbides. EN measured by galvanically coupling dissimilar microstructures suggests that the highest temperature ageing treatment (650°C) was most susceptible to metastable pitting events therefore has a higher probability of transitioning to stable pitting, which correlates with the trend in found in DOR.

Atmospheric induced stress corrosion cracking (AISCC) tests (4-point bend specimens with Cl⁻-salt deposits exposed to controlled temperature and RH) revealed that over-aged specimens (ageing temperature 650°C) were most resistant to cracking, whilst EN indicated they had greatest susceptibility to pitting. The opposite was found for under-aged specimens (ageing temperature 450 °C). The mode of AISCC transitioned from an intergranular (IG) pathway in under-aged specimens (450°C) to mixed IG + transgranular (TG) for those peak-aged (540°C); no cracks were observed under the same testing conditions in over-aged specimens. Overall these results are consistent with the theory that AISCC, like conventional SCC, only occurs under conditions of slow and stable localized corrosion [1].

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E18: Environmental effects of a simulated AGR coolant on oxidation and carburization behaviour of type 316H stainless steel

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This paper aims to further understand the environmental effects of oxidation and carburization of type 316H stainless steel, which is used within the super-heater and re-heater sections of the UK Advanced Gas-cooled Reactors. The effect of gas pressure and water vapour content, and applied stress on oxidation and carburization were investigated. Experiments were conducted using a simulated CO₂/1% CO, AGR gas mixture at a temperature of 550°C, which contained 300 vppm CH₄, 100 vppm H₂ and either 300, 500 or 700 ppm of water vapour. The results show that polishing the specimens with colloidal silica oxide polishing suspension (OPS) induced the formation of a duplex oxide structure, consisting of an outer magnetite and an inner chromium rich spinel layer. The thickness of the oxide layer followed a parabolic law with time, and changes in applied stress, did not affect the overall thickness. However, increased surface hardness beneath the scale, which was associated with a carburization process, was dependent on the applied stress. It is proposed that stress enhanced carburization is associated with the dislocation movement, which enhances carbon mobility. Furthermore, increasing the gas pressure led to thicker duplex oxide scales and most importantly, enhanced surface hardness beneath the scale, probably due to the higher carbon activity and associated diffusion through grain boundaries and pores in the oxide layer. Finally, unlike what found in other studies, no significant changes in oxidation or carburization as a function of water vapour in the gas were identified. The mechanistic interpretation of the environmental, total pressure and applied stress on oxidation and carburization is discussed.

E19: Elucidation of Charge-Transfer Mechanisms under Paint films by Conventional and Localised Electrochemical Impedance Spectroscopy

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The organic coating has been used to protect the metallic substrates from corrosive environments¹. Over time, the coating degrades and allows water and ions to ingress into the bulk of the paint film, eventually, causing the corrosion process to occur. However, this diffusion does not occur at the same time in every area of the paint film, hence, the concept of coating heterogeneity Direct conduction (D-type) and Inverse conduction (I-type) was established by Mayne², Mills^{3,4}, and Kinsella⁵.

In order to investigate the D and I behaviours, electrochemical impedance spectroscopy (EIS) and localised electrochemical techniques (LEIS) were deployed to elucidate the charge-transfer mechanisms as well as the diffusion process. The epoxy amine coating consisting of Bisphenol A diglycidyl ether (DER332) and m-xylenediamine (MXDA) samples were exposed to various salt solutions with different water activities. It has been found that solvent-based DER332-MXDA curing at 60 °C provided much lower coating resistance around 60-200 MΩ/cm² and the diffusion occurred faster than the system that was cured at 160 °C as the resistance went up to 1-13 GΩ/cm². The solvent-free system also provided higher resistance than solvent-based film compared to the same curing temperature. Although the majority of the tested films exhibited D-type behaviour, there is a higher chance to find the I-type film at high curing temperature but this behaviour stayed for a while until the diffusion process occurred resulting in a decrease in coating resistance and more importantly, switching from I to D type when the diffusion is fully developed without the appearance of rusts underneath the films. LEIS results show the impedance of the coating looks like 'hills and valleys' where the hills represent the high impedance areas and valleys represent the low impedance regions. However, this 'hills and valleys' mapping may arise from the surface roughness underneath the films.

In all coating systems, the resistance did not stay at the same value but reduced over time when the electrolyte concentrations along with water activities were changed. The results suggest that D and I type conduction are highly related to continuous pathway 'hole' rather than the structure of the polymer itself. The I type can be switched into D-type when the diffusion is fully developed and in some systems, both behaviours co-exist together which is rare to find. In summary, D-type conduction means 'defect' coating and I-type conduction means 'intact' coating.

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E20: The influence of radiation on the corrosion of carbon steel for nuclear waste geological disposal

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Nuclear energy is a vital technology for reducing global carbon emissions and is backed by substantial investment from both government and industry.¹⁻⁴ Effective management of high-level radioactive waste (HLW) necessitates a safe, secure approach and geological disposal is widely considered the best method.⁵ Therefore, understanding the corrosion properties of carbon steel as a candidate canister material is imperative for ensuring the longevity of HLW containers during geological disposal.

This study investigates the influence of radiation on carbon steel corrosion rates using a simplified aqueous system simulating geological disposal conditions. Results indicate that corrosion rates follow a power law decay curve as a function of exposure duration. A direct correlation between corrosion rate and radiation dose rate was observed, reaching a plateau between 100 - 1,000 Gy/h dose rate. Additionally, corrosion rate enhancement factors increase with both dose rate and total dose over short durations (up to 1,000 h). Interestingly, enhancement factors tended towards unity at lower dose rates (1-10 Gy/h).

Complementing the corrosion rate data, a suite of spectroscopic analyses have been used to provide a valuable insight into the corrosion behaviour of carbon steel canister material, identifying the iron corrosion product species and morphology of the surface corrosion layer. These initial results showed that for dose rates anticipated at the canister surface⁶, radiation induced corrosion did not cause a significant increase in the corrosion rate of carbon steel.

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Poster Abstracts

Symposium A – Advances in Electrolysers, Batteries and Supercapacitors

#	Presenting Author	Title	Affiliation
PA1	Rupa Kasturi Palanisamy	Nitrogen Doped rGO Sheets Embedded 3D Cubic Spinel CoMn_2O_4 Nanostructures, A Benchmark Electrocatalyst Towards OER Applications	Maynooth University
PA2	Marilia Barreto Dalla Benetta	Optimisation of Electrodeposited $\text{MoS}_2/\text{MoS}_x$ for the Hydrogen Evolution Reaction	Maynooth University
PA3	Jonathan Goh	Investigating the Impact of Impure Gas Mixtures on Single Cell PEM Fuel Cells	National Physical Laboratory
PA4	Kubilay Sahin	Ni-B-based Polyalloy Electrocatalyst Coatings Deposited by MSPVD for Efficient Oxygen Evolution Reaction	Coventry University, University of Mons
PA5	Walaa Alsaidi	Transition Metal Antimonates for Oxygen Electrocatalysis	University of Bristol
PA6	Thomas Doughty	Ferrocene-Based Metal Organic Frameworks for Electrocatalysis Applications	University of Lincoln
PA7	Carmen Murphy	Performance Improving for Proton-Exchange Membrane Fuel Cells Using Modelling and Diagnostics Tools	Johnson Matthey Technology Centre
PA8	Daisy Elizabeth Gray	Investigating the Stabilities of Carbon Support Materials Obtained From Fmoc-Amino Acid Hydrogels for Low-Temperature Acidic Oxygen Reduction Reaction Applications	University of Lincoln
PA9	Sami M. Alharbi	Structure Activity Relationship of $\text{La}_{1-x}\text{Nd}_x\text{CoO}_3$ Nanostructures Toward Oxygen Electrocatalysis	University of Bristol, Qassim University
PA10	Billie Sherin	In-Situ Reference Electrodes in Alkaline Water Electrolysis	National Physical Laboratory
PA11	Syed Sibte-e-Hassan	Structure Activity Relationship of Fe-C Catalysts Derived from ZIF-8 for the Oxygen Reduction Reaction	Manchester Metropolitan University
PA12	Metaxas Michalis	Preparation of High Performance Ultra-Low Loading PEM Fuel Cell Catalyst Layers	Imperial College London

PA13	Abhishek Rajput	CO ₂ removal from Aqueous Bicarbonates using Bipolar Membrane Electrodialysis	University of Glasgow
PA14	Obeten Mbang Eze	Decoupled Electrolysis for the Production of Zero-Carbon Hydrogen	University of Glasgow
PA15	Athi N. A. Rahmah	Enhancing La _{0.75} Ca _{0.25} Fe _{1-x} Ni _x O ₃ Catalytic Activity Towards Oxygen Electrocatalyst	University of Bristol
PA16	Xiaohong Li	Electrode Materials for Hydrogen Bromine Redox Flow Battery	University of Exeter
PA17	Jack Corbin	Hydrogen Generation from Seawater	University of Exeter
PA18	William Townsend	Exploring the Role of Redox-Shuttle Mediators in Lithium-Sulfur Batteries	University of Nottingham
PA19	Kiran Kumar Reddy Reddygunta	High Energy Density Supercapacitor With Wide Temperature Tolerance Enabled by Corn Husk Based Activated Carbon/Siloxene Electrodes and AWISElectrolyte	University of Strathclyde
PA20	Ali Al-Sikab	Best Practice for Finding Interfacial Contact Resistances Using Spatially Resolved Millimetre Scale Measurements	National Physical Laboratory
PA21	Megan R. Daw	Electrolytes for Rechargeable Magnesium Metal Batteries	University of Southampton
PA22	Hannah Burnett	Water-in-Salt Electrolytes for Redox Flow Batteries	University of Manchester
PA23	Rajeev K. Gautam	High-Voltage and High-Energy-Density Membrane-Free Nonaqueous Flow Batteries	University of Cincinnati
PA24	Chen Mi	The Effect on Performance 75Li ₂ S·25P ₂ S ₅ Solid-State Electrolyte System Through Doping Li ₂ O	University of Bristol
PA25	Rajat Kumar Mohanta	Exfoliation of Ca ₃ Co ₄ O ₉ to Two-Dimensional Single-Crystalline Misfit Calcium Cobaltates for Bifunctional Energy Storage	Indian Institute of Technology Bombay
PA26	Rigved Samant	Chirp-Driven EIS: Accelerating the Characterisation of Li-ion Batteries	Indian Institute of Technology Guwahati
PA27	Hyun-seung Kim	Morphological Failure of Li Deposits Induced by Positive Electrode-Li Metal Crosstalk Behaviour	Korea Electronics Technology Institute

PA28	Safeer Rahman Ottakath Cholakkal	Understanding Battery Health and Identification of Ageing History of Commercial Lithium-Ion Batteries Using Nonlinear Frequency Response Analysis (NFRA)	Coventry University
PA29	Iain M. Aldous	Challenges in Scale-Up and Manufacture of Lithium Metal Anode Protection Systems Targeting Lithium Sulfur Batteries	Swansea University
PA30	Ganesh Vailaya	Overcoming the Challenges of the Li-Air Battery	University of Nottingham, The Faraday Institution
PA31	Mian Muhammad Faisal	Influence of Electrolyte on the Electrochemical Performance of MoS ₂ decorated Carbon Cloth for Flexible Aqueous Supercapacitors	Durham University

Symposium B – Photoelectrochemistry and Sustainable Electrochemical Transformation

#	Presenting Author	Title	Affiliation
PB1	Seyed Mohamad Javad Sajjadi Shourije	Using Cu ₂ O Nano Particles as a Novel Non-Noble Metal Catalyst for Electroless Copper Plating on Textiles	Coventry University, University of Mons
PB2	Raphael T. M. Johnson	Suppression of Parasitic H ₂ Evolution Using Boron-Doped Diamond Electrode and Lithium bis(trifluoromethanesulfonyl)imide Electrolyte	University of Manchester
PB3	Insyirah Ismail	CO ₂ Reduction Reaction Using Channel Flow Cell	University of Manchester
PB4	James Finn	Electrochemical Capture and Release of Carbon Dioxide Using a Diselenide – Selenate Redox Cycle	Loughborough University
PB5	Toby Hodges	EcoFuel: Catalyst Development and Electrode Manufacturing for Electrochemical CO ₂ Reduction	Johnson Matthey Technology Centre
PB6	Zeliha Ertekin	Electrochemical Performance of Cobalt (II) 2,9,16,23-tetraamino Phthalocyanine Electrodes for Electrochemical CO ₂ Reduction: Effect of Electrode Preparation	University of Glasgow
PB7	Fiona Todman	Decoupled Biomass Oxidation and Hydrogen Production Mediated by Phosphomolybdic Acid	University of Glasgow
PB8	Tingran Liu	Redox Neutral Electrosynthesis without Added Electrolyte at Interdigitated Electrodes	University of Bath
PB9	Li Shao	Templated Electrodeposition of Nanoscale Materials	University of Southampton

Symposium C – Electrochemical Sensors and Electroactive Porous Materials

#	Presenting Author	Title	Affiliation
PC1	Han Shao	Electrochemical Sensor on Salt Content in Potato Chips and Crisps	Tyndall National Institute
PC2	Kai-Li Xin	Nanopore Electrochemical Analysis for Identifying Familial Point Mutations in Single Amyloid- β Peptides	Nanjing University
PC3	Muhammad Hashim Khan	Understanding the Transient Response of an Enzyme Electrode in Continuous Flow Using Approximate Analytical Solutions and Numerical Simulations	University of Southampton
PC4	Mehran Afra	Next-Generation In-Situ Sensors for Oxygen Concentration Measurements in PEM Fuel Cells	Coventry University
PC5	Kathleen Kennedy	Electrochemical-Based pH Control for the Analysis of Dairy Products	Tyndall National Institute
PC6	Tara Barwa	Development of 2D MoSe ₂ Nanosheets Combined with Reduced Graphene Oxide for Electrochemical Sensor Applications	Maynooth University
PC7	Yiran Luo	Development of Exfoliated 2D Nanosheets Molybdenum Disulfide Sensor for the Detection of Sulfanilamide in Water Environments	Maynooth University
PC8	Fan Gao	The Electrostatically Asymmetric Nanopore for Single Peptide Sensing	Nanjing University
PC9	Hongyan Niu	Directly Detection of Sulfotyrosine-Containing Peptides Based on Biological Nanopore Sensing	Nanjing University
PC10	Meng-Yin Li	Nanoconfinement Controlled Electrochemistry for Single-Molecule Measurement	Nanjing University
PC11	Luke Glennon	Electrochemical Detection of Ornidazole by means of a Reduced Graphene Oxide-Modified Electrode	Maynooth University
PC12	Ulzhalgas Karatayeva	Functionalised Porous Materials for CO ₂ Capture and Conversion	University of Bristol

PC13	Yubing Wang	Oxidized microporous polyaniline networks for CO ₂ capture and conversion	Xi'an Jiaotong University, University of Bristol
PC14	Elizabeth Christie	Advancement of Resistive Pulse Sensing for Particle Identification	Loughborough University

Symposium D – In-Situ Spectroelectrochemistry and Interfacial Electrochemistry

#	Presenting Author	Title	Affiliation
PD1	Connor Sherwin	Operando X-ray Studies of Gas Evolving and Consuming Electrocatalysts	University of Southampton
PD2	Hind Almalki	Electrochemical Dissolution of Fe in Concentrated Aqueous Electrolyte	University College London
PD3	Francesco Carlà	In-situ and Operando Characterization of Electrochemical Interfaces by Surface X-ray Diffraction and Scattering	Diamond Light Source
PD4	Lisa Hirsch	Measuring the Reaction Volume of Electrochemical Surface Processes	Karlsruhe Institute of Technology
PD5	Shane P. O'Neill	Proton Coupled Electron Transfer of Anthraquinone at a Glassy Carbon and Boron-Doped Diamond electrode interface	University College Dublin
PD6	Nashwa Awais	Exploring the Behaviour of Capped Metal Nanoparticles on Metallic Surfaces	University of Birmingham
PD7	James Counter	Spectro-electrochemical Cell for Soft X-ray XAS and XPS	Diamond Light Source, University of Reading, Johnson Matthey
PD8	Georgina K. Rhodes	Characterising the Fundamental Structural and Electrochemical Properties of Single Crystal Boron Doped Diamond	University of Warwick
PD9	Alister Dale-Evans	A Voltammetric Perspective of Multi-Electron and Proton Transfer in Protein Redox Chemistry: Insights From Computational Analysis of Escherichia coli HypD Fourier Transformed Alternating Current Voltammetry	University of Oxford

Symposium E – Corrosion Science and Technology

#	Presenting Author	Title	Affiliation
PE1	Luke S. Ronayne	Microstructural Influence on Corrosion Performance of Legacy Cast Iron Mains Water Pipe	University of Southampton
PE2	Hector Arriba Gutierrez	SS Great Britain - Decarbonising the Unique Conservation System for the World's First Iron Ship	Cranfield University
PE3	Harrison Sala	Electrochemical Monitoring Techniques for Evaluating Effectiveness of Petrolatum Coatings for Cast Iron Trunk Mains	University of Surrey
PE4	Dora Capone	Zinc and Cobalt Incorporation in 316 SS Oxide Formed in Simulated BWR Conditions	University of Manchester
PE5	Nafisah Mohd Rafiq	Corrosion Studies of Diamond-Like Carbon Coating on Ti ₆ Al ₄ V Alloy: A Promising Surface Coating in Biomedical and Aviation Industry	Institute of Materials Research and Engineering (IMRE-A*STAR)
PE6	Amber Sykes	The Effect of CO ₂ Partial Pressure on the Formation and Protective Characteristics of Iron Carbonate Corrosion Products	University of Leeds
PE7	Joseph Thevakumar	Casing corrosion of steels in geothermal environments containing sulphuric Acid	University of Leeds

PA1: Nitrogen Doped rGO sheets embedded 3D Cubic Spinel CoMn₂O₄ Nanostructures, a benchmark electrocatalyst towards OER applications

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The fabrication and engineering of highly efficient oxygen evolution reaction (OER) electrocatalysts has gained much attention in recent years, a revolutionary aspect concerning the future energy conversion world including solar fuels, fuel cells, and rechargeable metal-air batteries. Herein, we represent the fabrication and application of N doped rGO/3D-CoMn₂O₄ (N-rGO/CMO) spinel nanostructures as a benchmark electrocatalyst towards the OER. The N-rGO/CMO cubes were prepared by a facile hydrothermal approach with the subsequent thermal annealing at 600°C (Ar atmosphere). The as-prepared spinel cubes were homogeneously dispersed on the rGO sheets, with a diameter of 1.3-1.5 mm. Owing to the unique 3D cubic structure, N-rGO/CMO represented superior electrocatalytic activity towards OER with a high current density at a lower onset potential of 1.52 V (vs. RHE), a small Tafel slope and high durability (~20 h) close to the benchmark RuO₂. In addition, N-rGO/CMO dispersed on GCE substrates, showed a strong coupling and facile charge transfer. This indicates that N-rGO/CMO 3D cubes are promising electrocatalysts for OER, with the potential to give a reliable and cost effective large scale production towards commercial energy conversion applications.

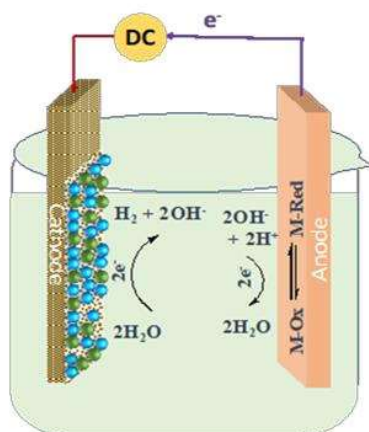
PA2: Optimisation of Electrodeposited MoS₂/MoS_x for the Hydrogen Evolution Reaction

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The development and design of cleaner and sustainable sources of energy has become a necessity due to Climate Change and the ever-increasing demands on energy. The Hydrogen Evolution Reaction (HER) is a promising green renewable source, and it might be the answer to the emerging energy crisis. Hydrogen which can be produced through the electrolysis of water with renewable energy sources, such as solar, wave or wind, is attracting considerable interest and has real potential in energy storage.



In electrolysis, water is split into hydrogen and oxygen using two half-cell reactions, with the hydrogen evolution reaction (HER) at the cathode, and the oxygen evolution reaction (OER) at the anode. The best performing electrocatalytic material for the HER, both in acid and alkaline environments, is platinum (Pt) or carbon-supported Pt nanoparticles. However, these Pt-based electrocatalytic materials are very expensive and are not cost-effective and sustainable.

In this project, MoS₂/MoS_x, a member of the dichalcogenide family of 2D materials, is investigated as an electrocatalyst for HER.

The MoS₂/MoS_x was electrodeposited onto working electrodes of different materials using ammonium tetra thiomolybdate dissolved in the presence of two different salts (sodium acetate and lithium perchlorate) and various conditions were investigated with the aim of optimising the electrodeposited film for the HER.¹ The electrodeposited MoS₂/MoS_x films were then used as electrocatalysts for the HER using different pH solutions and compared with Pt.

It was found that these optimised MoS₂/MoS_x films compared very favourably with the expensive Pt, with good long-term stability. Molybdenum and sulphur are considered as cost-effective and earth abundant materials, making the MoS₂ an interesting candidate in the electrochemical splitting of water. The incorporation of different metals oxides² is also being investigated aiming to further improve the electrodeposited film and getting the developed material closer to platinum which has been used as a reference material.³

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PA3: Investigating the impact of impure gas mixtures on single cell PEM fuel cells

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Polymer electrolyte membrane fuel cells (PEMFCs) have the potential to decarbonise a major portion of the transport sector owing to low-temperature operation, fast refuelling times and near zero emissions operation. As a guideline for hydrogen quality in vehicular applications, the ISO 14687:2019(D) standard specifies the maximum thresholds for contaminants in hydrogen that would damage fuel cells and hydrogen infrastructure, if exceeded. Previous works have studied the impact of various contaminants on fuel cell performance, but these were largely confined to binary and ternary mixtures [1]–[3]. Herein, we report the impact of (i) a complex mixture (CH_4 , CO , NH_3 , H_2S etc.) in hydrogen representing the ‘worst case’ hydrogen permissible under the ISO standard and (ii) various compounds (NO , NH_3 , SO_2 , C_7H_8) in air representing average levels of air pollution on the performance of a single cell PEMFC across a 300 h dynamic load cycling (DLC) test protocol. This work helps to quantify the difference between laboratory testing and ‘real-world’ use and represents one of the first instances where complex multi-component gas mixtures have been used for fuel cell testing. The fuel cell was characterised extensively by means of measuring polarisation curves, electrochemical impedance spectroscopy and cyclic voltammetry every 100 h. Reversible and irreversible losses (Figure 1) were also assessed, with the cell shut down completely for 10 h before resuming the next 100 h DLC. Voltage degradation profiles of the cell supplied with pure hydrogen, impure hydrogen and impure air will be discussed.

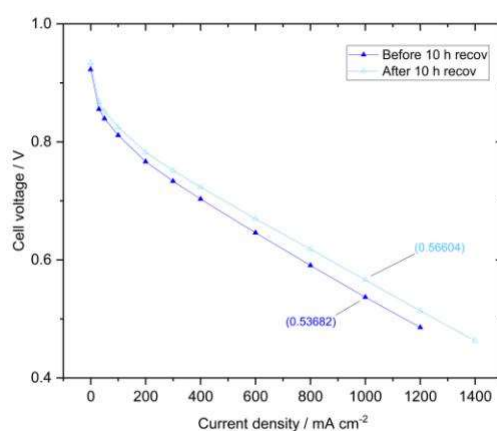


Figure 1 Polarisation curve measured immediately after 100 h DLC and following 10 h shut down; cell running on pure hydrogen

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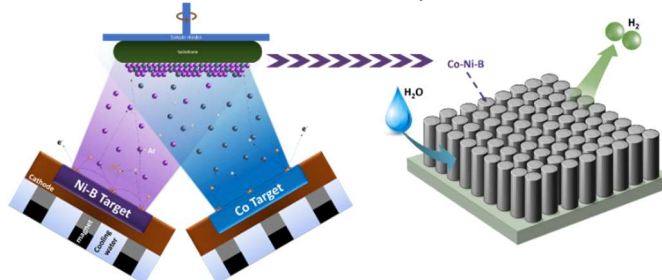
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PA4: Ni-B-based Polyalloy Electrocatalyst Coatings Deposited by MSPVD for Efficient Oxygen Evolution Reaction

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Molecular hydrogen as a green energy source has been considered one of the best energy sources due to its high energy density¹. Water splitting is a highly promising approach to generating molecular hydrogen without any damage to environmental health. However, highly active electrocatalyst materials, which are generally expensive noble elements, are required to complete the reactions efficiently and sustainably. Due to their excellent features such as low cost, high abundance, high corrosion resistance and durability, catalytic activity, and good synergistic effect with other elements, Nickel-based electrocatalysts have been reported as one of the most promising alternatives to expensive noble metals². Electrodeposition, electroless plating, hydrothermal deposition, and physical vapour deposition are some of the used techniques to synthesize Nickel-based electrocatalysts. Electroless nickel-boron (EN-B) plating is a highly beneficial technique to produce Ni-B coatings with outstanding features including hardness, wear resistance, and corrosion resistance. In recent studies, ENi-B coatings have also demonstrated encouraging catalytic activity with remarkable stability³. While N-B coatings have been extensively studied for various applications, there is not enough research on their catalytic applications. Furthermore, there is no existing literature regarding the deposition of Ni-B coating utilizing a technique other than electrodeposition or electroless plating. However, Magnetron Sputtering Physical Vapour Deposition (MSPVD) technique has the capability of producing Ni-B coatings with porous and tuneable structures together with an easy alloyability to further improve the electrochemical performance.

The current study is designed to investigate the electrocatalytic performance of Ni-B-based polyalloy coatings produced by MSPVD. Polyalloy coatings were co-deposited using a Ni-B target and a transition metal target such as Fe, Co, and Mo. The coatings were deposited at different deposition parameters such as pressure, substrate temperature and also at different chemical compositions. The electrocatalytic performance of the coatings was compared to see the effect of boron, alloying elements, morphology, and crystal structure for the Oxygen Evolution Reaction. Superior features like low overpotentials, high stabilities, and high surface areas were obtained after electrochemical analysis such as Linear sweep voltammetry, cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy under alkaline conditions. The results showed promising efficiencies and stabilities with highly tuneable, cost-effective electrocatalyst coatings.

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PA5: Transition Metal Antimonates for Oxygen Electrocatalysis

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A fuel cell is an electrochemical “device” that continuously converts chemical energy into electric energy. Due to their excellent energy efficiency, these devices are especially appealing for the future stationary power and transportation industries. Only after the creation of low-cost, widely available, and highly effective catalysts for oxygen reduction processes can devices be widely used. The best ORR catalysts available today are carbon-supported platinum-based compounds. Pt-based catalysts have significant energy losses and are limited in part because of the high cost and scarcity of Pt. Using an experimental approach, a novel electrocatalytic material for the ORR is explored in this study, composed of first-row transition metal antimonates that have the potential to be used for electrocatalytic applications, such as fuel cells and metal-air batteries. Studies indicate that transition metal antimonate catalysts, MSb_2O_6 , are active for ORR, therefore finding and developing stable, active, selective, and affordable Pt-free ORR catalysts is necessary to meet this problem. This class of materials, in particular, has the capacity to improve the performance of metal oxides by adjusting metal active sites and increasing activity at a metal site level. High current densities and low overpotentials demonstrated excellent catalytic properties for the materials in ORR. Oxygen reduction reaction in an alkaline environment has been thoroughly investigated with these materials as electrocatalysts in an alkaline solution. The results from CV and LSV suggest that varying electronic structure chemistry heightens ORR activity. MnSb_2O_6 stands out as an especially interesting candidate among first-row transition metal antimonates due to its good oxygen-binding energetics, conductivity, electronic structure, and stability. In terms of activity and selectivity, the MnSb_2O_6 electrocatalyst has the best performance toward the ORR.

Keywords: Oxygen Reduction Reaction, Transition metal antimonates, fuel cell, Electrocatalysis.

PA6: Ferrocene-Based Metal Organic Frameworks for Electrocatalysis Applications

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Electrochemical technologies for generation of fuels from renewable resources and upcycling of waste organic compounds offer promising routes to a more sustainable future. The splitting of water via electrolysis to produce green hydrogen, a desirable energy carrier, is currently hindered by the slow oxygen evolution reaction (OER) half reaction.¹ Meanwhile, upcycling of waste chemicals such as CO₂, polyethylene terephthalate (PET) and 5-hydroxymethylfurfural (HMF) typically utilise non-sustainable methods requiring high energy inputs or is extremely slow.²⁻⁴ A promising solution to many of these issues is to develop electrocatalysts.

Metal organic frameworks (MOFs) have been widely reported for electrocatalysis, owing to their porous structures and unrivalled tunability. Recently, ferrocene (Fc)-based MOFs have been employed as electrocatalysts primarily for water splitting.⁵⁻⁷ We explore MOFs utilising ferrocene dicarboxylate (FcDCA) linkers for a range of electrocatalytic processes, including water splitting, CO₂ reduction, plastic upcycling, and organic electrooxidation. We investigate four MOFs with FcDCA linkers, with nodes of Fe, Ni, Co and Cu. We also investigate the performance of the Fc-MOFs in a 2-electrode electrolyser for water splitting, using a bimetallic MOF electrode for the hydrogen evolution reaction (HER).

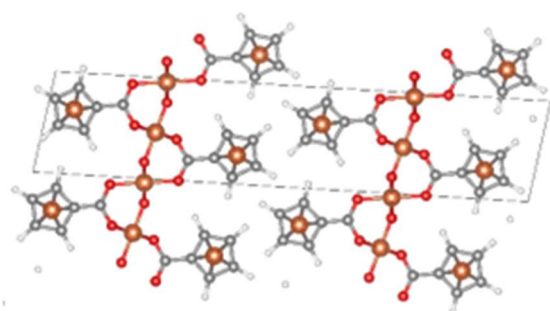


Figure 1 - Structure of FeFc MOF refined via DFT.
Black box shows unit cell

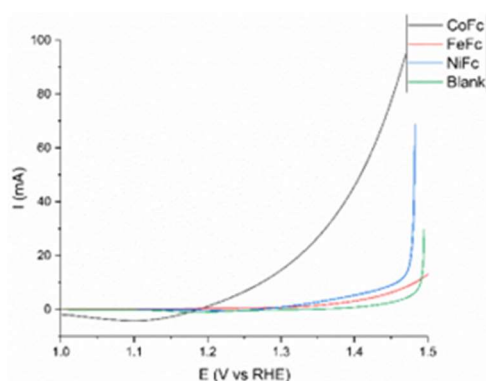


Figure 2 - LSV of Fc MOFs on Ni-Foam substrate for OER

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PA7: Performance improving for proton-exchange membrane fuel cells using modelling and diagnostics tools

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Performance and long-term durability targets present significant challenges for the large-scale commercialisation of proton-exchange membrane (PEM) fuel cells. For example, short term goals set by the the Million Mile Fuel Cell Truck Consortium (M2FCT)¹ are around 2.5 kilowatts per gram of PGM. This translates to current densities of 1.07 A cm^{-2} at 0.7 V after 25,000 hour-equivalent accelerated durability tests. To achieve this, improvements in beginning of life performance that is sustained throughout the fuel cell lifetime are required.

Usually, performance and durability are first evaluated at the membrane electrode assembly (MEA) level. Water, heat, and transport of species need to be considered. Electrodes must have high electronic and ionic conductivity to enable efficient catalyst utilization and must also be operationally robust to enable high performance under a range of operating conditions. Transport resistances affect voltage losses in the cell in a number of ways. These can be quantified using electrochemical impedance spectroscopy method and numerical modelling. Mass transport resistances are more difficult to quantify, for example, the oxygen transport resistance impeding the flow of oxygen to the surface of the catalyst. In addition, the water transport resistance impedes the flow of product water out of the cell, keeping the electrodes and membrane humidified, lowering their proton resistance, but if too severely impeded can lead to flooding of the electrode, which then hinders mass transport within the gas phase.

Transport resistances inside a series of MEAs with Pt loadings in the cathode catalyst layer of 0.4, 0.2 & 0.1 $\text{mg}_{\text{Pt}} \text{ cm}^{-2}$ were quantified using limiting current measurements and impedance spectroscopy under H_2/N_2 (anode/cathode). Additionally, the effects of Knudsen diffusion, oxygen dissolution rate and diffusion through the ionomer on limiting currents and polarisation curves were evaluated using modelling approaches. The methodology to determine transport resistances using the limiting current method within the catalyst layer is based on the experimental approach described by Baker². For bulk oxygen concentration C_{O_2} , the total oxygen transport resistance R_{Total} at i_{lim} limiting current (where the oxygen concentration on the platinum catalyst approaches zero) can be estimated using Fick's Law. The portion of the total resistance due to the local resistance at the platinum surface $R_{\text{O}_2^{\text{Pt}}}$ was determined experimentally to be between 7-9 S m^{-1} depending on the operating pressure. The effect this resistance has on the catalyst layer oxygen transport resistance was inversely proportionally to the platinum surface area and equates to voltage losses of around 6 mV at 0.8 A cm^{-2} limiting current for a $0.4 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ catalyst layer. A reduced area MEA was used to measure along-the-channel effects in terms of oxygen depletion and humidity variation.

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PA8: Investigating the Stabilities of Carbon Support Materials Obtained From Fmoc-Amino Acid Hydrogels for Low-Temperature Acidic Oxygen Reduction Reaction Applications

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Carbon support materials play a key role in the electrocatalytic reduction of oxygen at the cathode of low-temperature hydrogen fuel cells. A support material is expected to provide good electrical conductivity, prevent migration and detachment of the catalyst, possess suitable morphology to aid in exposure of active sites to the electrolyte, and resist corrosion. A major challenge for carbon support materials is poor durability under harsh fuel cell conditions such as applied voltage and low pH. Strategies to improve the durability of a carbon support include synthetically tailoring characteristics such as porosity and degree of graphitization.^{1,2}

Hydrogels consist of cross-linked polymeric materials with porous 3D structures within which water is absorbed.³ The ability of these polymeric networks to swell and hold relatively large amounts of water without structural damage means that nanostructured and porous carbon materials can be prepared from them.

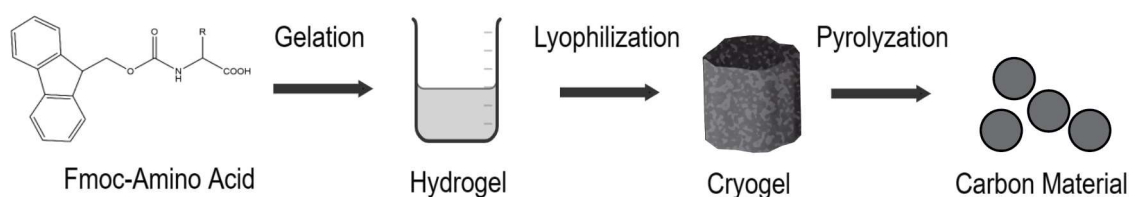


Figure 7. Diagram illustrating the general process followed in this work to produce carbon materials from Fmoc-protected amino acid hydrogels.

In this work carbon materials were obtained from a series of Fmoc-protected amino acid hydrogels following the process illustrated in Figure 1, and their chemical and physical properties and related stabilities have been investigated. Aside from the advantages of employing relatively cheap and non-toxic amino acids, this method of preparing carbon materials for fuel cell applications has the potential to allow reliable and well-defined tailoring of physical and chemical characteristics. These materials can be further functionalised or doped, and the pyrolyzation step employed to obtain the carbon network can be tailored to alter the degree of graphitization.

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PA9: Structure Activity Relationship of $\text{La}_{1-x}\text{Nd}_x\text{CoO}_3$ nanostructures Toward Oxygen Electrocatalysis

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Rationalizing the activity of transition metal oxides (TMOs) towards reactions such as the oxygen evolution (OER) and oxygen reduction (ORR) reactions in terms of their composition and crystal structure is one of the grand challenges in electrochemical energy conversion systems. TMO electrocatalysts are a vast family of compounds with a wide range of structural motifs, dimensionalities, and electronic properties, ranging from insulator to metallic conductivity.^{1, 2} In this contribution, we will provide a detailed study of the structure and activity of $\text{La}_{1-x}\text{Nd}_x\text{CoO}_3$ perovskites, with x ranging from 0 to 1. We will assess parameters such as coordination number, bonding and oxidation state of Co as a function of x . OER activity increases as the Nd content in the A-site increases up to approximately 50 %. We correlate this trend with evolution of Co d-states as a function of composition as probed by electrochemical measurements and DFT calculations. The electrochemical and computational results are supported by structural analysis obtained from X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and electron microscopy (EM).

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PA10: In-Situ Reference Electrodes in Alkaline Water Electrolysis

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The use of alkaline water electrolysis to split water into hydrogen and oxygen dates back to the late 19th century and has advantages over other water electrolysis technologies, including higher durability and cost-effectiveness due to the nature and availability of materials required for use.¹ An ability to better understand the mechanisms and behaviours that are taking place within the cell would be a great advantage in the development of more efficient and stable alkaline electrolyzers. This will in turn help in the energy transition from fossil fuels to renewables. In-situ reference electrodes can be used to provide deeper insights into the processes occurring at the anode and cathode of an alkaline water electrolysis cell.

In this study, two reversible hydrogen electrodes (RHE) were used to measure the electrode potential of the anode and the cathode of the cell by connection through Luggin capillaries. This avoided the insertion of a larger reference electrode directly into the cell, which is known to cause adverse effects.² This method also reduced the distance between the reference electrode and the electrode of interest, resulting in a smaller iR-drop. The obtention of a polarisation curve was conducted using a 1 M KOH electrolyte whilst holding current densities ranging from 0.05 A cm⁻² to 1 A cm⁻² for 60 seconds each. Figure 1 shows the iR-corrected cell voltage along with the individual anode and cathode cell potentials (vs. RHE), clearly showing that the anode contributes ~ 75% of the overpotential and the cathode ~ 25% at a current density of 0.5 A cm⁻².

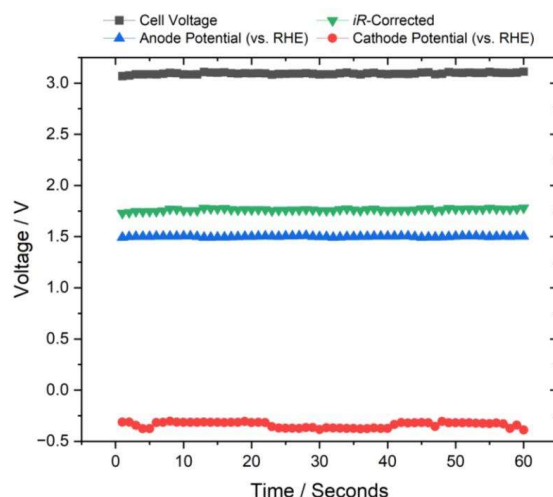


Figure 1 Cell voltage, iR-corrected cell voltage, and anode and cathode potentials (vs. RHE) of the alkaline electrolysis cell in 1 M KOH at 0.5 A cm⁻².

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PA11: Structure Activity Relationship of Fe-C Catalysts Derived from ZIF-8 for the Oxygen Reduction Reaction

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The need for greater energy production and the problems posed by climate change has motivated the global community to shift from fossil fuels towards low-carbon technologies such as the polymer electrolyte membrane (PEM) fuel cell. However, current PEM fuel cell technologies deploy costly platinum-based catalysts at both the anode and cathode. The discovery of platinum group metal (PGM)-free catalysts for the sluggish cathodic oxygen reduction reaction (ORR) is therefore an attractive route that requires urgent attention. This work examines ZIF-8 derived PGM-free catalysts which have recently gained significant attention for the ORR. We utilize a one-pot synthesis approach, deploying a range of different precursor salts of Fe to uncover how the Fe source affects the structure, morphology, and ORR activity of the Fe-doped carbonised ZIF-8 electrocatalysts. More precisely, two Fe (II) salts—ammonium iron (II) sulphate and iron (II) acetate—were chosen. Various material's characterisation techniques such as SEM (Scanning Electron Microscopy), EDS (Energy Dispersive X Ray Spectroscopy), XRF (X-ray fluorescence), XPS (X-ray photoelectron spectroscopy), were then deployed to characterize the carbonised ZIF-8 (CZ) and its Fe-doped derivatives, CZ-A (doped with ammonium iron (II) sulphate) and CZ-B (doped with iron (II) acetate). Furthermore, using a rotating disc electrode (RDE) and linear sweep voltammetry (LSV), the ORR activity of the same materials, was investigated in both acidic (0.5 M H₂SO₄) and basic (0.1 M KOH) electrolytes. The ORR activity of both the Fe-doped catalysts surpasses the pure CZ, with a significant activity in the basic electrolyte. The choice of Fe source has an influence on the performance of the catalysts as well i.e., CZ-A showed better performance over CZ-B in both pH conditions. These findings show the possible use of Fe-doped carbonised ZIF-8 catalysts for ORR in simple electrolytes and provide crucial information for the development of novel non-precious metal ORR catalyst materials.

PA12: Preparation of High Performance Ultra-Low Loading PEM Fuel Cell Catalyst Layers

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During the past decade the use of hydrogen as a vector for producing electricity has been extensively studied and has been exponentially improved, especially regarding its applications in the transport sector. Hence, several goals have been put in place by the Clean Hydrogen Joint Undertaking regarding both the performance and the cost of fuel cell stacks to further aid their commercialisation. The targets state that Pt content of the stack must be reduced to 0.08 gPt kW⁻¹ and the mass activity must be increased from 4.5 A mgPt⁻¹ to 15 A mgPt⁻¹ at 0.66V by 2024.[1] Here a new and simple preparation method for ultra-low Pt loading catalyst layers is introduced comprising of vacuum filtration, like the one used in the floating electrode method presented by Kucernak et al,[2] followed by a decal transfer method to produce catalyst layers with loadings down to 5 µgPt cm⁻² on the anode and cathode. Initial tests yielded both impressive and unexpected results, stressing the need for further investigation to take place to fully understand the kinetic response of catalysts under varying conditions and large potential ranges. For instance, these catalyst layers achieve high electrochemically active surface areas of 96.3 ± 0.4 m² gPt⁻¹ for the Pt/C electrodes prepared while, exhibiting impressive performances of 24.4 ± 1.8 A mgPt⁻¹ at 0.65 V under H₂/O₂ (1 barabs). The current densities and power outputs increased from polarisation curves measured in H₂/Air at 1 barabs to 2.5 barabs, followed by further increases from H₂/O₂ at 1 barabs to 2.5 barabs. The power density appeared to be dominated by electrokinetics over a very wide potential range, deeming it ideal to study the electrokinetics of oxygen within the fuel cell environment, enabling further understanding of the oxygen reduction reaction kinetics. As seen above the results obtained are closer to the targets set by the Clean Hydrogen Joint Undertaking, and about 4x higher than previously reported values in the literature.[3]

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PA13: CO₂ removal from Aqueous Bicarbonates using Bipolar Membrane Electrodialysis

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For over a decades, alkaline solutions viz. potassium hydroxide (KOH), sodium hydroxide (NaOH), sodium carbonate (Na₂CO₃), and potassium carbonate (K₂CO₃) been used to capture and sequester carbon dioxide (CO₂). Their remarkable properties have been harnessed by researchers, enabling significant strides in CO₂ capture and mitigation efforts. However, further development is required due to the slow reaction kinetics, low stability and high cost due to the necessary thermal regeneration of solvents. We employed bipolar membrane electrodialysis (BPMED) using aqueous potassium carbonate and bicarbonate solutions for CO₂ capture. Herein, under the influence of applied electric potential difference; the bicarbonate ions are transported through an ion exchange membrane to the concentrate side, where they are converted into the CO₂ gas in the presence of acid groups. The performance of the electrodialysis cell was evaluated for CO₂ removal through the current efficiency and the power consumption parameters.

Keywords: Carbon capture, membranes, electrodialysis.

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PA14: Decoupled Electrolysis for the Production of Zero-Carbon Hydrogen

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Electrolysis of water to produce hydrogen, notably water splitting, has great potential for addressing and mitigating potential energy crises and thus ameliorating environmental pollution. However, new electrolyzers that are more compatible with low current densities must be developed. This is because existing electrolyzers suffer from serious component degradation and hydrogen/oxygen mixing issues when operated in these current densities and at intermittent modes. Hence the poor performance of electrolyzers when coupled directly to low-power sources has hampered efforts to generate truly green hydrogen.

Here, we will build on the concept of Decoupled electrolysis to develop a system that can use low/high current densities for the electrolysis of water using silicotungstic acid as the redox mediator.^{1,2,3} By leveraging the ability of decoupled electrolysis to allow hydrogen and oxygen generation to take place in separate places, at separate times, and at rates that are not connected to each other, we aim in this project to demonstrate the production of pure and green hydrogen. This will open the door to future scale-up of these systems for safe and efficient production of zero-carbon Hydrogen driven by low /high current densities.

Keywords: Hydrogen Evolution Reaction, Decoupled Electrolysis, Polyoxometalate

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PA15: Enhancing $\text{La}_{0.75}\text{Ca}_{0.25}\text{Fe}_{1-x}\text{Ni}_x\text{O}_3$ Catalytic Activity Towards Oxygen Electrocatalyst

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Perovskite materials have garnered substantial attention as reliable catalysts for the oxygen evolution reaction (OER) due to their high catalytic activity, cost-effectiveness, stability, and eco- friendly [1,2]. This research delves into the enhancement of catalytic activity in $\text{La}_{0.75}\text{Ca}_{0.25}\text{Fe}_{1-x}\text{Ni}_x\text{O}_3$, a series of perovskite oxides, to uncover their potential as efficient oxygen electrocatalysts. The aim of this research is to systematically investigate the impact of the partial substitution of Fe with Ni towards OER. The sol-gel method was employed to synthesize the perovskite samples [3]. The findings of this study reveal that the strategic substitution of Fe with Ni can significantly enhance the catalytic activity of the $\text{La}_{0.75}\text{Ca}_{0.25}\text{Fe}_{1-x}\text{Ni}_x\text{O}_3$ series. The OER activity showed that as Ni increased, the catalytic performance also increased. Among the investigated compositions, $\text{La}_{0.75}\text{Ca}_{0.25}\text{Fe}_{0.5}\text{Ni}_{0.5}\text{O}_3$ emerged as the most promising electrocatalyst, exhibiting superior OER performance. Characterization techniques including X-ray diffraction (XRD), electrochemistry, transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), and energy-dispersive X-ray (EDX) were utilized to analyse the crystal structure, morphology, elemental composition, and electrochemical behaviour of the synthesized materials.

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PA16: Electrode Materials for Hydrogen Bromine Redox Flow Battery

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Redox flow batteries (RFBs) have been identified as one of the promising technologies for electrical energy storage because of their high efficiency, fast response, long cycle life, safe operation, and environmental friendliness. However, it is imperative that the electrolyte and the electrode materials used in an RFB are economical and abundant to ensure the energy storage system is sustainable and economically feasible. The hydrogen-bromine ($\text{H}_2\text{-Br}_2$) RFB meets these criteria owing to the abundance of hydrogen, bromine and the cheap, scalable, carbon-based electrode materials used for the bromine electrode, fast and reversible reaction kinetics of both the hydrogen and bromine electrodes, and detachment of power and capacity within the system. Compared to other electrochemical energy storage systems, the stored energy in $\text{H}_2\text{-Br}_2$ system, in theory, can be unlimited; in practice, it is very achievable in the range of kilowatt-hours to megawatt-hours as it is depending on the size of the storage tanks [1-3].

Due to the highly corrosive nature of bromine, the bromine electrode materials for $\text{H}_2\text{-Br}_2$ system need to be corrosion resistant, durable, and cheap along with good electrochemical activity. Noble metal platinum shows excellent electrochemical activity for bromine redox reactions but its instability in bromine electrolyte and high cost hampers its use. Carbon materials possess the advantages of low cost, excellent electrical conductivity, good inertness to corrosive media, wide operation potential range, controllable surface properties, high surface area, suitable porosity, and simple synthetic method. Carbon based materials have been used as bromine electrodes and improvise their properties in order to achieve high power density and stability thereby reducing the cost of the redox flow batteries. This presentation provides an overview of $\text{H}_2\text{-Br}_2$ RFB technology, with a focus on electrode materials to be used for design and development of $\text{H}_2\text{-Br}_2$ RFB system with improved performance.

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PA17: Hydrogen Generation from Seawater

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Water electrolysis is an effective approach to produce hydrogen sustainably and renewably. Scaling up green hydrogen production presents a risk and burden on freshwater resources, as a result, using the most abundant water source on the planet (seawater) as an electrolyte in electrolysis is a viable alternative for reducing cost and freshwater scarcity in the future but is limited by catalyst technology which is struggling to meet industrial requirements and long-term stability needed in a commercial application.

High volumes of negatively charged chloride anions present in seawater, introduce a challenge at the anode. The chlorine evolution reaction (CIER) is considered to be a competing reaction and negative to the oxygen evolution reaction (OER) performance. Anode catalysts must be highly selective and favour the OER to minimise the creation of toxic and corrosive hypochlorite during seawater electrolysis.

This study reports an investigation of the oxygen evolution reaction using low cost, nickel iron-based coatings cathodically electrodeposited on nickel substrates. In order to minimise IR drop and hence make more reliable comparison of materials at the high current densities of interest for water electrolyzers, the measurements were carried out with microelectrode (area $1.965 \times 10^{-5} \text{ cm}^2$).

Figure 1 illustrates a $\text{NiFe}(\text{OH})_2$ catalyst performance for OER in simulated seawater electrolytes, reaching current densities of $\sim 2.5 \text{ A cm}^{-2}$ at $\sim 345 \text{ mV}$. Further to this, the catalyst can be seen to achieve 500 mA cm^{-2} and 1 A cm^{-2} at overpotentials of 285 mV and 315 mV , respectively. Long term stability and performance in real seawater will be subsequently tested.

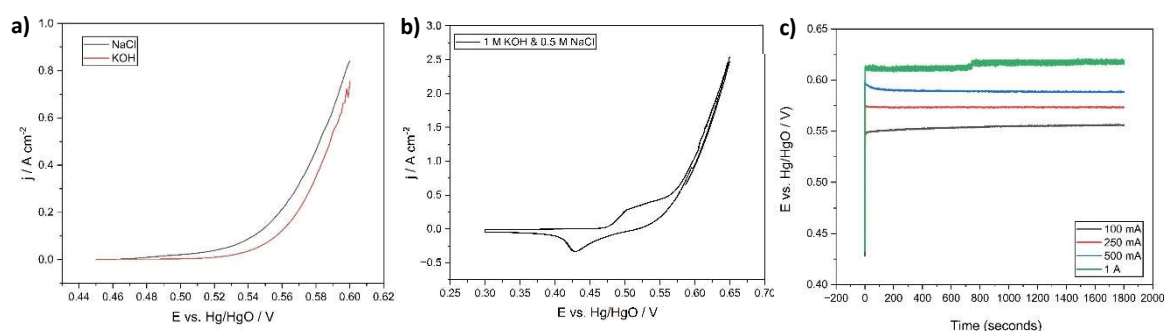


Figure 1. **a)** Linear sweep voltammetry curves of $\text{NiFe}(\text{OH})_2$ catalyst in 1 M KOH vs 1 M KOH & 0.5 M NaCl at 60°C at a scan rate of 1 mV s^{-1} . **b)** Cyclic voltammetry curve of $\text{NiFe}(\text{OH})_2$ catalyst in 1 M KOH & 0.5 M NaCl at 60°C at a scan rate of 100 mV s^{-1} . **c)** Chronopotentiometry tests of $\text{NiFe}(\text{OH})_2$ catalyst in 1 M KOH & 0.5 M NaCl at 60°C at current densities of $100, 250, 500 \text{ mA cm}^{-2}$ and 1 A cm^{-2} .

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PA18: Exploring the role of redox-shuttle mediators in lithium-sulfur batteries

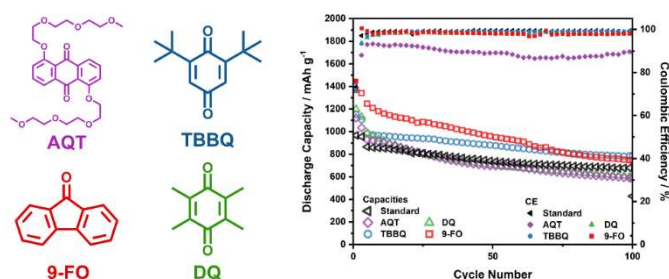
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The lithium-sulfur (Li-S) battery is one of the key contenders in replacing the lithium-ion battery. The combination of a theoretical high gravimetric energy density of $2567 \text{ W h kg}_{\text{cell}}^{-1}$, lower raw material costs and reduced environmental and sociopolitical impact make it an attractive battery technology. [1] Despite this promise, lithium-sulfur batteries still suffer from poor cycle life, rapid capacity fading and lower coulombic efficiencies largely due to the polysulfide shuttle effect. [2] Redox mediators have been proposed to mitigate these effects by delivering charge to both polysulfide intermediates in solution and insoluble sulfur/lithium sulfide during cell cycling, allowing for complete utilization of all sulfur species in the cell. [3] Currently there is a gap in the understanding of their property-performance relationship, how they affect polysulfide speciation and their compatibility with the metallic negative electrode within the cell.

Here we investigate a class of quinone-based compounds for use as molecular redox mediators in lithium sulfide cells, specifically 2,6-di-tert-butyl-1,4-benzoquinone (TBBQ), duroquinone (DQ), and 1,5-bis(2-(2-(2-methoxyethoxy) ethoxy) ethoxy) anthra-9,10-quinone (AQT) and 9-fluorenone (9-FO). [4] These were selected such that their redox potentials span the operating potential of the Li-S positive electrode ($1.8 \text{ V} - 2.6 \text{ V vs Li}^+|\text{Li}$). Interactions between the mediators and sulfur, lithium polysulfides, lithium sulfide and lithium metal were probed using chromatography, ultramicroelectrode voltammetry and cell cycling. Liquid chromatography-mass spectrometry confirmed that out of the chosen mediators, TBBQ and AQT can act effectively as both charge and discharge mediators. In real cells however, AQT showed poor coulombic efficiency as a result of shuttling, due to reaction with lithium and the high solubility of reduced AQT, as confirmed using ultra-



micro electrode voltammetry and solubility studies. Our findings demonstrate the importance of mediator redox chemistry, solubility, polysulfide conversion efficiency and compatibility with lithium metal when developing new mediators for Li-S batteries.

Figure 8. Structures of the redox mediators used in this study, along with cell performance, showing the maximum discharge capacity and coulombic efficiency of Li_2S coin cells with and without redox mediator, cycled at 0.1 C . Li_2S cells had a loading of 2.5 mg of Li_2S . The electrolyte comprised of 1.0 M LiTFSI , 0.5 M LiNO_3 in DOL:DME ($1:1 \text{ v/v}$) for the standard, with 50 mM of added redox mediator in mediated cells.

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PA19: High energy density supercapacitor with wide temperature tolerance enabled by corn husk based activated carbon/Siloxene electrodes and AWIS electrolyte

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Abstract: The development of high-performance biomass activated carbon-based supercapacitors with enhanced energy density and wide temperature tolerance is still a great challenge.¹ Recent research has concentrated on the production of multicomponent materials by combining biomass activated carbon with 2D materials in order to increase the electrochemical performance of the porous carbon materials.^{2,3} Herein, a novel corn husk derived activated carbon/2D siloxene composite electrode has been designed that delivers high specific capacitance of 415 F g⁻¹ at 0.25 A g⁻¹ and rate capability in 1 M Na₂SO₄ electrolyte. The high surface area (1508 m² g⁻¹) activated carbon derived from the corn husk (ACH-900) serves as a suitable framework for hosting siloxene nanosheets (S), where the siloxene nanosheet structures serves as a spacer and exposes the surface-active sites of ACH-900 for rapid electrochemical reactions and ensures high utilization of electrode materials. The symmetric supercapacitor with ACH-900/S composite electrodes and "acetonitrile/water-in-salt (AWIS)" electrolyte also demonstrated an energy density of 57.2 W h kg⁻¹ at 338 W kg⁻¹ power density and retained 92.8% capacitance after 10000 cycles at 5 A g⁻¹ current density. Besides, the fabricated ACH-900/S supercapacitor can operate over wide temperature range from 0 to 100 °C. The activated carbon/2D siloxene composite with AWIS electrolyte supercapacitor can become versatile functional devices in several high temperature energy conversion and storage applications.

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PA20: Best Practice for Finding Interfacial Contact Resistances Using Spatially Resolved Millimetre Scale Measurements

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The essential components which make up hydrogen fuel cells and electrolyzers, such as gas diffusion layers (GDLs), porous transport layers (PTLs) and bipolar plates (BPPs), are sandwiched together to conduct current, therefore maintaining a low interfacial contact resistance (ICR) between them is essential for high performance. By building upon existing techniques, we have established a robust methodology of measuring ICR with spatial resolution on the mm scale. This technique enables heterogeneity in ICR to be located and is therefore especially useful for quality control.

Figure 1 shows a schematic of how spatially resolved measurement of ICR was achieved. Segmented gold electrical contacts on custom made plastic circuit boards (PCBs) were used to contact the material. Gaskets were applied to give even pressure distribution along with pressure paper to evaluate its uniformity. A pneumatic press was used to set a consistent pressure and a low resistance ohmmeter enabled resistance measurements to be made.

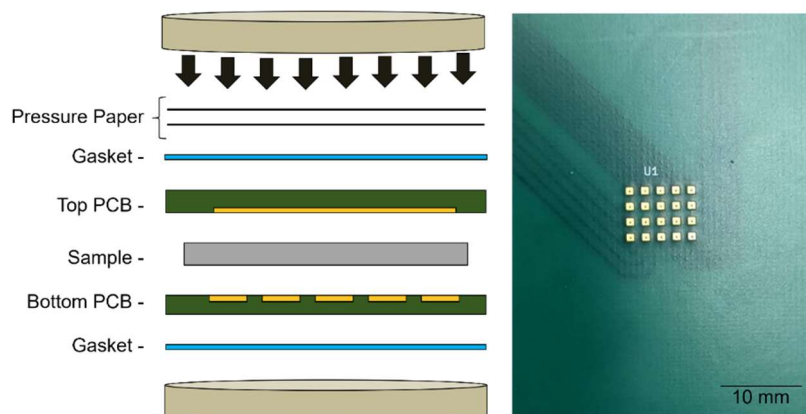


Figure 1: Left: Schematic showing set-up of the experiment. Right: Image of the bottom PCB used in the experiment.

This approach enables the consistent and reliable measurement of ICR and improves upon previously reported methods of ICR measurement.^{2,3} ICR is higher at lower clamping pressures, but the relationship is non-linear, with ICR uncertainty increasing significantly at low pressures, emphasising the need for accurate control of experimental parameters.⁵ Recommendations are therefore made for best practice in ICR measurement utilising spatially resolved methods to generate more representative data.

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PA21: Electrolytes for Rechargeable Magnesium Metal Batteries

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Currently, electric vehicles (EVs) are the centre of conversation surrounding sustainability in the UK with the Government's plan for transitioning to zero emission cars and vans by 2035.¹ Lithium-ion batteries have become the state-of-the-art in most devices, such as EVs, however, they no longer meet the increasing demand for the high energy density needed, i.e. range of an EV.² Rechargeable magnesium metal batteries (RMBs) have been identified as a promising alternative as, in comparison to lithium metal, magnesium metal is significantly more abundant, and has a higher volumetric capacity (2046 vs. 3833 mAh cm⁻³).³ However, identification of electrolytes that allow reversible magnesium plating and stripping whilst simultaneously having a good potential window, passivation of magnesium metal anodes, and lack of compatible cathodes pose a challenge.⁴ The development of new electrolyte materials for RMBs is required as the current candidates offer significant passivation, low capacities, or issues with corrosion due to the presence of chloride. Weakly coordinating anions have been identified as a promising candidate for Mg electrolytes as their large size and low charge, limits interactions with the cation reducing ion-pairing effects and boast relatively simple synthetic routes that are attractive for commercial applications. Recently, electrolytes of Mg(DME)3[Al(hfip)4]2 (**Figure 1**) in glyme solvents have been shown to allow reversible behaviour in cells with Mg foil and Chevrel phase (Mo6S8) electrodes.^{5, 6}

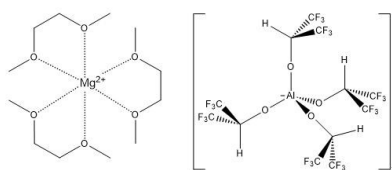


Figure 1: Mg(DME)3[Al(hfip)4]2

Magnesium electrolytes often use glyme solvents which are highly volatile, making them non-ideal for commercial applications. In addition, the vast excess of the strongly coordinating glymes can result in the sluggish release of Mg²⁺ at the electrode surfaces. Hence, the use of a solvent that will not compete with the ligand, improving the kinetics, is of interest.⁷

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PA22: Water-in-Salt Electrolytes for Redox Flow Batteries

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Redox flow batteries (RFB) are suited to grid scale energy storage, and in particular, can be integrated with renewable energy sources. RFBs store electrolyte solutions, containing the redox active material, in external tanks and pump them through the battery; this allows the energy capacity and power density of the battery to be scaled independently of each other. The two electrolyte solutions are typically separated by a membrane within the cell; the membrane is often a material called Nafion, which is expensive and can contribute up to 40% of the cost of the RFB system.[1] Current commercial RFBs use metals, often vanadium, as the redox active material in aqueous electrolytes. The main disadvantages of using metals in RFBs is that they are expensive and limited in abundance, which has led to organic molecules being explored as alternative redox mediators.

This work aims to produce a novel metal-free membraneless RFB using water-in-salt electrolytes (WiSE) which form an aqueous biphasic system (ABS) with a stable interface. Lithium chloride (LiCl) and Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) have previously been shown to form an ABS with each other.[2] We found that anthraquinone (AQ), a redox active organic molecule (ROM), was able to dissolve in LiTFSI WiSEs at low concentrations. Subsequently, the redox behaviour of AQ in LiTFSI was investigated; the redox reaction was found to be pH dependent and was fully reversible at pH8. This AQ/LiTFSI half-cell can therefore act as the negative couple in a membraneless RFB with LiBr/LiCl as the positive couple. This system has been initially tested in a static setup and yielded a battery system with a voltage of 1.6V. Future work aims to optimise and test this battery system before testing it under flow conditions.

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PA23: High-voltage and high-energy-density membrane-free nonaqueous flow batteries

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Lithium-metal-based nonaqueous redox flow batteries (LRFBs) have garnered considerable attention as potential alternatives to conventional aqueous redox flow batteries (RFBs) due to their high operating voltage and large theoretical energy density [1, 2]. However, the widespread applicability of LRFBs is hindered by the limited availability and high cost of the critical ion-selective membranes [3]. Consequently, membrane-free systems emerge as promising alternatives [4]. In this study, we present high-voltage membrane-free LRFBs based on an all-organic biphasic system that employs a Li metal anode and 2,4,6-tri-(1-cyclohexyloxy-4-imino-2,2,6,6-tetramethylpiperidine)-1,3,5-triazine (Tri-TEMPO) cathodes. The Li|Tri-TEMPO biphasic batteries demonstrate theoretical cell voltages of 3.53 V. Under static conditions, the Li|Tri-TEMPO batteries containing 0.5 M of redox-active material exhibit impressive capacity retention rates of 98% after 100 cycles over approximately 55 days. Moreover, the representative Li|Tri-TEMPO (0.5 M) flow battery displays a capacity retention rate of 81% after 100 cycles over approximately 45 days, along with a Coulombic efficiency of 96% and energy efficiency of 82%. This study marks significant advancements in biphasic systems for membrane-free batteries, achieving both high voltage and high energy density (approximately 33 Wh/L) under flow conditions.

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PA24: The effect on performance 75Li₂S·25P₂S₅ solid-state electrolyte system through doping Li₂O

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Since Sony launched the first lithium-ion batteries (LIBs) to the market in the early 1990s, they have attracted the attention of researchers due to their outstanding characteristics, including lightweight, high-energy density, long cycle life, environmental friendliness, and no memory effects ^[1-4]. Many countries have announced the orderly promotion of electric vehicles to replace fuel vehicles in recent years, prompting researchers to continuously develop battery materials and enhance battery performance to meet application needs ^[5-8]. All-solid-state lithium-ion batteries (ASSLIBs) using solid-state electrolytes (SSEs) promise the potential to replace traditional LIBs containing flammable organic liquid electrolytes and thereby improve the safety of next-generation high-energy batteries ^[9]. SSEs with high lithium-ion conductivities are essential to the development of ASSLIBs. The Li₂S·25P₂S₅ (LPS) system is regarded as one of the most promising SSE materials for future development. However, when compared to the conductivity of traditional liquid electrolytes, this is far from sufficient. Doping modification has been proposed to be a simple and effective approach to improving the performance of solid-state electrolytes. In this work, a series of (100-x)(0.75Li₂S·0.25P₂S₅)·xLi₂O (mol %) (x = 0, 0.5, 1, 2, 3) glass-ceramic electrolytes were synthesized by two-step ball milling technique (mechanical ball milling and subsequent heat treatment). Various characterization techniques (including powder X-ray diffraction, Raman, and solid-state nuclear magnetic resonance) have proved that the addition of Li₂O can stimulate 75Li₂S·25P₂S₅ system to generate the high ionic conductivity phase Li₇P₃S₁₁. The addition of Li₂O raised the amount of the easily lost light element Li and altered the element proportions in the 75Li₂S·25P₂S₅ system. The Li₇P₃S₁₁ phase with higher ionic conductivity was developed in the 75Li₂S·25P₂S₅ system, with a main structure of β-Li₃PS₄ and a little amount of Li₄P₂S₆, which is the primary reason for the increase in ionic conductivity of the doped material. Through doping optimization strategy, the ion conductivity (at room temperature) of 99(0.75Li₂S·0.25P₂S₅)·1Li₂O reached 1.01×10⁻⁴ S cm⁻¹, which is an order of magnitude higher than the undoped sample.

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PA25: Exfoliation of $\text{Ca}_3\text{Co}_4\text{O}_9$ to two-dimensional single-crystalline misfit calcium cobaltates for bifunctional energy storage.

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Layered materials are promising for various applications due to their unique properties. Misfit layered compounds (MLCs) are a type of layered material that exhibit intriguing properties such as super conductivity, magnetism, and good thermoelectric behaviour.[1,2,3] However, creating 2D materials from MLCs in large quantities has been challenging. In this work, we report the successful synthesis of few-layer misfit $\text{CaCoO}_2\text{-CoO}_2$ 2D nanosheets in bulk quantities from bulk Calcium Cobalt Oxide ($\text{Ca}_3\text{Co}_4\text{O}_9$). The newly synthesized 2D exfoliated misfit nanosheets were found to outperform the parent bulk CCO in electrochemical energy storage applications, particularly in Aqueous Zn-ion battery as cathode material. This material also showed high performance as a pseudocapacitor electrode material. The successful synthesis of few-layer misfit $\text{CaCoO}_2\text{-CoO}_2$ 2D nanosheets could pave the way for the creation of other 2D materials from MLCs and open up new avenues for their applications in various fields such as energystorage, catalysis, and sensing.

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PA26: Chirp-Driven EIS: Accelerating the Characterisation of Li-ion Batteries

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Electrochemical Impedance Spectroscopy (EIS) has long been acknowledged as an effective method for the Characterisation and analysis of a wide range of electrochemical systems, including Li-ion batteries [1]. However, a significant drawback of the conventional EIS method is the time-consuming nature of constructing an accurate impedance spectrum. This is primarily due to the method's dependence on a series of sinusoidal inputs with varying frequencies, where each frequency point is evaluated independently, resulting in lengthy measurement times. This time-extensive process is not suitable for applications requiring rapid evaluations or for online battery management systems [2].

This research focuses on the application of Chirp-based EIS for Li-ion battery analysis [3-5]. It is a comparative study against conventional EIS, a well-established but time-intensive method unsuitable for rapid evaluations. Hence, the main objective is to scrutinize Chirp-based EIS for its time efficiency and precision in simulating the impedance spectrum.

The methodology involves the usage of the Doyle-Fuller-Newman (DFN) [6] model run on PyBaMM [7] open-source software for Li-ion battery simulation. The DFN model was built using the parameters adopted from Ramadass et al. [8]: Sony 18650 Li-ion battery parameters. A single chirp signal, characterised by a constant amplitude but continuously varying frequency, is used in Chirp-based EIS. This approach significantly differs from the conventional EIS, which uses discrete signals, each characterised by a unique frequency. The simulations were conducted under controlled conditions, with a state of charge (SoC) set at 0.7 and an ambient temperature of 20°C.

The result depicted in Fig.1. demonstrates a strong correlation between the Chirp-based and conventional EIS techniques. A highlight of the study is the Chirp-based EIS's ability to achieve a 10-fold reduction in measurement time. Where conventional EIS took 15000 seconds for 75 logarithmically spaced signals for a frequency range of 1Hz to 0.01 Hz, the exponential chirp signal achieved the same in merely 1500 seconds. In conclusion, due to its speed, precision, and applicability, the Chirp-based EIS could potentially establish itself as a potent tool for real-time applications in battery prognostics.

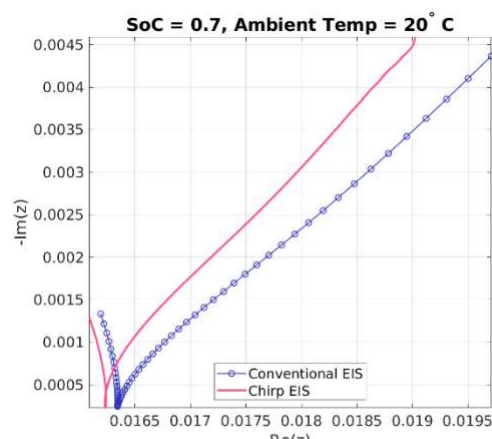


Fig. 1. Comparison of chirp EIS with conventional EIS on DFN Li-ion battery at frequency range of 1Hz to 0.01 Hz

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PA27: Morphological failure of Li deposits induced by positive electrode-Li metal crosstalk behavior

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The abnormal cross talk behaviour of common LiFSI-DME electrolyte comprised lithium metal cells are analysed. The oxidative decomposition of LiFSI-DME electrolyte forms the surface film on the positive electrode surface and the soluble decomposed product, simultaneously. The formation degree of soluble decomposed products is directly correlated with the cycle voltage range of positive electrode, hence the 4.2 V cycled high nickel-contented positive electrode demonstrates severe formation of degraded products. The soluble degraded products readily diffused to the Li metal negative electrode surface and reduced on the Li metal surface. The degraded products generate resistive film on the Li metal surface, thus the polarization of Li metal cycling is increased. The alternated Li metal cycling kinetics from the soluble decomposed products affect the deposition morphology of Li metal at negative electrode surface, hence the porous and dendritic Li deposits are formed with 4.2 V cycled NCM811 electrode; whereas the LFP and Li metal comprised cell shows rather smooth surface morphology. The new finding of soluble oxidative decomposed products from the LiFSI-DME based electrolyte induced failure should be mitigated for enhancing the stable cycling of high energy lithium metal batteries.

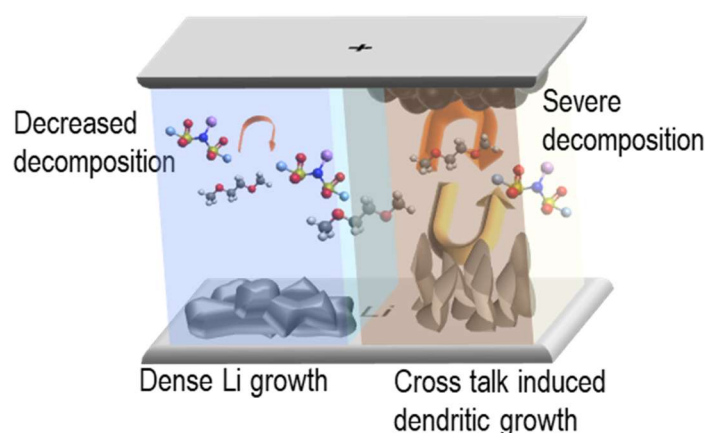


Figure 1. Scheme of the crosstalk induced failure of lithium metal electrode morphology

Acknowledgement

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PA28: Understanding battery health and identification of ageing history of commercial lithium-ion batteries using nonlinear frequency response analysis (NFRA)

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Lithium-ion batteries undergo several aging processes during their operational life, which negatively impact their overall performance, safety and remaining useful lifetime. State-of-the-art battery management systems (BMS) typically estimate the state-of-health (SOH) of the battery in terms of its capacity vs. beginning of life but are unable to resolve the different degradation mechanisms contributing to capacity fade. Reliable and easily adaptable diagnostic methods for better understanding of the ageing pathway are required for more precise determination of remaining useful life, enabling safer operation, and evaluating suitability of used batteries for second-life applications. In this study, commercial cylindrical cells were cycled at multiple ambient temperatures and charge-discharge rates to impose different ageing conditions. At regular intervals of degradation, the cells were discontinued from cyclic ageing and were subjected to NFRA analysis at different OCVs with different amplitudes to diagnose various ageing mechanisms. A model-based assessment is also conducted to further enhance the understanding of aging mechanisms and correlation with harmonics. The NFRA results revealed that state of health of the cells significantly impacted the harmonics obtained, particularly at a lower OCV. The higher harmonics and total harmonic distortion (YTHD) of the harmonic contents obtained in NFRA has shown that different ageing mechanisms display characteristic harmonics responses in frequency range 0.1 Hz to 200 Hz.

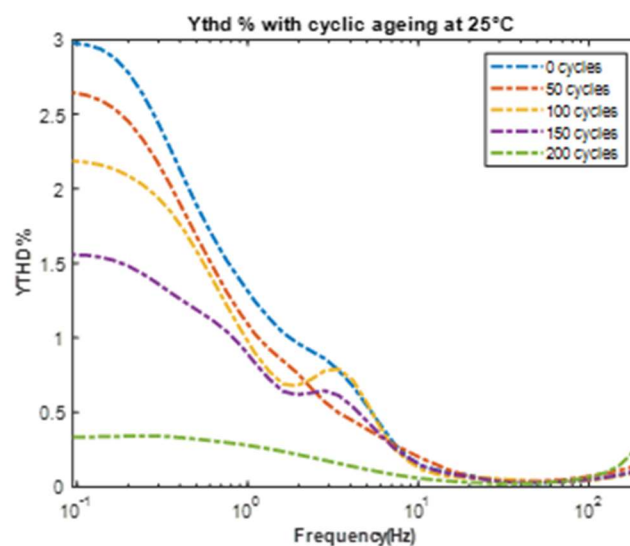


Figure 1: a) Change in YTHD % for cyclic ageing at ambient temperature of 25°C

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PA29: Challenges in scale-up and manufacture of lithium metal anode protection systems targeting lithium sulfur batteries

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Progress towards commercialising next generation energy storage devices is often decelerated by difficulty manufacturing stable, energy dense, alkali metal anodes at large scale. Despite accelerated progress in cathode engineering for conversion-based technologies, including Lithium-Gas (O₂, CO₂, N₂, F₂) and Lithium-Sulfur batteries the anode is the current rate limiting component in manufacturing next generation energy storage technologies.

Lithium metal anodes are limited in their practical application due to the growth of dendritic Li, electrolyte consumption, severe volume changes and subsequent safety risks¹. To mitigate the characterised failure mechanisms, scientific and engineering challenges apply strategies including interface engineering. The interest in developing controlled formation of artificial SEI's gives tailored solutions to individual next generation energy storage devices. These protection mechanisms can allow the utilisation of high energy density, limit dendrite growth, while alleviating safety risks within varying electrochemically and chemically extreme environments held within energy storage devices. The metrics of the impressive performance of engineered interfaces at the lab scale, do not match the metrics needed for pilot and production scale. The crossover of skillsets across researchers and knowledge of end-to-end processing creates difficulty in smoothly transitioning an anode protection mechanism from laboratory scale to commercialisation. By studying the differences in outcome of comparative laboratory and pilot level processing of anode protection systems we have identified critical elements as to how to maintain control at high throughput.

The presentation will provide a systematic approach to scaling both batch and roll-to-roll anode protection mechanisms for Lithium metal anodes, targeted at the metrics of commercial Lithium Sulfur batteries. It will explore zinc-based alloy anode protection mechanisms from a molecular vapour deposition (batch)² and a chemical alloy formation (roll-to-roll) process^{3,4}. It will explore both the fundamental control of competing formation reactions, alongside an assessment of how to maintain the same controlled environment and parameters when scaling up to a pilot scale level.

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PA30: Overcoming the challenges of the Li-air battery

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The lithium-air (Li-air) battery has the capability of being a key contender in replacing the lithium-ion battery. Compared to all practical next-generation battery technologies such as lithium-sulfur and magnesium-ion, it possesses the highest theoretical gravimetric energy density of ca. 3500 W h kg⁻¹, making it ideal for mass sensitive applications such as electric transportation.¹ The Li-air battery operates via the reduction of O₂ at the positive electrode to form Li₂O₂ during discharge, coupled with the simultaneous oxidation of lithium at the negative electrode. On charging the cell, Li₂O₂ is oxidised, releasing O₂. The battery is composed of a porous carbon cathode and metallic lithium anode, leading to lower material costs and a reduced environmental and geopolitical impact compared to existing battery technologies, making it an attractive target for future electrification.¹ Despite these promises, Li-air batteries are beset with difficulties. The insulating nature of Li₂O₂ leads to extremely high overpotentials on charge, driving electrolyte degradation. Furthermore, the Li-air battery ideally will utilise oxygen directly from the atmosphere. However, the presence of CO₂ and H₂O in the gas stream leads to unwanted discharge products that oxidise at potentials outside most electrolyte stability windows. These issues lead to very poor cycle lives, rapid capacity fading and low coulombic efficiencies of the cell.²

Here, we discuss our recent advances in understanding Li-O₂ battery chemistry. Redox mediators are a class of homogenous, electrochemically active molecules, which are capable of oxidising Li₂O₂ by shuttling electrons to isolated, insulating particles, thus lowering overpotentials on charge.³ We have focused on modifying the chemical structure of charge redox mediators, targeting certain redox potentials. In doing so, we aim to introduce mediators which drive Li₂O₂ oxidation, balancing the rate and applied overpotential observed during charge. With respect to tackling contaminants in the gas stream, the impact of water on driving the formation of unwanted discharge products in multiple wet solvent systems has been studied, leading to the identification of water-tolerant electrolytes in which Li₂O₂ is the main product formed, even at high water concentrations. Finally, we present a demonstrator gas-handling system and cell, which can be used to evaluate the impact of humidity, gas flow, gas stream composition and electrolyte composition.

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PA31: Influence of Electrolyte on the Electrochemical Performance of MoS₂ decorated Carbon Cloth for Flexible Aqueous Supercapacitors

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The development of robust, mechanically flexible electrical energy storage devices is a key requirement for the development of wearable and implantable electronics¹. Such an energy storage device should be safe in the case of leakage and ideally produced from sustainable and Earth-abundant materials. Hence, aqueous supercapacitors based on flexible electrodes are a particularly promising solution.

Here we report the synthesis, characterisation and evaluation of an aqueous supercapacitor electrode material consisting of a pseudocapacitive material, MoS₂, supported on a carbon cloth 'backbone'. In particular, by varying the ions within the aqueous electrolyte, we examine the influence of ion size and chemistry on energy storage performance.

MoS₂ decorated carbon cloth (CC) electrodes have been produced by hydrothermal synthesis at a range of mass-loadings and characterised by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and Raman spectroscopy. SEM micrographs reveal the layered structure of MoS₂, which decorates the CC surface in the form of quasi-spherical aggregations, covering the whole surface at longer synthesis times. The composition and structure of the MoS₂ is confirmed by XRD², EDX and Raman spectroscopies, with the latter indicating that the thickness of the MoS₂ structural units is at least 5 monolayers³.

The electrochemical performance of the electrode material, operating as an anode, was investigated using cyclic voltammetry (CV), galvanostatic charging/discharging (GCD) and electrochemical impedance spectroscopy (EIS). Charge storage behaviour has been evaluated in several neutral electrolytes (3.0 M Li₂SO₄, 1.0 M Na₂SO₄, and 1.0 M KCl) to understand the impact of cation size and anion chemistry on specific capacitance, effective series resistance and, particularly cycle life. Results indicate that the electrode material displays intrinsic pseudocapacitive behaviour in all the electrolytes tested, as expected, and possesses sufficient charge storage capability to be promising for flexible energy storage devices. However, the electrode rate capability was found to be poor in 3.0 M Li₂SO₄, whereas the in the case of 1.0 M Na₂SO₄, and 1.0 M KCl the electrodes displayed significantly improved behaviour. EIS analysis indicates better capacitive behaviour in 1.0 M Na₂SO₄ electrolyte in comparison with 3.0 M Li₂SO₄ and 1.0 M KCl with the highest gravimetric capacitances obtained in 3.0 M Li₂SO₄, 1.0 M Na₂SO₄, and 1.0 M KCl at a rate of 0.625 A g⁻¹ found to be 213 F g⁻¹, 222 F g⁻¹ and 188 F g⁻¹, respectively. The origins of the differences in capacitance and rate performance are discussed and comparisons made with results obtained in acidic and alkaline aqueous electrolytes.

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PB1: Using Cu₂O nano particles as a novel non-noble metal catalyst for electroless copper plating on textiles

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Electroless deposition on to substrates such as polymers and textiles require a critical activation step in which the substrate is activated by using a catalyst. Palladium is widely used as the catalyst for electroless deposition of such substrates, but it is a very expensive element, a critical raw material and is also hazardous for the environment. Thus, in this work, the potential usage of Cu₂O nano particles as a novel catalyst for electroless copper plating on polyester textile substrates was investigated as a replacement for palladium. First, the electrocatalytic performance of Cu₂O nano particles toward the oxidation of formaldehyde was investigated. In the next step, Cu₂O nano particles were used in order to activate a polyester textile for metallisation via an electroless copper process. The effects of the type of dispersion of the Cu₂O nano particles including magnetic stirrer agitation as well as sonication (300 W power and 40 kHz frequency) during the activation step was investigated with regard to final properties of copper deposits including resistivity of the coating and surface coverage were determined. The results showed that Cu₂O can successfully initiate the electroless copper process on the textile and produced a uniform copper deposition on the fibres within the textile. In addition, it was found that the dispersion method of Cu₂O nano particles plays a significant role in the quality of the final copper deposits. In particular, the results showed that the resistivity values for the electroless coatings were decreased significantly by using sonication during the activation step and produced values that were very similar to those found when the textile was activated by a palladium catalyst. This indicated that using sonication not only leads to surface coverage improvement, but it can act as a surface treatment process at the same time during the activation step which can improve the adhesion and conductivity of the final coating.

PB2: Suppression of parasitic H₂ evolution using boron-doped diamond electrode and lithium bis(trifluoromethanesulfonyl)imide electrolyte

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Electrochemical CO₂ reduction (CO₂RR) research is receiving increasing attention as this technique can be used to store renewable energy via chemical bonds and allows carbon dioxide to be used as a feedstock molecule; both of these aspects make CO₂RR interesting from a perspective of mitigating climate change. In order for CO₂RR to be viable, a stable catalyst which operates selectively at a low overpotential must be used. Boron-doped diamond (BDD) emerges as a promising catalyst choice as a mechanically and chemically robust material with poor performance towards hydrogen evolution (the main parasitic reaction for aqueous electrochemical CO₂RR).

The choice of catalyst is not the only factor of importance for achieving efficient CO₂RR; the type and concentration of the electrolyte used is of vital importance towards the activity and selectivity of CO₂RR. This poster will present the performance of a BDD electrode (compared with Cu foil) as a CO₂RR catalyst in different electrolyte solutions. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), which has not previously been studied as a CO₂RR electrolyte, is of particular interest. LiTFSI has been shown to have excellent solubility in water and can be dissolved at appropriately high concentrations to form water-in-salt electrolytes (WISE), where the mass of salt in solution is larger than the mass of water; these WISEs have been shown to suppress H₂ evolution in aqueous batteries [1]. By utilizing a combination of boron-doped diamond with a 10 m LiTFSI electrolyte, CO₂RR progressed without the parasitic H₂ evolution reaction, even at -1.7 V vs Ag/AgCl, which was not observed using a Cu electrode or when BDD was used in conjunction with other electrolyte solutions. This provides a novel method of controlling the selectivity during electrochemical CO₂RR.

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PB3: CO₂ Reduction Reaction using Channel Flow Cell

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It is well known in CO₂ reduction field that flow cells could significantly increase the mass transport of CO₂ due to the continuous flow of electrolyte across the catalyst [1]. Here, we designed a channel flow cell with a well defined mass transport characteristics in order to study the effect of electrolyte flowrate and therefore mass transport on CO₂RR. With the channel flow cell, it is also possible of making use of the double electrode experiments which has similar concept with the rotating ring disk electrode (RRDE) [2]. The main advantage of channel flow cell compared to RRDE is it does not suffer from bubbles blocking as the electrolyte got flushed away during the process. In the channel flow cell, Cu foil works as the working electrode 1, whereas Pt foil acts as the working electrode 2. The generated CO₂RR products from Cu Foil would be transported to the Pt Foil and thus unique electrochemical fingerprints on Pt could be observed. This method would minimize the time needed to identify the product.

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BP4: Electrochemical Capture and Release of Carbon Dioxide Using a Diselenide – selenate Redox Cycle

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Here we experimentally demonstrate a new electrochemical cycle that enables the capture and release of carbon dioxide. The redox carriers or 'capture agents', phenyl-selenate and benzyl-selenate, are generated through the reduction of diphenyl-diselenide and dibenzyl-diselenide, respectively. Following electrochemical analysis, it is proposed that, like disulfides [1] (a periodic analogue), the alkyl-selenate will ligate with carbon dioxide forming a binding complex. Oxidation of the alkyl-selenate causes the release of the carbon dioxide and the reformation of the dialkyl-diselenide (RSeSeR). The capture and release cycle and redox mechanism was investigated in an ionic solution of tetrabutylammonium hexafluorophosphate (NBu₄PF₆) in dimethylformamide.

Here, we also investigated the impacts of substituting the alkyl groups on the reaction procedure and redox cycle. Reduction potential for carbon capture of diphenyl-diselenide and dibenzyl-diselenide was found to be -2.0 V and -2.6 V (vs. Fc⁺/Fc) respectively. Additionally, it was found that dibenzyl-diselenide had significantly worse Nernstian reversibility and stability, with side oxidations posing a problem for long-term stability, as compared to phenyl-diselenide.

This work develops our understanding of the capacity for larger chalcogens to capture and release carbon more effectively than sulphur counterparts and the redox mechanisms of these dialkyl-diselenides. This builds on experimental and practical work conducted by Singh et al. [1] investigating the sulphur analogue, dibenzyl-disulfide. As well as work by Harris and Bushnell [2], who computationally demonstrated the possibility for dialkyl-diselenides to capture and release carbon dioxide.

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PB5: EcoFuel: Catalyst development and electrode manufacturing for electrochemical CO₂ reduction

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Electrochemical CO₂ reduction is an attractive technology to produce energy dense carbon products, such as ethylene, alcohols, and syngas from renewable energy and carbon dioxide. Such products are key industrial feedstocks that, if produced renewably, can greatly contribute towards a net-zero transition. This is the goal of the Horizon 2020 Ecofuel Project, which aims to optimise the complete process chain comprising of a) the supply of CO₂ from the atmosphere via a novel direct air capture approach, b) direct electro-catalytic reduction of CO₂ to C₂/C₃ products at close to ambient temperatures, and c) thermo-catalytic liquefaction of alkenes, upgrading and fractionation into transport fuels, targeting developments up to TRL 4/5.

This talk will focus on the electrocatalytic reduction of CO₂, detailing advancements in catalyst development and electrode manufacturing, with the aim to increase the electrode stability up to 1000+ hours and product selectivity up to 85% C₂/C₃ products.

PB6: Electrochemical performance of Cobalt (II) 2,9,16,23-tetraamino phthalocyanine electrodes for electrochemical CO₂ reduction: Effect of electrode preparation

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The manufacturing of electrodes for the electroreduction of CO₂ is a crucial stage in achieving deeper reduction products¹. By optimizing the preparation of electrodes, significant enhancements can be achieved in terms of both the yield obtained and the faradaic efficiency of the products². Covalent attachment of molecular catalysts to electrodes could facilitate multiple rapid electron transfers and hence promote multi-electron reduction of bound carbon dioxide³. In this study, the surface of a glassy carbon electrode was modified using a cobalt phthalocyanine compound through electrografting and ink preparation techniques (Figure 1). The modified electrode surfaces were characterized by SEM-EDX, FTIR and XRD analysis. The catalytic activity of these modified electrodes for CO₂ reduction was evaluated through cyclic voltammetry, linear sweep voltammetry, and impedance spectroscopy measurements. The findings of this study highlight the significance of electrode preparation in determining the electrochemical performance of cobalt-substituted phthalocyanine electrodes for CO₂ reduction.

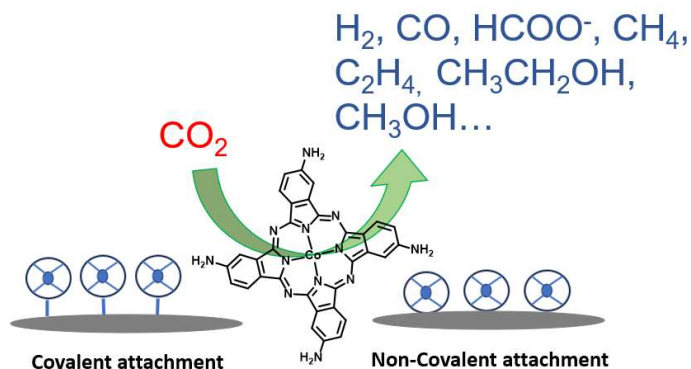


Figure 1. The preparation of cobalt-substituted phthalocyanine on glassy carbon electrode through electrografting and ink preparation techniques.

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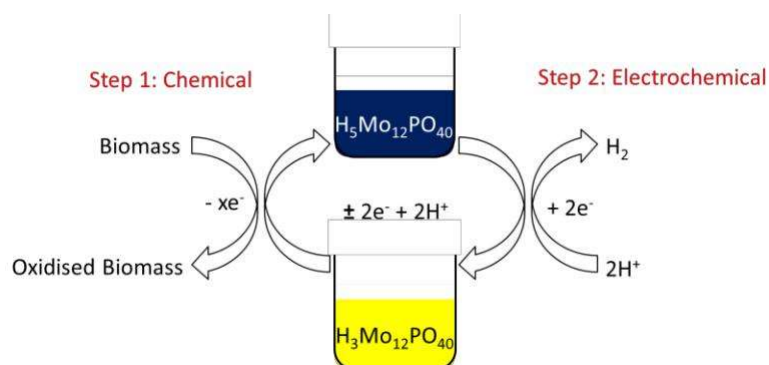
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PB7: Decoupled Biomass Oxidation and Hydrogen Production Mediated by Phosphomolybdic Acid

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Hydrogen evolution via the electrolysis of water is one way to address the intermittency of renewable energy sources, and the hydrogen produced can be utilised as both a clean fuel and a feedstock for ammonia. However, improvements in electrolyser performance through further research and development are essential if hydrogen is to become a viable commercial solution for energy storage. Decoupled water electrolysis improves the flexibility and safety of traditional electrolysis by utilizing a redox mediator to separate the oxygen and hydrogen evolution reactions into two distinct steps. The polyoxometalate phosphomolybdic acid is an established redox mediator for this process.¹

Decoupled biomass oxidation and hydrogen production is a further adaptation to decoupled electrolysis, that can also be mediated by phosphomolybdic acid. In this system the first step is the spontaneous reduction of the phosphomolybdic acid mediator by a biomass material, which is itself oxidised. In the second stage the reduced mediator is electrochemically re-oxidised, forming hydrogen gas and regenerating the phosphomolybdic acid. The advantage of this approach over traditional electrolysis is that oxidation of the biomass releases additional electrons which lower the energy required to produce hydrogen. This has previously been demonstrated using waste organic materials such as lignin² and corn straw.³

Seaweed exists in abundance in the UK, so it is an excellent potential biomass source for decoupled biomass oxidation and hydrogen production. The seaweed derivatives sodium alginate and agar are widely used in the food industry, cheap, commercially available, and readily oxidisable. In this work the ability of sodium alginate and agar to reduce phosphomolybdic acid was evaluated using UV/Vis spectroscopy, and the oxidation products of the seaweed derivatives were analysed by NMR and gas chromatography.

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PB8: Redox Neutral Electrosynthesis without Added Electrolyte at Interdigitated Electrodes

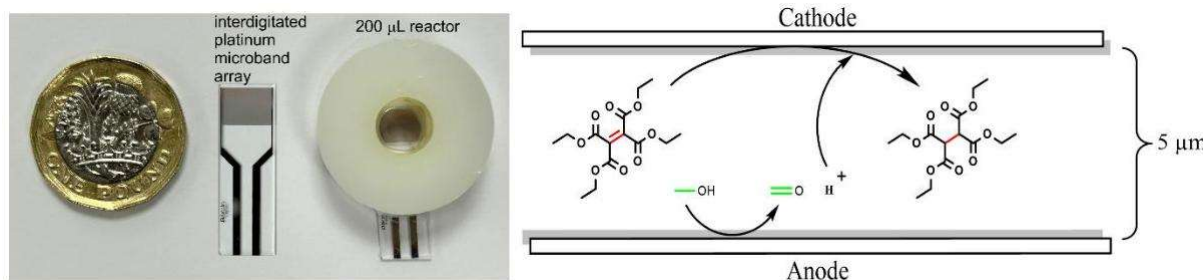
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Pioneering work by Belmont and Girault in 1994 introduced interdigitated band electrodes into electrosynthesis ^[1]. Today, interdigitated microband electrodes have been accepted as powerful tools in electrosynthesis, especially for paired and redox neutral oxidation/reduction processes ^[2,3].



Here, a microreactor based on a symmetric Pt-Pt interdigitated microband array electrode (5 mm bands with 5 mm gaps; Figure 1) is employed with typically 200 mL reaction volume. Olefin reduction is investigated in aliphatic alcohol solvents. The absence of intentionally added electrolyte has no detrimental effects on the process. Constant current mode and constant voltage mode synthesis are compared. Impedance spectroscopy is employed to investigate the reaction layer. In a typical electrolysis reaction, tetraethyl-ethylene-tetracarboxylate is reduced to tetraethyl-succinate in >95% yield. Effects of reaction time and substrate concentration are investigated.

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BP9: Templated electrodeposition of nanoscale materials

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Our project (ADEPT, EPSRC EP/N035437/1) aims to fabricate nanoelectronics (thermoelectric, phase change memory and IR sensor devices) by using electrodeposition of a range of p-block compounds.^[1-3] This work focuses on fabricating nanoscale materials by templated electrodeposition. Published work generally uses commercial membranes as templates for electrodeposition of nanostructures, which usually have pore sizes larger than 10 nm, and in most cases significantly larger. However, mesoporous silica films can provide small pore sizes in the range of 2-10 nm and different pore structures. In this work, highly-ordered 3D mesoporous silica templates with accessible pores are fabricated through evaporation-induced self-assembly (EISA) approach. The mesoporous silica films have small mesopores (~8 nm) and complex 3D mesopore channels (Fmmm mesostructure with the [0 1 0] axis perpendicular to the substrate). Using the silica films as templates, Au nanoparticles are deposited through the mesoporous channels by conducting two-step pulse electrodeposition in the aqueous electrolyte system. The gold particles are characterised by electron microscopy and grazing incidence small-angle X-ray scattering (GISAXS). GISAXS shows changes in the lattice parameters after gold electrodeposition, which relates to swelling or compression of the mesostructured perpendicular to the 1 1 1, 0 2 0 and 0 2 2 lattice planes. Top-view SEM (Figure 1(a)) shows large areas of gold nanoparticles were deposited into the film and they were growing towards the surface.^[4] After removing the silica film, the gold nanoparticles display interesting fractal morphologies: the linked gold nanonetworks form a branched structure, as shown in Figure 1(b). The lengths of branches vary from the applied nucleation deposition conditions. Bi, Te and Bi₂Te₃ were electrodeposited into the mesoporous channels from a non-aqueous electrolyte system. Different PED conditions were used to optimize the nucleation and growth process. FE-SEM image in Figure 1(c) shows that the deposited Bi₂Te₃ nanoparticles filling into the nanopores of the silica films.

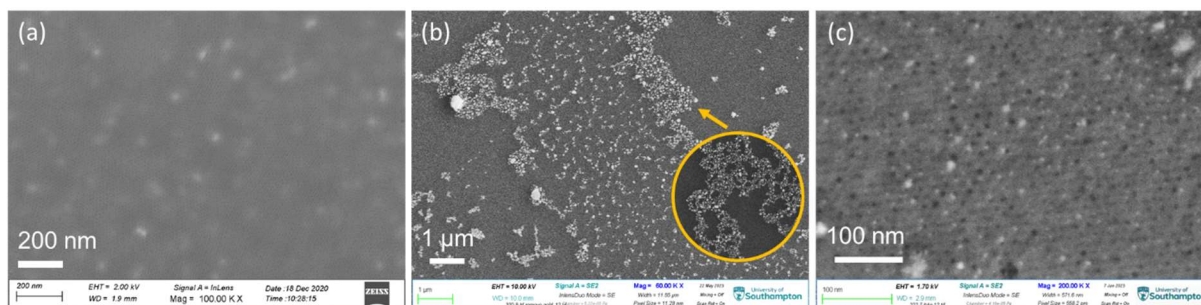


Figure 1. Top-view FE-SEM images of (a) gold particles electrodeposited into the mesoporous silica film; (b) the deposited gold nanonetworks after removing the silica film template; (c) Bi₂Te₃ nanoparticles electrodeposited into the mesoporous silica film .

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PC1: Electrochemical Sensor on Salt Content in Potato Chips and Crisps

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High level of sodium in diet leads to high blood pressure, heart disease and stroke, and salt (sodium chloride) is the major source of sodium across different types of dietary contributors (meals, breads, snacks, etc.). The World Health Organisation recommends that adults should consume less than 5 grams of salt every day and most people consume too much (on average 9 to 12 grams). Reducing salt intake to the recommended level can help to improve population health, and an estimated 2.5 million deaths could be prevented each year globally.[1]

As one of the most popular snacks across the world, the growing trend of consuming potato chips and crisps began in the western world and quickly spread to the rest of the world with an estimated market size of USD 35.5 billion in 2023, which is foreseen to reach USD 44.2 billion by 2028.[2] In this market, the manufacturers are continuously developing a wide range of different potato chips and crisps to keep their customers and market occupancy. In recent years, with the growing demand of healthy snacks, manufacturers are expanding their products offering by introducing vegetables and fruits. However, potato chips and crisps still attract customers' interest and manufacturers need to control the salt content in the final products. Therefore, a rapid assay of sodium chloride on the production line is required.

Electrochemical sensors are ideal for this application due to the rapid analysis, great accuracy, easy operation, and cost efficiency.[3] In this work, we have successfully developed a chip-based (1x2cm) novel smart sensor platform for chloride analysis. The sensor has been investigated and challenged in both buffer solution and real sample solution prepared with five different flavoured crisps. This work clearly demonstrated that the silicon chip digital technologies have tremendous potential by enabling rapid analysis to provide real-time analytical data.

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PC2: Nanopore Electrochemical Analysis for Identifying Familial Point Mutations in Single Amyloid- β Peptides

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Nanopores are acquainted as sensitive single-entity electrochemistry analysis tools for label-free molecule discrimination. The sensing principle of this method is based on single molecules consecutively traversing through a nanopore driven by a bias voltage, resulting in ionic current reduction. Hence, it is of great significance to explore more effective features to characterize the current blockage event for promoting nanopore sensitivity. Based on our previous understanding of “current noise” in nanopores, a new third practical parameter, standard deviation (σ_b), was proposed to describe current blockade fluctuations of single molecular signals. Here, to clarify the capability of σ_b , single amyloid- β (A β) peptides associated with familial Alzheimer’s disease were detected by the mutant aerolysin nanopore. The result demonstrated that the qualitative and quantitative determination of the Flemish version (A21G) and wild type A β peptide could be realized by introducing σ_b . By combining the conventional parameters blockage current and duration time, with standard deviation (σ_b), a 3D blockage mapping strategy was constructed to identify up to four kinds of single-point mutant A β peptides simultaneously. This work provided an easy and reliable strategy to promote nanopore sensitivity of peptide mutants, leading to a more precise analysis of pathogenic mutations for developing effective diagnosis and treatment.

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PC3: Understanding the transient response of an enzyme electrode in continuous flow using approximate analytical solutions and numerical simulations

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Electrochemical response for tubular enzyme membrane systems were investigated using mathematical models and transient numerical simulations. This study explores the potential of such systems to serve as the basis for implantable devices that continuously harness glucose from the bloodstream to power biomedical devices inside the body [1]. Furthermore, the effect of viscosity change on the Amperometric output has also been observed and reported. The viscosity was altered by adding glycerol and xanthan gum concentration in the flowing electrolyte. The observed effect has been attributed to alterations in the diffusion coefficient of the substrate within the film because of the viscosity change. To prove this, we used microelectrodes to calculate the change in diffusion coefficient in the electrolyte solution with varying concentration of glycerol and xanthan gum. Key experimental parameters have been extracted by fitting the approximate models to the steady state response. These parameters were then used to obtain ranges of normalized variables to fit the entire chronoamperograms (obtained against varying substrate concentrations) to the transient simulations. The results from these numerical simulations enable the calculation and evaluation of experimental concentration profiles for both the substrate (glucose) and the mediator membrane as they evolve through time.

Acknowledgement

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PC4: Next-generation in-situ Sensors for Oxygen Concentration Measurements in PEM Fuel Cells

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Proton Exchange Membrane Fuel Cells (PEMFCs) hold promise for clean power generation in a range of applications including aerospace, marine, heavy duty automotive and stationary power. The electrochemical reactions of hydrogen and oxygen responsible for power generation in PEMFCs take place at the surface of electrodes with geometric surface areas of several hundred cm² ¹. The distribution of these reactions across each electrode is not uniform, giving rise to significant spatial variation in critical operating parameters such as temperature, current density, and reactant concentrations ². Local oxygen starvation at the cathode catalyst layer (CL) can result in poor performance and accelerated degradation ³. As a result, maintaining a uniform oxygen concentration is important for maximizing PEMFCs' performance and extending their lifetime. Techniques for direct, spatially-resolved measurement of oxygen concentration have not received as much attention as current or temperature. At present, there are no direct means to make spatially-resolved measurements of oxygen concentration across the plane of PEMFC electrodes, particularly at the interface of the CL and membrane. The goal of this research is to develop in-situ sensors and instrumentation to measure and map oxygen concentration inside a 250 cm² PEMFC. Micrometer platinum wires and inkjet printing technology will be implemented for developing the oxygen sensors. Initially, the developed oxygen sensors are evaluated ex-situ using a 3-electrode cell and liquid electrolyte. Electrochemical techniques are applied to characterise the sensor elements and evaluate their performance for oxygen concentration measurement.

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PC5: Electrochemical-based pH control for the analysis of dairy products

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One of the key parameters that influences what dairy products can be created from milk during manufacturing is pH. The pH of milk is influenced by the temperature, mineral composition, and amino acid profile.¹ Constant monitoring must be conducted during processing as pH can change resulting in a final product with undesirable characteristics. The tailoring and analysis of pH, without the need for additional reagents diluting the sample, would allow for the determination of acid coagulation conditions during processing. A sensor that would allow for pH to be controlled using an electrochemical means would have clear advantages over the current method of altering the pH of dairy products.

For this work the sensing devices consist of gold interdigitated electrode arrays, a counter electrode and a reference electrode meaning all electrochemical elements are contained on the one chip.² In-situ pH control is achieved by applying a high positive potential to one of the interdigitated electrode combs resulting in water electrolysis occurring at one electrode, producing hydrogen ions which diffuse away and acidify the solution surrounding the electrode. The other electrode comb in the interdigitated setup can be used as an in-situ pH probe by monitoring the potential at which the gold oxide reduction peak occurs when undergoing cyclic voltammetry, as seen in Figure 1 and 2.³ The combination of these two factors allows for pH control to be implemented using interdigitated electrochemical chips, allowing for the facile analysis of milk. We have successfully shown the pH of complex matrixes such as low-fat milk and whey protein isolate solution can be altered in the range of pH 6.8 down to pH 5.0 in 0.2 pH units with results comparable to analysis needed in industry.

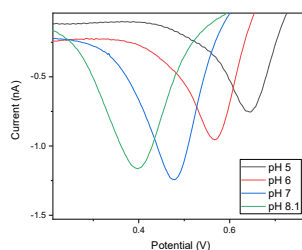


Figure 1: gold oxide reductions peaks

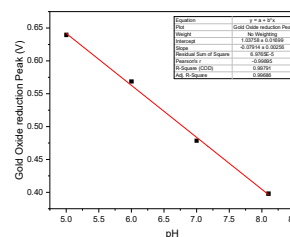


Figure 2: linear relationship between pH and gold oxide potential

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PC6: Development of 2D MoSe₂ Nanosheets combined with reduced graphene oxide for Electrochemical Sensor Applications

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Environmental monitoring is crucial for ensuring the health and safety of both human populations and the natural world. Recently, 2D materials have emerged as promising candidates for environmental sensing, due to their unique properties and potential applications. Transition-metal dichalcogenides or TMDs, are two-dimensional (2D) materials comprising of MX₂, with M a transition metal atom e.g. Mo, W etc. and X, a chalcogen atom S, Se or Te [1]. The M atoms are sandwiched between two layers of X atoms with strong covalent bonds (in-plane) and weak van der Waals forces between the planes. Among these materials, molybdenum diselenide (MoSe₂) shows excellent properties, such as high electronic conductivity, large capacitance, high surface area, and chemical stability.

In this study MoSe₂ was combined with reduced graphene oxide, another 2D carbon-based material with equally exceptional electrical and mechanical properties [2], to create a hybrid structure for the development of sensors. This MoSe₂/rGO hybrid was used to detect dimetridazole (DMZ), an antibiotic drug often used as a poultry feed additive and for the treatment of bacterial/protozoal infections in humans and animals, as illustrated in Figure 1. Excess DMZ has carcinogenic effects and ensuring that DMZ remains at a very low level in the environment is essential for public health.

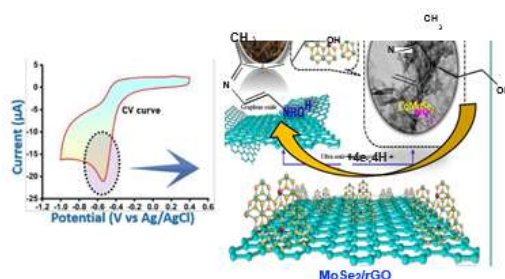


Figure 1: Electrochemical reduction of DMZ at MoSe₂/rGO

The MoSe₂ nanosheets were fabricated by simple and low-cost sonication-assisted liquid phase exfoliation of bulk powders in ethanol and water, and subsequently drop casted on a glassy carbon electrode. Reduced graphene oxide was then electrodeposited on the nanosheets to form a composite material on the electrode. We will show that this MoSe₂/rGO hybrid material has excellent potential for the development of electrochemical sensors.

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PC7: Development of Exfoliated 2D Nanosheets Molybdenum Disulfide Sensor for the Detection of Sulfanilamide in Water Environments

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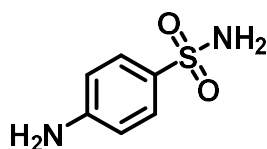
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Transition-metal dichalcogenides (TMDs) are a class of materials with excellent physical and chemical properties, currently being explored for applications as sensors, energy storage and catalysis among others [1]. TMDs comprise of MX_2 , where M is a transition metal (e.g., Mo, W) and X is a chalcogen (e.g., S, Se, and Te). They have strong covalent bonds in plane, and weak van der Waals forces between sheets. Exfoliated molybdenum disulphide (MoS_2) is a two-dimensional (2D) material with unique properties, such as high surface area, excellent electrical conductivity, and good chemical stability. In this study, we propose the development of an exfoliated MoS_2 -based sensor for detecting sulfanilamide.

Sulfanilamide (SFD) is a sulfonamide antibiotic commonly used in veterinary and human medicine to treat bacterial infections. The presence of antibiotic residues, including SFD, in aquatic environments has raised serious concerns due to their potential impact on human health, aquatic life, and the emergence of antibiotic-resistant bacteria. Consequently, the development of sensitive and selective sensors for the detection of SFD in water is of vital importance for environmental monitoring and water quality management. This molecule has an amino group, $-NH_2$, that can be electrochemically oxidized, and this was used in the electroanalysis of the drugs [2].



Sulfanilamide (SFD)

The aim of this poster presented here, is to develop a new sensor using exfoliated MoS_2 2D nanosheets, for the detection of the antibiotic drug SFD, which is available in the market and is used for treating bacterial and protozoal infections [3]. The bulk MoS_2 was exfoliated using biomolecules to give an impressive sensor for the detection of SFD. The exfoliated MoS_2 sheets were further improved by forming a MoS_2 reduced graphene oxide (rGO) composite to give a sensor with excellent long-term stability.

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PC8: The Electrostatically Asymmetric Nanopore for Single Peptide Sensing

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Proteins participate in almost all biological processes. In view of the Implementation of nanopore DNA sequencing, more studies turn to single protein sensing and sequencing based on biological nanopores.^[1,2] It remains a challenge to read the sequence directly by nanopores due to the complex building blocks of 20 amino acids and the corresponding sophisticated structures. And biological nanopores hardly provide effective ionic current responses to all heterogeneously charged peptides compared to the uniformly charged polynucleotides. By regulating the dynamic non-covalent interactions inside the biological nanopore,^[1-3] we designed an electrostatically asymmetric constriction zone inside OmpF. The positively charged ladder and the negatively charged pocket on the opposite side forms a strong lateral electrostatic field at CZ. This laterally asymmetric electrostatic field forces the sidechains of the amino acids in peptides to specific orientations within OmpF, causing distinct ionic current fluctuations.^[4] Using statistical analysis of the respective ionic current variations allows distinguishing the presence and position of a single amino acid with different chiralities. To explore potential applications, the disease-related peptide β -Amyloid and its D -Asp¹ mutant and a mixture of the icatibant peptide drug and its D -Ser⁷ isomer have been discriminated, which shows quite high chiral amino acid resolution and analysis efficiency. These findings highlight a novel sensing mechanism for identifying single chiral amino acids in peptides and even for single-molecule proteomic studies.

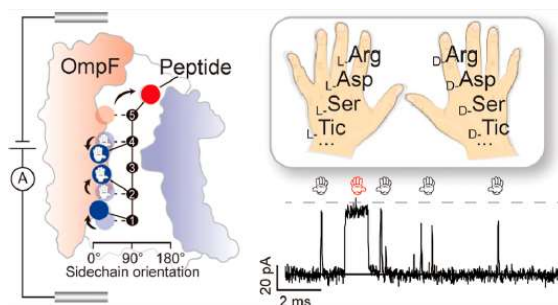


Figure 1. The electrostatically asymmetric nanopore for the identification of single amino acid.^[4]

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PC9: Directly detection of sulfotyrosine-containing peptides based on biological nanopore sensing

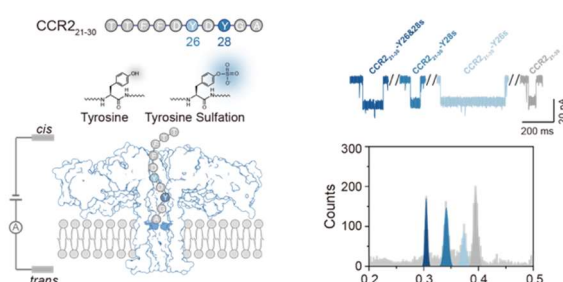
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Sulfotyrosine is one of the significant post-translational modifications (PTMs) that participates in and mediates various life activities in cells. Although many methods like radioactive isotope-label and mass spectrometry have been explored to detect sulfotyrosine, the in-depth characterization of this post-translational modification is still rare due to the lack of general, label-free methods. Specifically, for mass spectrometry, sulfotyrosine is easily broken down at high temperatures and low pH, which may lead to the loss of sulfated modification. Moreover, since sulfotyrosine and phosphotyrosine have a similar mass change (sulfotyrosine: 79.9568 Da; phosphotyrosine: 79.9663 Da), it is quite difficult to directly discriminate them unless using ultra-high accuracy mass measurements. Nanopore, as a single-molecule sensing approach, has been widely used for DNA sequencing, peptide sensing, PTMs detection, etc [1-3]. When a single analyte enters the nanopore, the current could be partially blocked. The inherent properties of the analyte (structures, charges, size, etc) could be directly reflected by the current blockage. Here, we used a mutant aerolysin nanopore to detect sulfotyrosine without labelling. It should be noted that the experiments are performed under mild conditions (1 mol/L KCl, 10 mmol Tris, 10 mmol EDTA, pH 8.0) without impact on the stability of sulfotyrosine. We could map of the sites of sulfated tyrosine in a decapeptide sequence from the C-C chemokine receptor type 2 protein (CCR2₂₁₋₃₀). Furthermore, all-atom molecular dynamics simulations were further employed to validate the design strategy of nanopore and provide insights into the corresponding molecular mechanism. These findings offer a path to the single-molecule, label-free identification of sulfotyrosine.



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PC10: Nanoconfinement Controlled Electrochemistry for Single-Molecule Measurement

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Changes in the nanopore ionic current during entry of a target molecule underlie the sensing capability and dominate the intensity and extent of applications of the nanopore approach^{1,2}. The volume exclusion model has been proposed and corrected to describe the nanopore current blockage. However, increasing evidence shows nonconformity with this model, suggesting that the ionic current within a nanopore should be entirely reconsidered. Here, we revisit the origin of nanopore current blockage from a theoretical perspective and propose that the noncovalent interactions between a nanopore and a target molecule affect the conductance of the solution inside the nanopore, leading to enhanced current blockage³. Moreover, by considering the example of an aerolysin nanopore discriminating the cytosine DNA and methylcytosine DNA that differ by a single methyl group, we completely demonstrate, by nanopore experiments and molecular dynamics simulations, the essential nature of this noncovalent interaction for discrimination. Furthermore, based on this interaction-volume exclusion model, we design an interaction enhanced mutant aerolysin for homo- and hetero-DNA sensing, which could achieve the identification of several base modifications in a random DNA sequence in mixture⁴. Our conductance model suggests multiplicative effects of both volume exclusion and noncovalent interaction on the current blockage and provides a new strategy to achieve volume difference sensing at the atomic level with highly specific current events⁵, which would promote the nanopore protein sequencing and its applications in real-life systems..

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PC11: Electrochemical detection of Ornidazole by means of a reduced graphene oxide-modified electrode

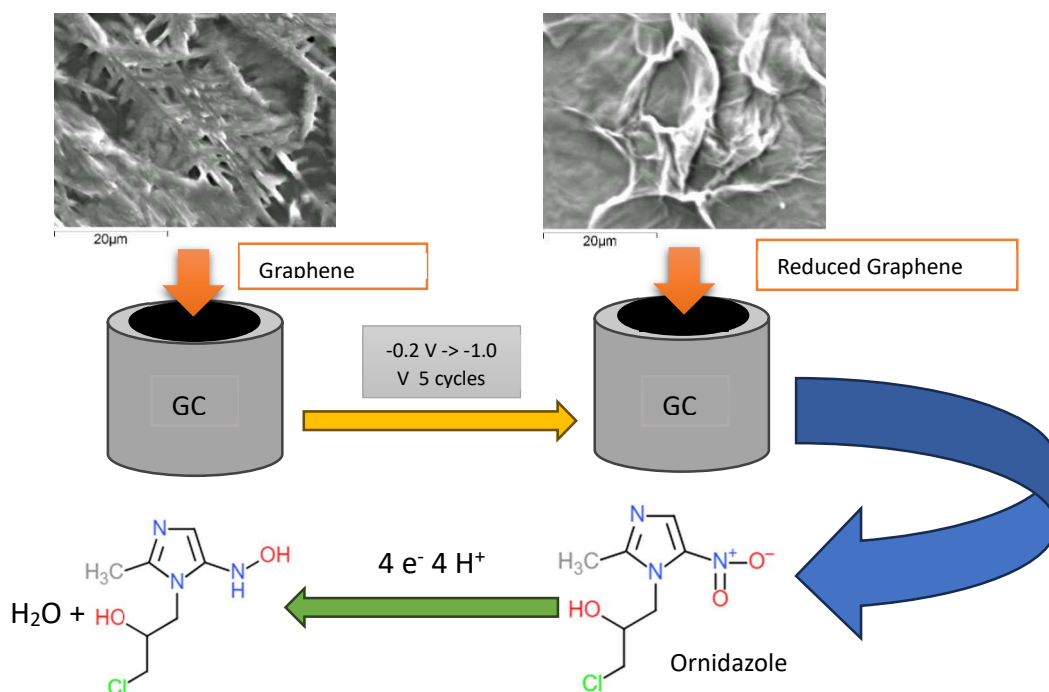
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Ornidazole (ORZ) is a member of the 5-nitroimidazole antibiotics that are heavily employed in the treatment of infections in both humans and animals, especially cattle [1]. As a result of the widespread use of these antibiotics, their concentration can build up in the environment, making a detection system capable of sensing ORZ essential to monitor environmental pollution [2]. Reduced graphene oxide (rGO) is an exciting and promising material that has large theoretical surface area and good electrical conductivity [3] which can improve the electrochemical sensing capabilities of electrodes, thus its ability to enhance the detection of ORZ is investigated in this study. Graphene oxide was synthesised via the Hummers method with potassium permanganate and sulphuric acid. This was then dispersed in sulphate solution and drop casted onto the surface of a glassy carbon electrode before being reduced on the electrode surface by the application of potential to form an rGO-modified electrode.

Following optimisation of the application of rGO, investigations were performed into the influence of pH of the ORZ solution to determine the electron transfer mechanism, the influence of scan rate to determine the kinetics of the detection, and a calibration curve was produced to determine limit of detection and sensitivity. Characterisation studies were performed on the rGO using SEM and FTIR, and the stability of the rGO on the electrode surface was studied.



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PC12: Functionalised Porous Materials for CO₂ Capture and Conversion

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Economic growth is intricately tied to greenhouse gas (GHG) emissions, particularly carbon dioxide (CO₂) resulting from fossil fuel combustion. With the atmospheric concentration of CO₂ currently at 422 ppm, it has become the most significant contributor to global GHG emissions.[1] Consequently, there is a pressing need for research and technological advancements in capturing, storing, and converting CO₂. Promising materials in this field are porous organic polymers (POPs), specifically conjugated microporous polymers (CMPs). CMPs possess advantageous properties, including π -conjugated structures, permanent porosity, as well as thermal and chemical stability.[2] Among CMPs, polytriphenylamine (PTPA) networks represent an intriguing class due to their adjustable characteristics, such as redox activity and conductivity.[3] These polymers hold potential for catalytic applications, enabling the capture and conversion of CO₂ into valuable products. Furthermore, the incorporation of heteroatoms and functional groups into the framework can enhance the ability of these materials to adsorb and convert CO₂. Notably, the inclusion of carboxylic acid functional groups demonstrates promise, as they exhibit high binding capabilities with CO₂ molecules.[4]

In this study, we present a novel class of carboxylic acid functionalised PTPAs synthesised via the Pd-catalyzed Buchwald-Hartwig cross-coupling reaction. By changing reaction conditions such as reactant ratios, solvents, and the introduction of inorganic salts, in addition to implementing post-synthetic modifications, we successfully obtained a series of polymers with moderate surface areas and very good CO₂ uptake capacities (up to 543 m²g⁻¹ and 15.59 wt%, respectively).

Our preliminary investigations into the electrochemical reduction of CO₂, utilising these networks as catalytic surfaces, reveal promising electrocatalytic activity for formate production. Moreover, the synthesised materials exhibit excellent catalytic efficiency (93% conversion) in CO₂ fixation reactions with epoxides (epichlorohydrin), resulting in cyclic carbonates (here chloromethyl ethylene carbonate), without the need for any additives under mild reaction conditions.

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PC13: Oxidized microporous polyaniline networks for CO₂ capture and conversion

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Carbon dioxide (CO₂) is the main anthropogenic greenhouse gas¹. Consequently, the past decades have witnessed a continuous build-up of excessive CO₂ concentration in the atmosphere, which has resulted in global warming, ocean acidification, extreme weather, and species extinction²⁻³. Thus, CO₂ capture, and further utilization are widely regarded to be major challenges with urgent solutions required. Conjugated microporous polymers (CMPs), a type of three-dimensional network material, have attracted considerable attention owing to their combined extended π -conjugation with a permanently microporous skeleton⁴.

We propose a strategy to introduce more oxygen-containing sites in our CMPs to enhance CO₂ capture and conversion by a post-synthesis oxidation approach. To construct CMPs with multiple nitrogen-containing functional groups and gradient pore characteristics, the Buchwald-Hartwig coupling method was chosen. We are currently exploring oxidation methods and the potential of CMPA in the electrocatalytic reduction of CO₂ into valuable chemical feedstock materials using a standard H-cell setup⁵. Our cyclic voltammetry studies of the synthesized materials indicate that CMPA is electrocatalytically active towards CO₂ reduction to yield methanol. Our future work will encompass chronoamperometric investigations and detailed product determination using NMR spectrometry.

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PC14: Advancement of Resistive Pulse Sensing for Particle Identification:

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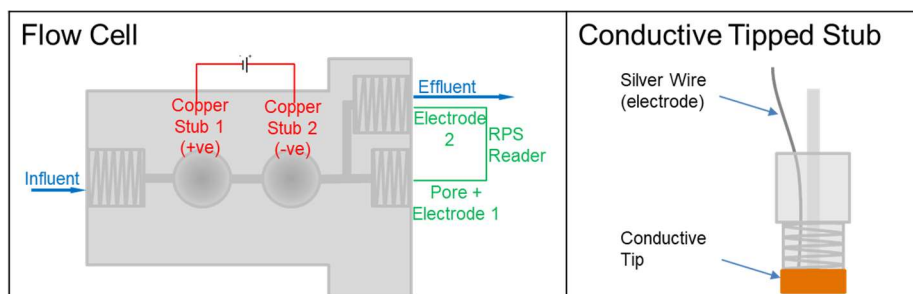


Figure 1 - Diagram of optimised flow-RPS system

Here we present improved techniques for identification, quantification, and characterization of Nanoplastics using Flow Resistive Pulse Sensing¹ (RPS), a method that is capable of measuring particle size and concentration on a nano scale. Our work advances RPS for particle identification, specifically for plastics. The World Health Organization (WHO) and the United Nations (UN) have called for more research on 'plastic pollution'.² Whilst there are efforts being made to understand scale, there is a disproportionate volume of research focused on the macro and micro scale, and not enough on nano plastics, despite their likely increased threat to health.³ Additionally, most research to date uses the current principal technique, Dynamic Light Scattering⁴ (DLS), which is limited as the technique only provides information on particles size and is not suitable for non-monodispersed samples, due to its low resolution.

We observed that polystyrene particles are consistently attracted to charged surfaces, therefore we successfully integrated a charged surface within a preexisting flow RPS set up using conductive tipped electrode stubs, as displayed in fig.1. The conductive electrode stubs were connected to a battery whilst the plastic contaminated samples were pushed through the cell, flowing across the charged tips. The particle removal was then either observed in real time, or post flow; corroborated with tunable RPS. Thus far, conductive tipped electrodes have been integrated, and optimized for salinity, flow pressure, conductive material, and applied voltage. From the data obtained it was decided that for optimal results the operating conditions should be as follows: A copper conductive material, with a pressure of 50 mbar, salinity concentration of 100 mM (KCl) and an applied voltage of 3 V.

In summary these developments of flow RPS are worthy of further assessment, by investigating optimized conditions with a variety of particle types and sizes. Additionally, further evaluation of the degree of plastic selectivity of the overall technique will allow improvement and refinement of the system design.

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PD1: Operando X-ray Studies of Gas Evolving and Consuming Electrocatalysts

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The inherent intermittency of renewable energy production is one of the major challenges facing a future powered by renewable sources. Electrolysers are a potential solution to buffer this intermittency through production of green hydrogen. The electrochemical conversion of carbon dioxide (CO₂) to useful chemicals and fuels is another promising route toward the achievement of carbon neutral and carbon negative energy technologies. Fully understanding the catalytic and degradation mechanisms at current densities relevant for industrial application of these processes is therefore paramount for further catalyst improvement.

In this project we have developed a novel operando x-ray absorption spectroscopy (XAS) electrochemical cell which aims to increase the mass transport limiting current density of gas evolving and consuming reactions through an improved three-phase interface between catalyst, electrolyte, and produced/consumed gas. To achieve this, a gas diffusion electrode comprised of a PTFE membrane coated in a metal thin film to act as a current collector has been used to benchmark the cell by measuring the Pt L₃ XAS during the oxygen reduction reaction (ORR) and the hydrogen evolution reaction (HER). The cell's use was then expanded to help characterise through operando XAS an iridium oxide electrode in strongly oxygen evolving conditions and copper oxide for CO₂ reduction. Results from this have shown how the disorder of iridium oxides affect the catalyst speciation and the kinetics behind the formation of active catalysts for CO₂ reduction.

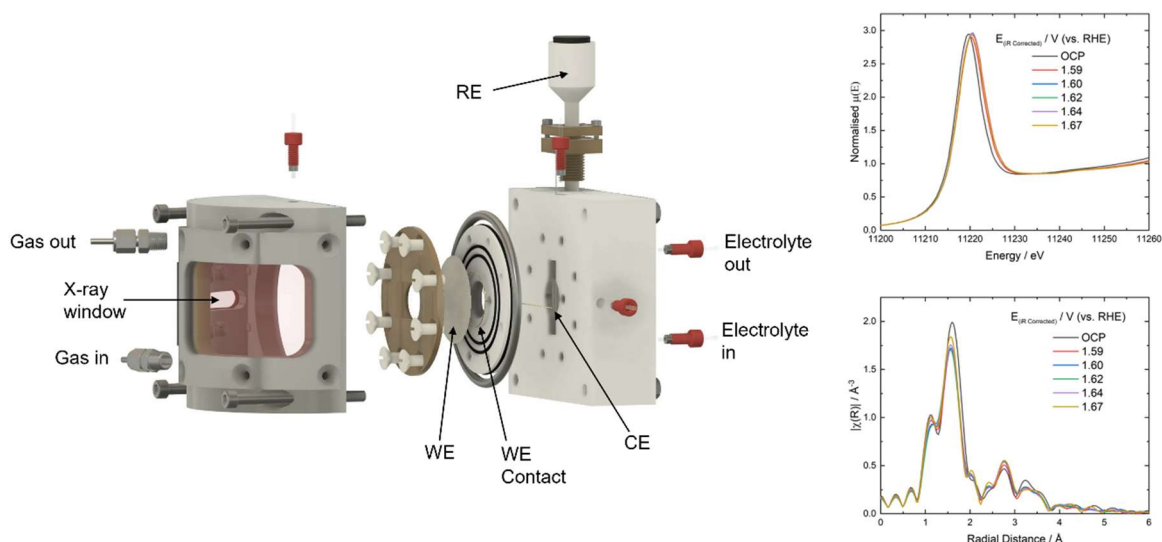


Figure 1: Schematic of the operando XAS electrochemical cell. Normalised Ir L₃ XANES (top) and EXAFS (bottom) collected in the operando XAS cell in 0.1 M H₂SO₄ under flowing N₂ at during the OER.

PD2: Electrochemical dissolution of Fe in concentrated aqueous electrolyte

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All-iron aqueous redox flow batteries provide a low-cost, safe solution for energy storage by utilising Fe(II)/Fe(0) couple ($\text{Fe}^0 \rightarrow \text{Fe}^{2+} + 2\text{e}^-$) at the anode and Fe(III)/Fe(II) couple ($\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$) at the cathode [1,2]. While the simplicity of this battery design is attractive, several fundamental challenges must be overcome to allow full exploitation. These include slow kinetics for the $\text{Fe}^{2+}/\text{Fe}^0$ plating and stripping reaction leading to decreased coulombic efficiency (CE) and competing H_2O reduction at the Fe electrode leading to harmful H_2 generation.

In this study we show that the $\text{Fe}^{2+}/\text{Fe}^0$ redox response, measured using cyclic voltammetry, varies with electrolyte concentration (over range of 0.1 M to 2.5 M Li_2SO_4). Our in-situ IR spectroscopy data shows changes to water and electrolyte structure at potentials at which Fe dissolution takes place. These methods show that electrolyte concentration has an influence on the kinetics of iron plating and stripping. Raman spectroscopy of the iron electrode after both oxidation and reduction shows formation of iron oxides and hydroxides, which indicates that competing reactions with the aqueous electrolyte are taking place. This is also influenced by the electrolyte concentration.

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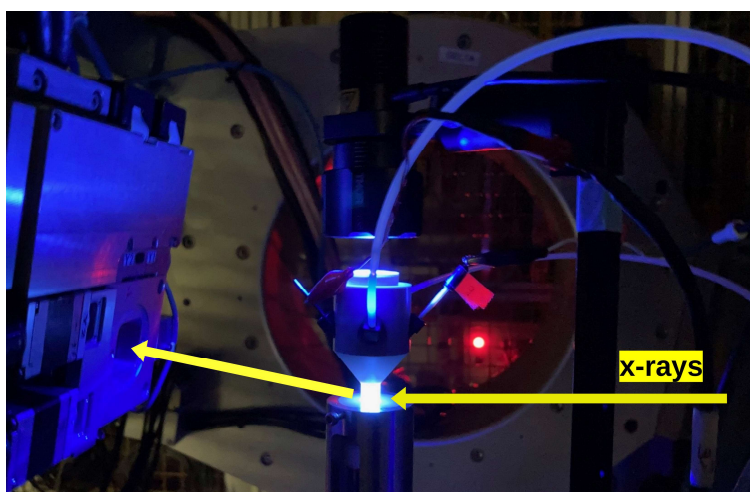
PD3: In-situ and Operando Characterization of Electrochemical Interfaces by Surface X-ray Diffraction and Scattering

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The high transmission through solid and liquid materials makes high energy x-rays an incredibly versatile tools for the characterization of electrochemical surfaces and interfaces during operando and in-situ experiments. The I07 beamline at Diamond Light Source [1], is dedicated to the structural study of interfaces using surface and grazing incidence x-ray diffraction and scattering techniques. The beamline is open to external users and offers a variety of different sample environments for the investigation of chemical processes in real reaction conditions, including different cells and systems for electrochemical experiments. In this contribution the different capabilities of the beamline and the diffraction/scattering techniques will be presented. The possible applications to the characterization of surface dynamics in electrochemical systems will be also showcased using results from recent experiments in photo-electrochemistry and electrodeposition.



Flow cell for combined surface x-ray diffraction and photo-electrochemical experiments

Reference

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PD4: Measuring the reaction volume of electrochemical surface processes

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The reaction volume of reactions at electrochemical interfaces is determined by the volume changes of the involved species and the change of the electrostriction of solvent molecules in the high electric fields around ions in the electric double layer. The reaction volume of electrochemical reactions thus contains information upon the processes themselves as well as the participation of solvent. However, for electrochemical surface reactions data on this thermodynamic property is quite limited. [1-3]

We are able to measure the pressure dependence of the electrode's equilibrium potential with a specifically designed cell. By applying pressure pulses of moderate amplitudes (5 bar) and durations of several seconds, the resulting pressure coefficient is used to directly calculate the reaction volume of the electrode process. For (111)-textured Au-films in CuSO₄/H₂SO₄ the reaction volume has been determined at different resting potentials, including electrochemical reactions such as bulk metal deposition, underpotential deposition of copper, coadsorption of copper and sulphate as well as sole anion adsorption.

Within the Cu UPD region, the reaction volume approximately maintains the value of bulk deposition. Deviation indicate coadsorption of sulphate and copper. At potentials where solely the adsorption of sulphate takes place, the reaction volume decreases to 0 cm³/mol for a fully sulphate covered surface, showing that in the latter case the solvation state of sulphate does not change during adsorption.

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PD5: Proton Coupled Electron Transfer of Anthraquinone at a Glassy Carbon and Boron-Doped Diamond electrode interface

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In recent times, there has been a growing prominence in the use of carbon-based electrodes over traditional noble metal electrode materials like gold and platinum. This shift is driven by the numerous benefits associated with carbon-based electrodes over traditional electrodes. Two particularly interesting carbon materials are glassy carbon (GC) and boron-doped diamond (BDD), the former made up predominantly of sp^2 hybridised carbon and the latter comprised of sp^3 hybridised carbon.¹ Surface modification routes have been developed to investigate the inherent underlying properties of electrode materials. Extensive studies have been conducted regarding modifications on GC.^{2, 3} However, the same cannot be said for BDD due to the inherent inert nature of the material.^{4, 5} Although the grafting of diazonium has been demonstrated for both GC and BDD, there has been no comparison of the chemical and electrochemical properties of redox moieties attached to the surface of BDD with that of GC. Herein, this poster presents a reliable and reproducible route to the modification of the surface of both GC and BDD with an anthraquinone layer, following the reduction of an aryl diazonium linker and subsequent solid phase synthesis. While the surface density of the anthraquinone layer grafted on the two materials is near identical (GC: $1.0 \pm 0.1 \times 10^{14}$ molecules cm^{-2} and BDD: $0.9 \pm 0.3 \times 10^{14}$ molecules cm^{-2}), properties, such as the electron transfer kinetics, differ between the two electrode materials. Further, when the pK_a of anthraquinone is determined, an interesting phenomenon is observed where the bulk pK_a of anthraquinone ($pK_a = 7.7$) shifts to a more basic value when immobilised on GC ($pK_a = 9.1$) and a more acidic value when immobilised on BDD ($pK_a = 6.3$). Our results highlight the importance of caution when translating known surface modification strategies from sp^2 carbon materials to sp^3 materials and the impact of the underlying substate in, for example, electrochemical sensor design.

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PD6: Exploring the Behaviour of Capped Metal Nanoparticles on Metallic Surfaces

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Metal nanoparticles in the size range of 1-10 nm possess unique electronic and catalytic properties that make them attractive for the design of functional surfaces.¹ Previous work has shown that when immobilised onto an Au (111) disc, thiolated Au nanoparticles (~3.5 nm dia.) undergo a redistribution effect where the capping layer moves onto the substrate surface.² This process was shown to be dependent on the substrate reactivity, as well as entropic and enthalpic considerations.

The focus of the current work is to evaluate the stability of thiolated metal nanoparticles on various metal surfaces. To date, we have evaluated Au particles on a Pt microelectrode surface, and vice versa. The modified electrode surfaces were studied via cyclic voltammetry, looking at their behaviour towards the electro-oxidation of glycerol in alkaline media.

A Pt electrode modified with Au nanoparticles showed no significant change in the voltametric features. Lower observed current intensities in the CV indicate the presence of a species on the electrode surface, which we believe to be protected and intact Au particles. The Au electrode modified with Pt particles exhibited a new voltametric peak, attributed to the oxidation of glycerol by electrochemically active Pt. This indicates exposed Pt particles present on the surface as a result of a redistribution effect.³ Recent work has focused on the inclusion of in-air scanning tunnelling microscopy (STM) to image the modified surfaces. Images show the Pt particles on the Au surface are not fully intact. We look now towards including more materials (i.e. Ni and Ag) as well as further characterisation of the modified surfaces using XPS and STM.

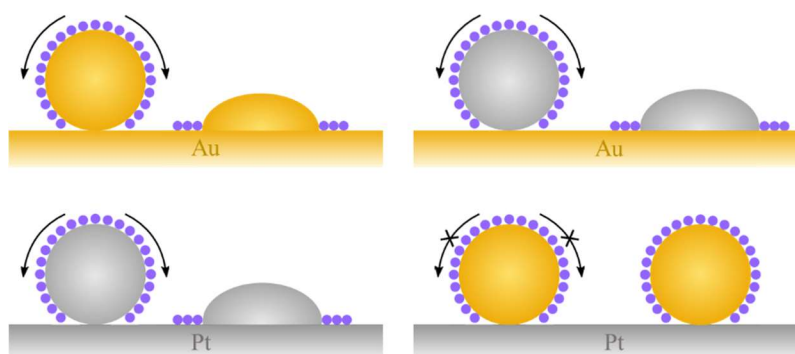


Figure 9. Proposed scenarios of the redistribution effect of the capping layer (purple) of thiolated nanoparticles (Au, Pt) deposited onto a metal (Au, Pt) substrate.

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PD7: Spectro-electrochemical cell for soft X-ray XAS and XPS

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The B07 versatile soft X-ray (VERSOX) beamline utilises the high brilliance of the Diamond Light Source synchrotron for X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) experiments at near-ambient pressures. The beamline utilises soft X-rays to probe the electronic structure of materials. We have developed a 3-electrode electrochemical flow cell for operando studies to probe the electronic structure of electrocatalytic materials during electrochemical reactions (Figure 1). B07 is a soft X-ray beamline which can probe key edges such as the O and C K X-ray absorption edges, and is very surface sensitive, which allows us to probe the catalyst-electrolyte interface. [1]

Our standard XAS experiments use a thin layer of electrocatalyst on a gold coated silicon nitride window. An example of this is some of our work on CuO_x catalysts for CO_2 reduction. We can measure changes in X-ray absorption at fixed photon energies during cyclic voltammetry. Therefore, we can measure the changes in oxidation state with direct comparison to electrochemical potential: this is demonstrated in the fixed energy X-ray absorption voltammetry (FEXRAV) data shown in Figure 2. [2]

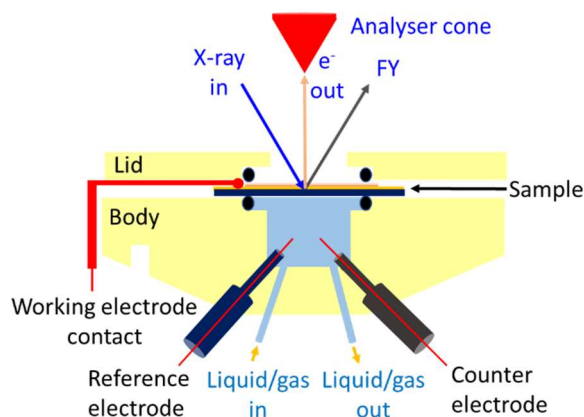


Figure 1 – Schematic of B07 electrochemical cell for silicon nitride window experiments.

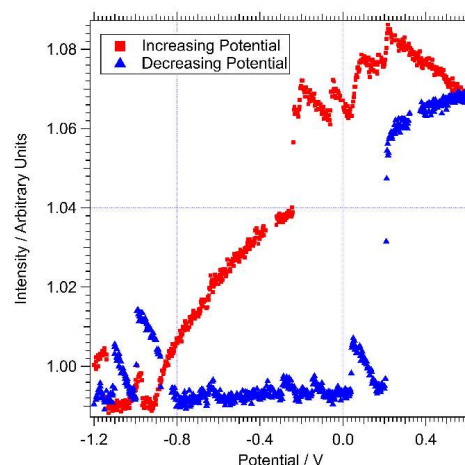


Figure 2 – FEXRAV of CuO_x at 931.25 eV – Cu(II) main peak (Cu $L\alpha$ edge). Potential vs. Ag/AgCl.

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PD8: Characterising the Fundamental Structural and Electrochemical Properties of Single Crystal Boron Doped Diamond

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Boron doped diamond (BDD) has many favourable properties that lend themselves to electrochemical applications: low background currents, a wide solvent window, resistance to corrosion and fouling, and metal-like behaviour upon doping above 10^{20} B atoms cm^{-3} .^{1–4} As a result, BDD has found applications in areas such as electroanalysis, sensors and electro-organic synthesis.⁵ Typically, research revolves around the use of polycrystalline BDD since it can be readily grown at the large wafer size. However, polycrystalline BDD is inherently inhomogeneous. The presence of grains, with varying amounts of boron doping, present challenges when studying the fundamental properties of BDD on a macroscale. Grain boundaries may also contain sp^2 carbon impurities, which increase the background currents, decrease the solvent window, and further adds to the surface's heterogeneity. Therefore, to study the fundamental behaviour of BDD, one approach is to use single crystal (SC) surfaces.

Growing appropriately doped SC BDD of the correct orientation and post processing it such that the surface is smooth and free from defects and surface damage is challenging, and very few studies have achieved this.^{6,7} This work outlines the growth, processing and characterisation of three freestanding homoepitaxially chemical vapour deposition-grown BDD SC samples of (111), (110) and (100) orientation that were polished to sub-nanometre roughness. First, the orientation of each sample was confirmed using x-ray diffraction and any off-angle orientation corrected for by further polishing of the crystal. The samples were further characterised using low energy electron diffraction, Raman spectroscopy, atomic force microscopy and x-ray photoelectron spectroscopy to confirm crystal quality, surface finish and chemical functionality. Electrochemical characterisation was made at both the macroscale using outer and inner sphere redox couples and nanoscale, using scanning electrochemical cell microscopy to spatially map the electron transfer kinetics across the surface using an outer-sphere redox couple.⁸

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PD9: A Voltammetric Perspective of Multi-Electron and Proton Transfer in Protein Redox Chemistry: Insights From Computational Analysis of *Escherichia coli* HypD Fourier Transformed Alternating Current Voltammetry

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Our work is concerned with the mechanism of electron transfer in metalloproteins, we have successfully distinguished a concerted two electron-transfer mechanism from a two sequential one electron-transfer process and deconvoluted the square scheme using voltammetry techniques.[1] This paper explores the impact of pH on the mechanism of reversible disulphide bond (CysS-SCys) reductive breaking and oxidative formation in *E. coli* hydrogenase maturation factor HypD, a protein which forms a highly stable adsorbed film on a graphite electrode. To achieve this, low frequency (8.96 Hz) ramped Fourier Transformed alternating current Voltammetric (r-FTacV) experimental data was used in combination with modelling approaches based on Butler-Volmer theory with a dual polynomial capacitance model, utilizing an automated two-step fitting process conducted within a Bayesian framework. We previously showed that at pH 6.0 the protein data is best modelled by a redox reaction of two separate, stepwise one-electron, one-proton transfer terms ($E_{app2}^0 > E_{app1}^0$). [2] Remarkably, rather than collapsing to a concerted two-electron redox reaction at a more extreme pH, the same two-stepwise one-electron transfer model with. Remarkably, rather than collapsing to a concerted two-electron redox reaction at a more extreme pH, the same two-stepwise one-electron transfer model with $E_{app2}^0 > E_{app1}^0$ continues to provide the best fit to r-FTacV data measured across a proton concentration from pH 4.0 to pH 9.0. A similar, small level of crossover in reversible potentials is also displayed in overall two-electron transitions in other proteins and enzymes, and this provides access to a small but finite amount of the one-electron reduced intermediate state.

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PE1: Microstructural influence on corrosion performance of legacy cast iron mains water pipe

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Grey cast irons have been extensively used for potable water pipe networks worldwide, due to their low-cost and ease of manufacture. With the introduction of ductile iron and PVC pipes the installation of cast iron pipes has for the most part ceased, thus discouraging continued research using more advanced techniques. At present, pipe failures are increasing as the cast iron pipe network has reached and often surpassed its service life limit. Plus, interestingly, there is a renewed attention in the use of cast irons as a more environmentally-friendly alternative to plastics. Consequently, there is a greater urgency to better understand the corrosion performance and the influence of aggressive soil environments. Previous work has established the 'leak before burst' concept associated with localised corrosion features 10s of millimetres in diameter; however, how these leaks occur and the key factors aggravating the formation of a pinhole leak has yet to be fully determined.

The focus of this work is to characterise grey cast iron microstructures, which typically consist of three phases: ferrite (α -phase), pearlite (an alternating ferrite and Fe₃C platelet structure) and graphite and assess the microgalvanic behaviours between these phases on the corrosion performance. In addition, the aggressive soil conditions have been characterised into key parameters that govern the surface degradation. Thus, a study of pit geometries in varying conditions was conducted, and the effect of the interplay between the three distinct phases on the nucleation, evolution and morphology of corrosion pits was examined.

Several legacy cast irons, representative of a typical in-service pipeline material, were exposed for 96 h to a 0.03 M NaCl solution, adjusted to pH 8.5; this electrolyte solution has a similar conductivity and pH to typical soil conditions of buried water pipelines. Linear polarisation resistance and potentiodynamic polarisations was used to evaluate the initial corrosion performance and mechanisms. Optical and electron microscopy were undertaken establish the extent of the microgalvanic corrosion and the presence of any protective oxide films. Estimates of the initial corrosion rate on the surface have been made, as well as studying its variation over the test duration. Previous work has shown that the long-term corrosion rate of grey cast iron in seawater is between 60 and 80 $\mu\text{m y}^{-1}$, and the rate in a water-clogged clay soil to be as high as 1000 $\mu\text{m y}^{-1}$. As such, it is imperative to re-evaluate and assess cast iron corrosion performances using modern techniques to gain a better understanding of the initial corrosion mechanism and pit depths in simulant soil conditions.

PE2: SS Great Britain - Decarbonising the unique conservation system for the world's first iron ship

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The wrought iron hull of Brunel's SS Great Britain, the first and largest screw-propelled iron steamship, was recovered in 1970 from the Falkland Islands, and is in the Bristol dry dock where it was built in 1843. Originally designed for Atlantic crossings but later refitted and repurposed, the ship enjoyed an extraordinarily long working life, travelling over a million miles and circumnavigating the globe 32 times thanks to the strength and longevity of the iron structure. The ship has now been accessible to the public for over 50 years, with a bespoke system built to protect the salt impregnated wrought iron structure from ongoing corrosion¹. The dry dock and ship's interior have been converted into a climate-controlled envelope, with a glass plate sealing the dry dock at waterline level and air, supplied by two dehumidifiers set at 20% relative humidity (RH), protecting the most vulnerable parts of the iron from corrosion.

Planned maintenance and unplanned system outages result in short excursions from 20% RH at least annually. The system cooling is passive and can be limited in effectiveness, there is also significant temperature variation. The system has a significant carbon footprint, most notably from the gas burners which provide heat for the drying action of the dehumidifiers. The SS Great Britain Trust, responsible for the ships conservation has an interest in understanding of the effectiveness of the system, to identify and minimise any active corrosion and reduce the carbon footprint. This research aims to recommend ways to reduce the energy and environmental impact of the conservation system.

To ensure a minimum intervention philosophy for the conservation of the asset, environmental control of the relative humidity (RH) is the main focus of this research. Different approaches are explored:

- The impact of the RH level over the current 20%, evaluating the deliquescence of a range of salts, to avoid the formation of highly active electrolyte.
- Management of water infiltration in the dry dock to reduce the RH of the enclosure and load on the desiccation system.
- The possibility of employing vapour phase corrosion inhibitors (VpCI) in case of failure of the desiccation system is discussed.

These recommendations are discussed with the aim of reducing the environmental impact of the conservation of this exceptional ship.

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PE3: Electrochemical Monitoring Techniques for Evaluating Effectiveness of Petrolatum Coatings for Cast Iron Trunk Mains

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Passive electrochemical monitoring was utilised to evaluate the effectiveness of a petrolatum-based coating system in mitigating corrosion in uncorroded cast iron sections exposed to a corrosive soil environment, to replicate in-situ conditions. Petrolatum based coating systems are commonly used for corrosion prevention, hence it's vital to holistically understand their effectiveness of corrosion mitigation and if it can influence corrosion rates in adjacent areas.

Typically, corrosion mitigation studies focus on how effective the mitigation on the area it's protecting, however this study also looks at partial coatings to evaluate if there is an impact on the adjacent unprotected regions to the coating. Mitigating corrosion for water networks typically means doing spot repairs on high-risk areas, hence it's imperative to understand the complete effect of spot repairs, whether they solely prevent corrosion locally or if they influence the adjacent regions in a positive or negative way. Thus coating was applied to the sections in ways to investigate this relationship; including a baseline uncoated, half coated, full coated, and poorly coated, to replicate poor workmanship scenarios.

The techniques utilised were open circuit potential and ZRA electrochemical noise, whereby the potentials of a pair of nominally identical cast iron electrodes are held at the same potential to monitor the current noise between them. Performance of the electrochemical techniques varied and were chosen with the idea of monitoring the noise under the coatings, however there was little connection between the pair of fully coated electrodes, thus some currents were negligible and heavy polarisation was needed to hold the samples at the same potential.

The experiments are ongoing and have been exposed for 8-months, hence analysis of the results was limited due to the ongoing nature of the experiments and the inability to visually assess the corrosion. Analysis of electrochemical data has been completed through looking at the potential and current over an elapsed time. Interpretation of the results are based on the idea that the potential should remain consistent as long as there is an exposed area, whereas the current will be proportional to the amount of corrosion activity dependent on the size of the surface area exposed. Based on this model of interpretation, the potential data showed constant values between uncoated and partially coated samples and the coated samples showed potential below that of corrosion potential values. Current noise has increased over time for all samples, including comparable and measurable current noise for coated samples.

Future work will involve Linear Polarization Resistance (LPR) measurements to verify current noise measurements, continued monitoring with the same techniques as described, and subsequent evaluation through weight loss and microscopy after the yearlong exposure period is complete.

PE4: Zinc and Cobalt incorporation in 316 SS Oxide formed in simulated BWR Conditions

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The oxidation of 316 stainless steel (SS) was investigated in simulated Boiling Water Reactor (BWR) environments using coupons exposed to multistage oxidation tests under mixed water chemistry (H:O molar ratio ~8) at 288 °C. The coupons were initially oxidized for 500 h, then treated for 200 h to simulate On-Line NobleChem™ (OLNC) (either with or without 10 ppb Zn), and subsequently re-oxidized for 500 h in the same water chemistry as for the first stage, but this time with 0.2 ppb Co injection. The microstructure and chemical composition of the oxide was analysed after each stage using a variety of characterisation techniques (SEM, TEM, STEM-EDX). In pure water, the duplex oxide formed without OLNC treatment was composed of a chromite spinel-based inner layer whilst the outer layer was a mixture of ferrite and magnetite. In contrast, the injection of Zn resulted in a thinner oxide and suppressed the formation of the outer magnetite in which Zn was not incorporated because it has low miscibility in magnetite which has an inverse spinel structure. A bilayer inner oxide developed after exposure to OLNC, which was attributed to the electrochemical potential gradient established near the surface where the Pt nanoparticles were deposited. It was also observed that, in Zn-free water, Co was incorporated in the outer layer of the inner oxide whereas a negligible concentration of Co was detected in the oxide formed in Zn-dosed water, thus confirming the beneficial effects of Zn on the suppression of Co uptake in the oxide.

PE5: Corrosion studies of diamond-like carbon coating on Ti₆Al₄V alloy: A promising surface coating in biomedical and aviation industry

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Due to its biocompatibility and non-toxicity nature, titanium grade alloy (Ti₆Al₄V) has been widely utilised in orthopaedic implants. As a load-bearing requirement, metallic implants are subjected to complex reactions chemically and biologically. The few contributing factors resulting in corrosion mechanism are the material's electrochemical behaviour with the human body fluid, consequently inducing implant deterioration progressively. Additionally, a high coefficient of friction and poor wear resistance stimulate the release of metallic ions from implants, subsequently prolonging the healing and accelerating its infection. As such, materials with good wear resistance and chemical inertness are critical for attributing osteointegration capability. While in aviation and marine industries, Ti₆Al₄V alloy are generally used for structural application. However, it is also prone to aggressive and seawater environments, therefore making it vulnerable to corrosion mechanisms.

Carbon-based materials have unique allotropes which allow electrical and mechanical properties modification to be used for various commercial applications.¹ Diamond-like carbon (DLC), which contains a sp³ bond commonly deposited through a sputtering method,² has recently garnered interest to promote the adherence of the coating and long lifespan of both implants and structural parts. Although Ti₆Al₄V forms a passivation layer naturally within a nanometre range, the thin layer is insufficient to act as a protective layer against corrosion.³ As such, surface coatings that yield suitable candidates on Ti₆Al₄V have been increasingly explored in recent years. The coating functions as a critical barrier layer of protection to prevent the degradation of metallic alloys.

In this work, we study the corrosion resistance of DLC coatings under different types of corrosive medium by mimicking human body fluids as well as aggressive environments. The experimental electrochemical procedures conducted are open circuit potential and linear polarization. This provides an understanding of the corrosion initiation under different electrolyte conditions. Additionally, both qualitative and quantitative will be supplemented through electrochemical impedance spectroscopy to understand the adherence of the coating through a circuit fit model. Other surface characterization such as atomic force microscopy, micrographs and hardness testing will be used to understand the surface morphology and properties.

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PE6: The effect of CO₂ partial pressure on the formation and protective characteristics of iron carbonate corrosion products

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The presence of dissolved carbon dioxide (CO₂) in geothermal energy facilities acidifies the aqueous environment and accelerates the corrosion of carbon steel pipes. Under certain conditions, the precipitation of iron carbonate (FeCO₃) corrosion products onto pipe walls can form a dense layer that protects the underlying metal surface from further corrosion. However, the level of protection offered by the corrosion product layer is highly sensitive to changes in environmental conditions.

This study investigates how CO₂ partial pressure affects the formation and characteristics of FeCO₃ layers that form on X65 carbon steel. Autoclave corrosion testing is performed using CO₂-saturated, 3wt.% sodium chloride solution at an operating temperature of 80°C and partial pressures ranging from 5.5 to 15.5 bar. In-situ linear polarisation resistance analysis reveals the distinct stages of FeCO₃ layer development and demonstrates how operating pressure influences the rate of FeCO₃ formation. Electrochemical Impedance Spectroscopy (EIS) provides an insight into the mechanism by which the FeCO₃ layer protects the metal substrate. This was found to transition from initially blocking steel active sites, to providing additional corrosion suppression by limiting the diffusion of electrochemically active ions. The formation of an effective diffusion barrier is accelerated at high CO₂ partial pressures.

PE7: Casing corrosion of steels in geothermal environments containing sulphuric acid

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Geothermal pipelines as part of production or injection wells can undergo corrosion due to interactions with high-temperature/low-pH geothermal fluids. Areas in Taiwan and Indonesia are known to have low-pH geothermal fluids containing sulphuric acid (H_2SO_4) stemming from the mixture of underground waters and magmatic gases. However, there is limited knowledge about the corrosion behaviour of carbon steel within H_2SO_4 waters within the pH range of 2-4. This work is conducted with the aim of gathering insight into steel corrosion concerning geothermal conditions, especially focusing around fluids containing H_2SO_4 . A tantalum-lined autoclave was used to perform static corrosion tests with N80 carbon steel submerged in acidic solutions (pH 2-4) and temperatures up to 150°C. Real-time in-situ electrochemical measurements of linear polarisation resistance and electrochemical impedance spectroscopy were recorded as means of relating corrosion rates and reaction mechanisms for the tested material. Surfaces of the corroded steel were analysed with scanning electron microscopy and white light interferometry to visualise the physical impacts of corrosion. The N80 carbon steel was seen to encounter high corrosion rates (>90 mm/year) along with severe signs of localised corrosion when exposed to the pH 2 test solution tested at 150°C. Additionally, the corrosion behaviour of alternative corrosion resistant alloys is explored to provide material selection options for demanding geothermal environments.

Delegate list

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