UNIVERSITY OF LIVERPOOL

Stephenson Institute for Renewable Energy

Annual Reports 2022 and 2023

LIFE CHANGING
World Shaping

The Stephenson Institute for Renewable Energy Report: 2022 and 2023

Contents

The Annual Report 2022 and 2023 was collated and edited by Ken Durose

Cover and contents page images: Brad Lewis

Director’s Welcome

Welcome to the SIRE Report for 2022/23 - a snapshot of our work on the chemistry and physics of energy storage, conversion, and sustainability. Our objective is to work on topics that transform energy futures through fundamental science, understanding and controlling interfaces, new materials, and devices. With our unique focus on the physical sciences for energy research, SIRE exploits the research expertise on technologies such as solar energy, solar fuels, batteries, catalysis, electrolysers, and electrochemical capacitors.

2023 has been a milestone year for the Stephenson Institute for Renewable Energy as we celebrated our 10-Year anniversary of the opening of our brand-sparklingly new energy research building. Looking at our photos in the directory of expertise (page 39) some of us have not aged a day and have kept in as good condition as our institute! We are very proud of the research conducted over the past decade, in a short space of time a healthy research income grew to over £20 million leading to a constant annual scientific output of over 60 papers, numerous academic and industrial collaborations from UK and across the globe. The greatest pleasure (or maybe the only pleasure) in the role of Director is seeing the development of our early career academics through PhDs and postdoctoral positions within SIRE and then following their subsequent later flourishing careers. It was a delight to welcome back some of our alumni to our 10-year event as either speakers or attendees from countries spanning the globe from Japan, Taiwan, China, mainland Europe and various corners of North America. The 10-Year event also gave us an opportunity to pay thanks to our professional services colleagues who keep the proverbial *wheels on the road*, notably to our technician Vince Vasey who has been with us since day one.

Thirty-three of our early-stage research colleagues successfully defended their theses in 2022 and 2023: Natalie Bavis, Jack Beane, Zhenyu Chen, Scott Christy, Romy Dop, Benjamin Duff, Holly Edwards, Julia Fernandez Vidal, Nicole Fleck, Benjamin Greeves, Adrian Hannah, Joseph Horne, Leanne Jones, Jacob Leaver, Monica Lisauskaite, Sarah Livesley, Yi-Ting Lu, Qurat Nadeem, Omer Omar, Dora Garcia Osorio, Andrea Pugliese, Kieran Routledge, Khezar Saeed, Arne Sandschulte, Abbie Scholes, James Smith, Luke Thomas, Katherine Tustain, Rebekah Upton, Peiyao Yan, Haofan Yang, Bowen Zhang, Hongda Zhou.

Their thesis titles and photos appear towards the end of this report. Everyone in the team congratulates them and wishes them all well in their future careers!

Thank you for reading our annual report. I do hope that if you wish to know more or to collaborate with us you will feel welcome to get in touch with any of the Institute’s researchers using the directory of expertise on page 39.

10 Years is quite a milestone for a research centre, and I look very much forward to the next 10 years!

Laurence Hardwick,

News and Events

SIRE 10th Anniversary Celebrations and New Lab Opening

Wednesday 15th November 2023 saw the Stephenson Institute for Renewable Energy celebrate their 10 Year Anniversary opening of the main building! To celebrate the event, current members of the Institute were joined by former PhD students and colleagues (including Professor Tzu-Ho Wu, National Yunlin University of Science and Technology (NYUST), Taiwan, pictured), to hear about their time in SIRE and also where their various career paths and research had taken them.

The name 'Stephenson' connects the institute to Liverpool's long history of innovation. Stephenson's nearby rail terminus scored several world firsts: the first intercity line, first double track, first with a timetable, first with signals, and of course the first to be steam-only (no horses allowed). Continuing that tradition, much innovation was on show as colleagues around the globe joined us, starting in Taiwan, then Japan and finishing in Oregon, US. The institute were fortunate enough to host online and virtual talks on a range of topics, such as numerous world records in solar cell efficiencies, advanced spectroscopy to study the orientation of complex proteins on surfaces, development of aqueous rechargeable Zn-ion cells and the underpinning theory for controlling photochemistry in space and much more besides. In attendance was also Vice-Chancellor Professor Tim Jones, whom the institute would like to extend their thanks to for officially opening their new Sustainable Fuels Laboratory, touring their solar and electrochemistry research laboratories, and delivering the welcome address.

Throughout the day, guests had the opportunity to walk through the building and view the 30+ posters covering the walls which showcased the fantastic work of our present generation of PhDs and PDRAs and partake in lively discussions in the coffee and lunch breaks.

Sincere congratulations to the best poster prize winners: Baltazar Correa Mendes Pereira Guedes (Probing the Structure of the Electrochemical Interface) and Dr Alex Neale (Operando Kerr Gated Raman Spectroscopy to Probe the High States of Charge in Graphite Electrodes for Li-ion Batteries).

While the event celebrated ten years of the opening of the SIRE main building, the Institute's first staff came to Liverpool in February 2011 when Ken Durose initiated the photovoltaic materials and devices activity in what is now Lab 1 in SIRE. Since then the team has expanded to a total of 16 academic members of staff and they maintain a standing portfolio of > £30m in research grants, SIRE publishes a total of 60-70 research papers and graduates around 15 PhD students annually.

Laurence Hardwick and
Ken Durose Nov 2023

Speakers at the event were:

Prof. Tzu-Ho Wu, National Yunlin University of Science and Technology (NYUST), Taiwan - "Strategies Toward High-Performance Aqueous Zn-Ion Batteries"

Dr Silvia Mariotti, OIST, Japan - "Fabricating perovskite solar cells around the World: a toxic job"

Dr Filipe Braga Nogueira, University of Liverpool - "Interface between academia and industry as a post-doctoral researcher in energy storage materials"

Dr Ben Williams, Oxford PV - "Thin-film photovoltaics, from academia to industry"

Dr Leanne Jones, University of Oxford - "The Journey of an X-ray Spectroscopist : an illuminating career path"

Dr Ben Duff, University of Liverpool - "Towards Understanding of the Local Structure and Li+ Ion Dynamics in Solid Electrolyte Candidates using Solid-State NMR"

Dr Khezar Saeed, University of Copenhagen, Denmark - "Probing the interfacial activation of proteins at lipid surfaces with VSFG spectroscopy"

Dr Gaia Neri, JM - "Power-to-Fuels from academia to industry"

Dr Gilberto Teobaldi, STFC - "Riverrun, past Eve and Adam's, from swerve of shore to bend of bay"

Prof. Gary Harlow, University of Oregon, USA - "Adventures in surface x-ray diffraction and electrochemistry"

Dr Phillipe Braga Nogueira outlining industrial/academic interaction in SIRE at our 10th anniversary event.

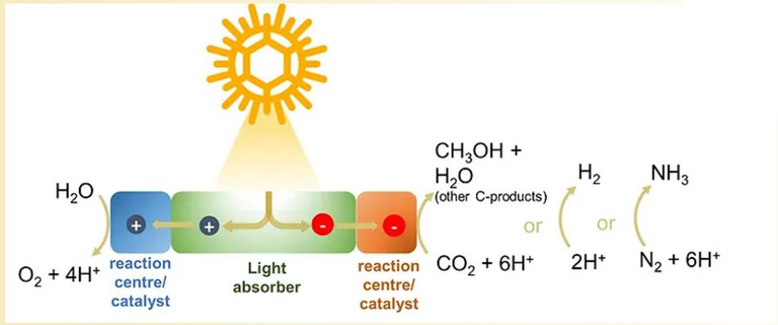
University Vice Chancellor Tim Jones cuts the ribbon to open a new lab extension in SIRE with our Director, Laurence Hardwick.

The Solar Chemicals Network

Alex Cowan has been successful in gaining UKRI-EPSRC funding for The Solar Chemicals Network (SCN) which aims to develop an effective community of solar chemicals researchers from both academia and industry. The Network seeks to raise the profile of the solar chemicals research community nationally and internationally, to promote collaboration and co-operation with other research disciplines, industry and international solar chemicals programmes, and to contribute towards the development of a UK solar chemicals technology and policy roadmap.

Nature has evolved an array of machineries and mechanisms for sustainably generating chemicals in a versatile manner from water, carbon dioxide and nitrogen from the most abundant energy resource available - solar. In contrast industrialised society relies on chemicals that are derived from fossil resources in energy intensive processes. The demand for key chemicals such as methanol, ammonia and polymer precursors is growing rapidly, driven by increased needs for use in agriculture, manufacturing and consumer products. It follows that there is an urgent need to find sustainable ways to generate the chemicals which we rely on in modern life. Scientific progress towards artificial, or semi-artificial light-driven materials that achieve these transformations is underway. But success will require input from a wide range of fields including chemistry, biology, chemical engineering and physics. This network proposes to bring together the key researchers to build a diverse community that can deliver the underpinning science and technology for a solar chemicals industry. We will support the community and facilitate it to generate novel activities that advance the field through a series of events and travel grants. We will also work to raise awareness of this potentially transformative approach to sustainable chemicals and fuels production with the public and policy makers through a range of policy and outreach documents and events co-created with UK and international partners.

Alex Cowan/Glenda Wall
The Solar Chemicals Network



Common features across solar to chemicals systems include a light absorber (green) able to generate oxidising and reducing equivalents that can be utilised at catalytic centres for water oxidation (blue) and a range of reduction reactions (brown).

Director	Prof Alex Cowan, Liverpool
Deputy Director	Dr Jenny Zhang, Cambridge
Project Manager	Dr Glenda Wall, Liverpool
Biocatalysis Theme Lead	Prof Julea Butt, UEA
Electrocatalysis Theme Lead	Dr Ifan Stephens, Imperial College
Light Harvesting Theme Lead	Prof Libby Gibson, Newcastle
Devices and Carbon Capture Co-Lead	Dr Alex Forse, Cambridge
Devices and Carbon Capture Co-Lead	Prof Gianluca Li Puma, Loughborough

The Network is open to any interested academic or industrial partners in the UK.
For more details, please visit https://www.solarchemicals.co.uk

EPSRC Centre for Doctoral Training in New and Sustainable Photovoltaics – CDT-PV

The Centre for Doctoral Training in New and Sustainable Photovoltaics (CDT-PV) is nearing the end of its lifetime. Most of the doctoral students have either graduated or are about to graduate. Based on a recent survey, 51 alumni are employed of whom 21 in academia, 26 outside of academia, and in addition 4 have both, an academic and a non-academic affiliation. Out of these 51 alumni, 30 have a position in which they work either with PV, energy, or sustainability. The most common job titles are researcher (17), engineer (11) and consultant (5).

The main CDT-PV event of the past two years was the Final Showcase held in Central Hall Westminster, London. This event brought together the CDT-PV alumni, students, supervisors, industry members, and the UKRI-EPSRC representatives. In addition to the talks and posters from students, the programme contained several insightful invited talks and two lively panel discussions in which also the audience contributed enthusiastically. The industry panel discussed about the future of low carbon, and the alumni panel shared their experiences in the job market after PhD. The evening finished with a round-table discussion and dinner.

Other notable CDT-PV events and trainings from the past two years include the following:

- 'Multi-CDT Conference on Clean Energy and Sustainable Infrastructure' was held in April 2022 at the University of Sheffield in collaboration with two other CDTs, Energy Storage and Its Applications and Sustainable Infrastructure Systems.
- A PhD Thesis Writing Retreat was held in September 2022 in the Peak District and contained professional development and outdoor team building activities.
- An online Project Management Training was held in January 2022 and covered such topics as project management methods, implementation, lifecycle, and practicalities.

In terms of published scientific papers, one highlight was the research conducted by Tomi Baikie (University of Cambridge) et. al. who published their paper 'Photosynthesis re-wired on the pico-second timescale' in the journal Nature (Nature 615, 836-840, 2023). Their work gave new insight into the photosynthesis of plants and speculated on how this could be used in the future to develop more efficient processes for creating biofuels. Their work received a lot of media attention both here and abroad (DW News, CNET).

Another paper that was quickly noticed by media (e.g. Physics World, pv magazine) was 'Next steps in the footprint project: A feasibility study of installing solar panels on Bath Abbey' by Matthew J. Smiles (University of Liverpool) et. al published in the journal Energy Science & Engineering (Energy Science & Engineering 10, 3, 892-902). This paper is a great example of a CDT-PV wide collaboration: the paper was co-authored by 7 CDT-PV students from 5 different partner universities. The paper originated from the training module at Bath where the students from all 5 cohorts visited Bath Abbey to discuss its Footprint project, see the roof, and the used PVSyst software combined with architectural diagrams and energy usage provided by the Abbey to predict cell output.

Ville Rimpilainen,
Deputy Director, CDT-PV

The industry panel discussed about the future of low carbon, PV and other options. The panel was chaired by Lewis Irvine from Oxford PV (right) and the panelists (from right to left) were David Bossanyi (Renewable Energy Systems), Heather Goodwin (Element Energy), KT Tan (Viridian Solar), Paul Warren (NSG Group) and Chris Rider (Cambridge Photon).

Electrochemistry North West Meeting 2022, Liverpool

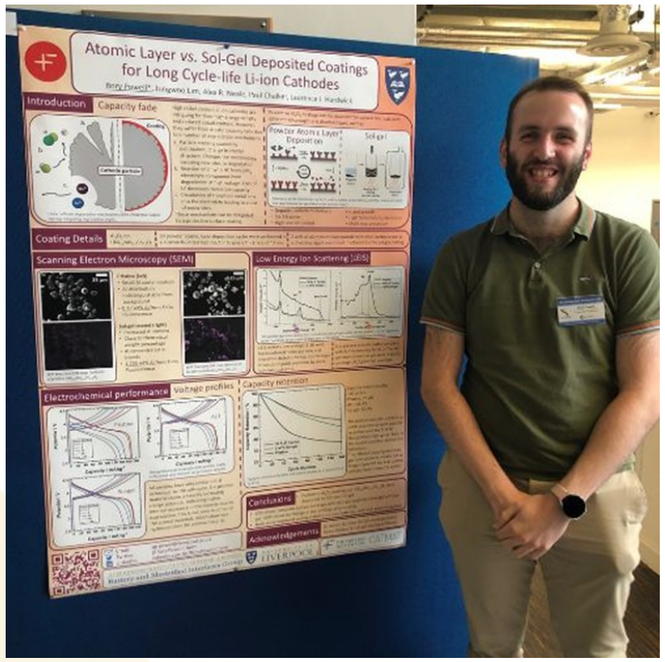
On Thursday 14th July 2022, Electrochemistry North West was held in the Stephenson Institute for Renewable Energy with some 85 participants. It was brought about through the hard work and organisation of Hardwick Group's Dr Alex Neale along with Dr Mangayarkarasi Nagarathinam (Lancaster University) and Dr Hussain Al Nasser (University of Manchester).
The day kicked off with refreshments and a morning full of interesting and thoughtful talks chaired by Professor Laurence Hardwick. Dr Nuria Garcia-Araez (University of Southampton) started this session as the invited speaker and gave a great in-depth and eye-opening talk about 'Fundamental Developments of Next Generation of Batteries and Lithium Production Methods'.

During lunch, the poster session, which featured over 20 posters, was in full swing. There were many discussions challenging the minds of each poster presenter, in addition to sharing ideas and knowledge. Group member Rory Powell took second place in the poster competition for his poster 'Atomic Layer vs. Sol-Gel Deposited Coatings for Long Cycle-life Li-ion Cathodes' which was judged by the exhibitors Alvatek, BioLogic Science Instruments, Cellerate, Hiden Analytical, and Metrohm; who also put on marvellous displays of their products and services as well as providing sponsorship and prizes for the day. Support was also received by the Royal Society of Chemistry's (RSC) Applied Materials Chemistry Group and by the RSC Electrochemistry Interest Group.

In the afternoon, Dr Alex Neale chaired the second talks session where invited speaker Dr Kathryn Toghill (Lancaster University) gave an insightful talk into 'The challenge of electrocatalytic CO_2 reduction'. During this session, Group member Julia Fernandez-Vidal gave a talk on 'Investigating the Presence of Adsorbed Species on Pt Steps at Low Potentials' and won first place in the afternoon talks competition which was judged by fellow academics in attendance.

Overall, a great day was had by all. There was an amazing and varied turnout of poster presentations and 11 interesting and thought-provoking talks, along with great attendance from those across the North West and beyond.

Dr Alex Neale

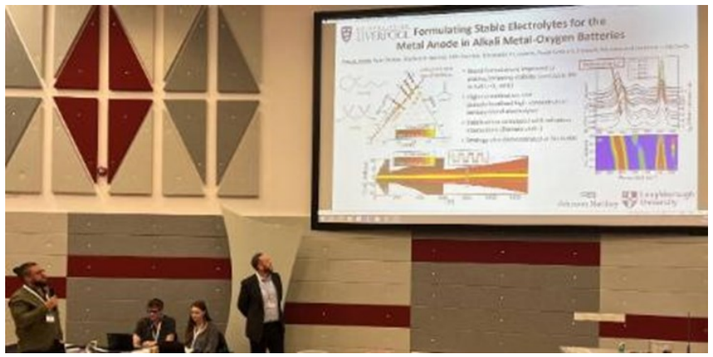


Rory Powell with his prize-winning post-

Julia Fernández-Vidal presenting at Electrochemistry North West.

Electrochemistry Faraday Discussion 'Rechargeable non-aqueous metal-oxygen batteries'

Lucy Walters receiving her poster prize from Professor Dame Clare Grey FRS (University of Cambridge).



Laurence Hardwick Chairing the Flash poster presentation. Dr Alex Neale (University of Liverpool) is presenting on "Formulating stable electrolytes for the metal anode in alkali metal–oxygen batteries".

The Faraday Discussion on 'Rechargeable non-aqueous metal-oxygen batteries' coordinated by Laurence Hardwick as the Chair of Scientific Committee took place 18-20th of Sept. at the National STEM Learning Centre, University of York with over 80 attendees present in the UK. There was a high-profile international audience form North and South America, Asia, and the EU.

The Discussion addressed the following four key themes: Mechanism of oxygen reduction and evolution reactions in non-aqueous electrolyte, materials for stable metal–oxygen battery cathodes, metal anodes and protected interfaces and reaching practical metal–oxygen batteries.

The event was attended by several members of the Hardwick Group. Group member Lucy Walters was awarded *The Faraday Community for Physical Chemistry Poster Prize for the best poster* was awarded to Lucy Walters of the University of Liverpool for her poster entitled "Operando surface enhanced infrared investigations of nonaqueous Na–O_2 batteries" and Prof Gary Attard (Dept Physics, Liverpool) presented a joint discussion paper based on collaborative work on single crystal electrochemistry and spectroscopy work carried out by PhD graduate Dr Julia Fernández Vidal ("Effect of alkali-metal cation on oxygen adsorption at Pt single-crystal electrodes in non-aqueous electrolytes").

Highly stimulating scientific discussions were held on reaction mechanisms and new materials for lithium, sodium and potassium air cells, as well as room temperature and high temperature all solid-state metal air cells. Discussions also concentrated on advanced physical chemistry methods to understand reaction mechanisms, degradation reactions and the role of singlet oxygen. Achieve stable metal plating and stripping at the negative electrode was examined in detail.

Laurence Hardwick

Research Group Expertise and Highlights

Crystal growth, magnetism and thermoelectrics

Jonathan Alaria

We specialise in single crystal bulk growth, thin film growth by pulsed laser deposition and physical characterisation. High quality crystals are an essential part of our research, enabling us to determine fundamental properties of new or previously misunderstood materials with important physical properties or applications in renewable energy. Physics understanding and methodologies (such as quantum oscillations) are combined with chemistry know-how and intuition. Our main focus in renewable energy materials is the design of novel ways to break the conventional interdependence of thermal and electronic conductivity in order to develop improved thermo-electric materials.

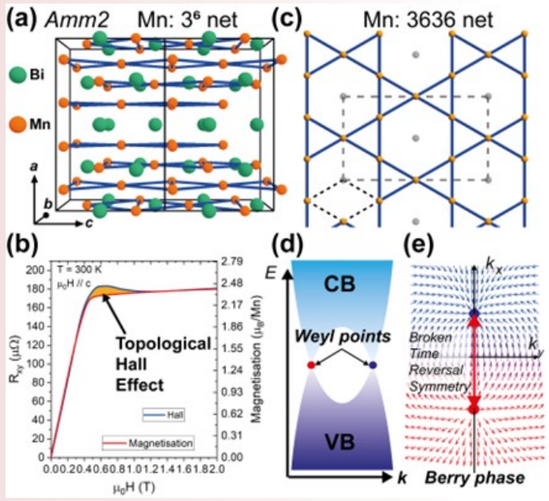
Highlight: Electronic and thermal transport in novel Kagome magnets

One of the consequences of technology commodification and ease of access to the internet is that worldwide data creation is forecasted to grow to 175 zettabytes by 2025 (prediction by the International Data Corporation) and with their associated continuously increasing energy consumption needs, the development of “Green Computing” is a pressing matter to build an energy-efficient society. The development of quantum information processing hardware has allowed to demonstrate the unique opportunities offered by quantum technology to provide energy efficient computing. One of the next milestones for this technology to mature is to tackle the materials challenge.

Materials with efficient spin-charge conversion (large Anomalous Hall Effect (AHE), Spin Hall Effect (SHE), and Topological Hall Effect (THE)) are needed for next generation low energy computing devices. Two new materials containing a Kagome net have been identified and the coupling between the magnetic ordering and their electronic and thermal properties have been investigated.

$Mn_{1.05}Bi$ shows magnetic properties markedly different from hexagonal, NiAs-type MnBi, driven by ordered interstitials and vacancies of Mn, stabilizing a likely complex magnetic structure with strongly temperature-dependent spin dynamics and room temperature THE.

To investigate the possibility to tune the electronic structure of Kagome metals, we studied the magnetic, electronic and thermal properties of Fe_3Ge_2Sb, with buckled Kagome layers and found similar properties to unbuckled hexagonal FeGe making the family of compounds $Fe_3Ge_{3-x}Sb_x$ a good host to study various physical effects in Kagome metals.



$Mn_{1.1}Bi$ has a chiral structure (a) that affords the topological Hall effect at 300K (orange field) (b). Defect order (removing the grey sites) in this NiAs-related structure will offer Kagome-related (blue) nets (c) generating Weyl crossings (d) and large Berry curvature (e).

Magnetic resonance for energy materials and catalysis

Frédéric Blanc

Magnetic resonance spectroscopy enables advances in the understanding of the structure, dynamics and behaviour of a large range of chemical systems to be obtained. We exploit the atomic resolution sensitivity of magnetic resonance to probe the mobility of lithium and oxide ions in electrolytes materials for application in energy storage and conversion devices; to follow the dynamics of supramolecular assemblies with molecular capture and release properties; and to identify catalytic intermediates in heterogeneous catalysts as well as their host guest interactions. Recent research highlights also include the development of hyperpolarisation magnetic techniques to detect the nuclear spins of extremely insensitive nuclei.

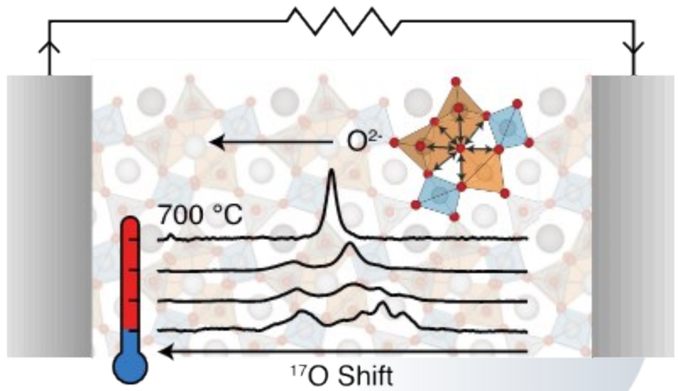
Highlight: Oxide ion diffusion mechanism from ^{17}O NMR under non-ambient conditions

Fast oxygen transport materials play key roles as electrolytes in solid oxide fuel cells devices. One of such materials that has a layered tetrahedral network melilite structure is the front runner candidate exhibiting the flexibility required to accommodate interstitial oxide anions leading to excellent ionic transport properties at moderate temperatures. Work led by PhD student Lucia Corti exploiting new high temperature Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) capabilities available at the UK High Field Solid-State NMR National Research Facility solved the conduction mechanism in this important class of melilite structure.

Firstly, a combined experimental and computational MAS NMR approach first aimed at elucidating the local configurational disorder in a key member of this structural family possessing the $La_{1.54}Sr_{0.46}Ga_3O_{7.27}$ composition. The ^{17}O and ^{71}Ga MAS NMR spectra display complex spectral line shapes that could be accurately predicted using a computational ensemble-based approach to model site disorder across multiple cationic and anionic sites, thereby enabling the assignment of bridging/non-bridging oxygens and the identification of distinct gallium coordination environments. The ^{17}O and ^{71}Ga MAS NMR spectra of $La_{1.54}Sr_{0.46}Ga_3O_{7.27}$ display additional features not observed for the parent $LaSrGa_3O_7$ phase which are attributed to interstitial oxide ions incorporated upon cation doping and stabilised by the formation of five-coordinate Ga centres conferring framework flexibility.

Secondly, ^{17}O high temperature MAS NMR experiments capture exchange within the bridging oxygens at 130 °C and reveal coalescence of all oxygen signals in $La_{1.54}Sr_{0.46}Ga_3O_{7.27}$ above approximately 300 °C with significant line narrowing at 700 °C (at which solid oxide fuel cells devices operate) indicative of the participation of both interstitial and framework oxide ions in the transport process.

These results unequivocally provide evidence for the conduction mechanism in $La_{1.54}Sr_{0.46}Ga_3O_{7.27}$ and highlight the potential of ^{17}O MAS NMR spectroscopy to enhance the understanding of ionic motion in solid electrolytes.



Layered tetrahedral network melilite is a promising structural family of fast ion conductors that exhibits the flexibility required to accommodate interstitial oxide anions, leading to excellent ionic transport properties at moderate temperatures.

Sustainable Fuels and Chemicals

Alex Cowan

Alex's team is studying pathways for the conversion of waste and abundant molecules such as carbon dioxide and water into useful fuels and chemical feedstocks such as green H_2 and carbon products (e.g. syngas). The groups work spans from fundamentals of light driven materials (solar-to-x), that absorb sunlight to drive the chemical transformation, through to applied studies and catalyst development activities in the field of power-to-x, where catalysts are used in electrolysers for the transformation.

Alongside developing catalysts and electrolysers we have interests in developing in-situ spectroscopic measurements of the electrodes and photoactive materials.

Highlight: Bipolar membrane electrolysers for CO_2 conversion

CO_2 electrolysers are an emerging technology with the potential to generate useful products for the chemicals industry. At the anode the oxidation of water yields oxygen as a product and provides a source of electrons for the reduction of carbon dioxide at the cathode, to generate a range of products from carbon monoxide, formic acid to ethylene depending on the catalyst used. In this way it is possible to generate a recycled feedstock for the chemicals industry that displaces the currently used fossil resources.

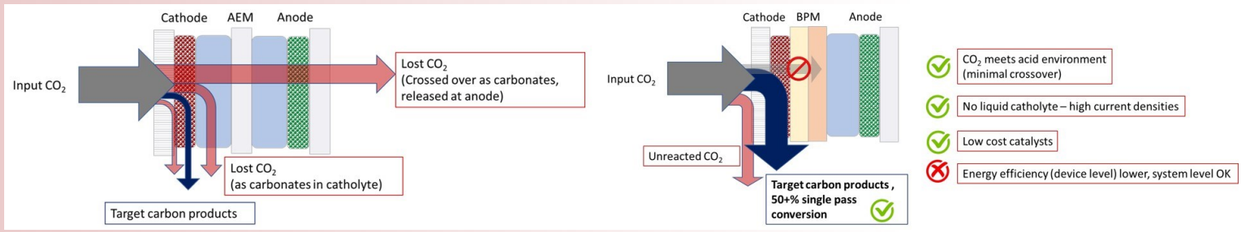
To operate at high rates (current densities) CO_2 electrolysers use a gas-diffusion-electrode that allows for rapid delivery of the CO_2 gas to the active catalytic site on the cathode electrode. Typically an anion-exchange membrane (AEM) is then used to separate the two parts (anode/cathode) of the electrolyser to prevent product-cross over, figure below. The AEM also leads to a high pH (alkaline) environment at the cathode. This has benefits - it minimises competitive hydrogen evolution but the disadvantage is that CO_2 rapidly is converted to carbonates and becomes unavailable for reduction at the cathode (figure, left).

Working as part of the UKRI Interdisciplinary Centre for Circular Chemical Economy (https://www.circular-chemical.org/) the team at Liverpool has develop a type of bipolar membrane electrolyser that minimises this loss pathway (figure right). The bipolar membrane is reverse biases and its acidic side is contacted to the cathode preventing carbonate formation. In principle this seems like a simple solution but the challenge becomes finding a catalyst that can operate to convert carbon dioxide in the acidic environment.

During 2022 our proof-of-principle work identified a molecular catalyst that has a Nickel active site that could operate in the acidic electrolyser (*J. Am. Chem. Soc*. 2022, 144, 17, 7551–7556). Although the catalyst has issues with stability the concept has generated significant interest as it allowed a CO_2 electrolyser to be tested that only required pure water and CO_2 as the reagents, potentially simplifying the system (*Nature Catalysis,* 2022, 5, 356).

As the bipolar membrane electrolyser prevents carbonate formation it is able to achieve high CO_2 conversion efficiencies and follow up studies at the start of 2023 with a more stable Cobalt catalyst achieved >50% single pass conversion efficiencies and greatly improved current densities and current densities of 200 mA cm^{-2} (*Adv. Mat. Interfaces.,* 2023, 10 (15), 2300203).

Significant technical challenges remain to be addressed, principally the low stability of the overall device due to poor water management and the losses induced by the commercial membrane. But despite this work is now underway to explore how bipolar membrane electrolysers operate with real-world gas sources as a first step to wards implementation.



Left: carbon dioxide electrolysers have tended to use an alkali environment at the cathode. This enables high Faradic efficiencies through the suppression of hydrogen evolution, but the carbon dioxide rapidly forms carbonates and is lost to other parts of the device. Right: the approach developed uses a bipolar membrane to engineer the local pH and achieve high conversion efficiencies.

Photoemission measurements for advanced functional materials

Vin Dhanak

We specialise in photoemission measurements of novel advanced materials related to solar conversion and battery storage research as well as gate dielectrics for both low and high-power metal-oxide-semiconductor field-effect transistors. Photoemission (XPS, UPS) and inverse photoemission (IPES) are used to measure the chemical and electronic properties of a range of materials with applications in electronic devices and energy materials. The measurements elucidate not only composition and oxidation states, but also band line-up determination at interfaces and its relation to other physical properties, as well as the density of states on either side of the Fermi level.

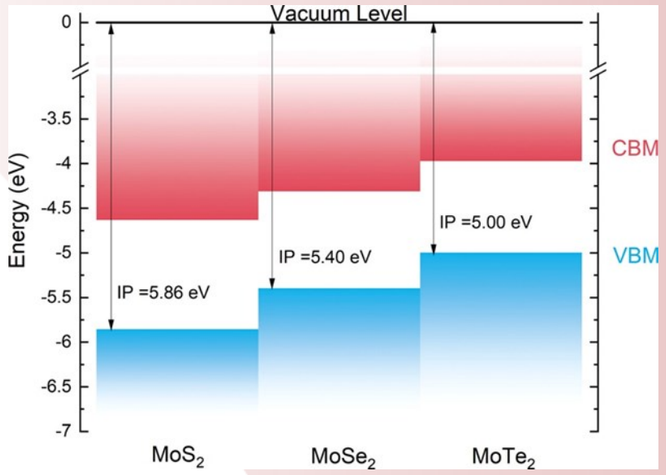
Highlight: Electronic structure of molybdenum di-chalcogenides

Interest in transition metal dichalcogenides (TMDs) was reignited by the discovery of graphene which shares the honeycomb / van der Waals sheet structure. TMDs exhibit a remarkable range of properties (e.g. conductivity mechanisms, high surface area/volume ratio) enabling unique applications. MoS_2 is of interest for photovoltaic devices, and $MoSe_2$ for energy storage due to its larger interlayer spacing. $MoTe_2$ is of interest for Li-ion storage anodes, gas sensors, and photodetectors. Understanding the bulk electronic structure is crucial for developing all three: We used soft and hard X-ray photoelectron spectroscopy (SXPS and HAXPES) measurements to probe them. Core level measurements and valence band spectra were compared to density functional theory calculations of the occupied density of states.

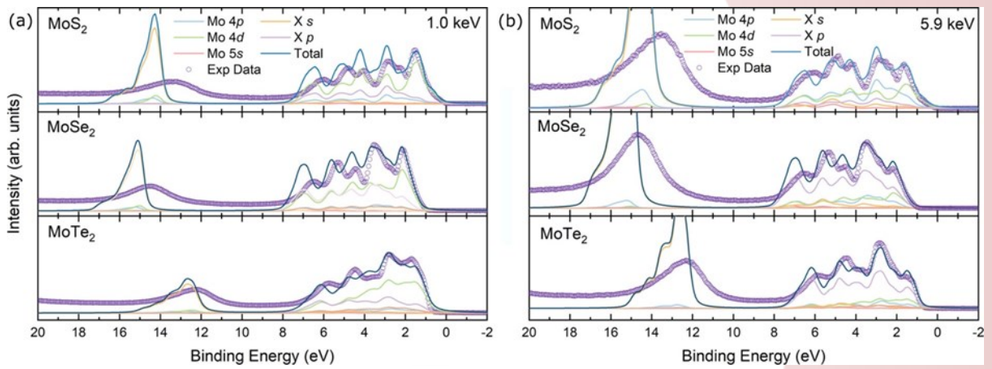
Measurements of the ionization potential allowed for the determination of the band alignment of MoS_2, $MoSe_2$ and $MoTe_2$. Importantly, the orbital contributions were investigated, and the role of p-d hybridization was found to explain the trend in band offsets.

It was deduced that the strength of the p-d hybridization increased when traversing from the sulphide to the telluride due to a greater presence of chalcogen p orbitals at the valence band edge.

Band alignments, electronic structure, and core-level spectra of bulk molybdenum dichalcogenides (MoS_2, $MoSe_2$, and $MoTe_2$), LAH Jones et al., J. Phys. Chem. C, 126 (2022) 21022.



Band alignment between the three bulk dichalcogenides determined from the experimental ionization potentials.



Broadened and cross-section-corrected theoretical density of states for MoS_2, $MoSe_2$, and $MoTe_2$ compared with (a) the SXPS and (b) HAXPES valence band spectra.

Thin film solar photovoltaic materials and devices

Ken Durose

Ken's group specialises on developing new materials and devices for solar electricity generation. We are able to take this all the way from the synthesis of new and emerging materials, all the way though to incorporating them into working photovoltaic devices at the lab scale. The laboratory has full capabilities for bulk materials synthesis, thin film deposition, device making and testing the performance of the photovoltaic devices and materials. We have worked on a wide range of materials, including transparent conductors and solar absorbers, most notably CdTe, Sb_2Se_3, inorganic perovskites and organic device partner layers. The case study below reports our work on novel device architecture design.

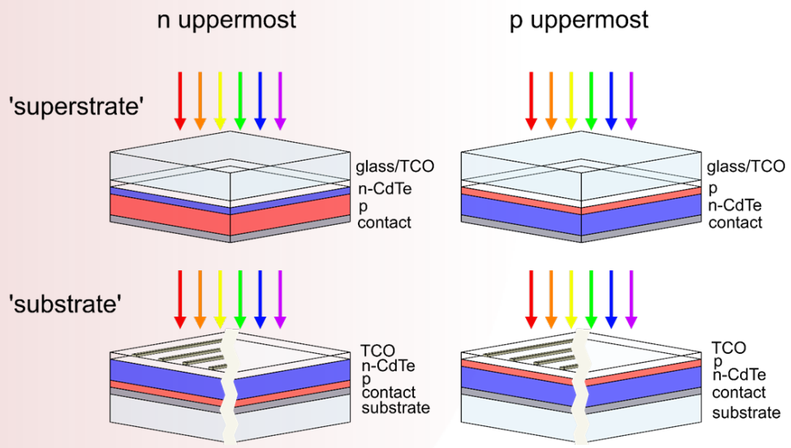
Highlight: Thin film solar cells with n-type absorber layers

Throughout the 50 year history of low cost thin film p-n junction solar cells, the absorbing layer has always been chosen to have p-type conductivity. There are good reasons for this, but some problems too. Use of p-type absorbers makes sense since they are compatible with transparent electrodes, which have to be n-type (p-doping of wide bandgap materials is very ineffective). However, the choice of p-type absorber layers comes with some built-in setbacks, especially for CdTe. These are: a) there is an upper limit to the p-doping level achievable, and this limits the photovoltage achievable, and b) it is difficult to form low resistance Ohmic contacts to p-type CdTe.

In order to get around these problems, we started a new project to redesign the CdTe solar cell using n-type absorbers rather than p-type. The aim was to take advantage of the high n-type doping levels and low-resistance contacts achievable for CdTe which promise to allow higher photovoltages to be developed.

Those working on the project were postdoc Dr Theo Hobson, supported by an EPSRC grant, and PhD student Mr Luke Thomas, funded by the EPSRC Centre for Doctoral Training in New and Sustainable Photovoltaics.

The initial challenge was to dope the CdTe n-type with indium and to verify that thin films made from it were indeed n-type. We trialled a number of post-growth and in-situ doping methods, settling on sublimation of pre-doped CdTe:In to form the films. A key process step was to do the sublimation transfer in an oxygen-free or else reducing environment in order to avoid the formation of oxides which blocked dopant transfer. While demonstration of n-type conduction in our bulk samples was easy to prove, for the thin films the grain boundaries present made the usual methods of Hall and hot probe analysis impossible. Hence we resorted to hard x-ray photoemission studies to determine the Fermi level position in the thin films. By measuring the Fermi level as a function of depth in the samples, it was possible to account for the effects of surface band bending which could otherwise confound the measurements. An unexpected finding at this stage of the work was that chlorine treatment, which is universally applied to CdTe solar cells to achieve high efficiency - did not work for n-type CdTe. Indeed, it acted to compensate n-doping, nullifying the intended effect. Since chlorine usually acts to electrically passify harmful grain boundaries, it remains a challenge for the n-type paradigm to achieve both n-doping and grain boundary passivation. Nevertheless, modelling of the devices shows that the n-type designs are capable of achieving open circuit voltages in excess of 1V, which would represent a significant advance over the present practical limit of about 0.86 V.



Alternative design types for thin films solar cells having n-type rather than p-type absorber layers.

Atomic structure and charge distribution at the electrochemical interface

Yvonne Grunder

The structure of the electrode and electrolyte, as well as stability effects and charge transfer mechanism are the underlying properties and processes which can crucially affect reactivity and performance of electrochemical applications. We employ in-situ surface x-ray diffraction to enable atomic/molecular-level understanding of the interface under reactive conditions. Experiments are conducted in-situ at synchrotron lightsources. We have recently developed a new technique, a combination of x-ray diffraction and spectroscopy, allowing to gain inside into the charge distribution and bonding mechanism at the interface.

Highlight: Surface resonant X-ray diffraction — probing the charge distribution at an electrochemical interface

Although there have been several theoretical studies of the charge transfer mechanism at the electrochemical interface, few experimental electrochemical investigations are reported. The complexity of the electrochemical environment makes the interface inaccessible to traditional electron-based probes of charge transfer. A fundamental understanding of the nature of the charge transfer and the electron distribution at the interface is therefore a major goal in electrochemistry.

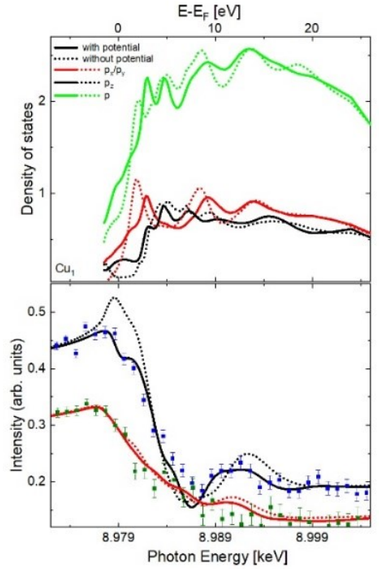


Fig. 1: The spectra at the surface sensitive anti-Bragg position (1 1 0.2) measured in horizontal and vertical polarisation modes are shown (lower panel) together with the modelled data obtained both with and without the additional Helmholtz potential.

We have employed Surface Resonant X-Ray Diffraction (SRXRD) in combination with self-consistent DFT calculations to assess the charge distribution and bonding mechanism for the adsorption of bromide anions onto a single crystal Cu(001) electrode surface. The X-ray scattering amplitude depends on the electron density of the contributing atoms: any modification of charge distribution should be observable in a change of the scattered intensity close to the adsorption edge of the involved atoms. The intensity variation at each position in reciprocal space is thus specific to the spectroscopic response of the probed atoms and to the modification of their atomic form factor due to the change in the electron arrangement at the interface (**Fig. 1**).

The electrochemical environment was mimicked by a simple double layer model at the electrochemical interface (Helmholtz), which has been implemented into the FDMNES code introducing an additional potential. Its effect on the electron distribution at the interface (**Fig. 2**) can be obtained. The charge distribution at the atoms has been altered, not only by adding or subtracting charges, resulting in simply a charged atom, but by a rearrangement of the electron densities.

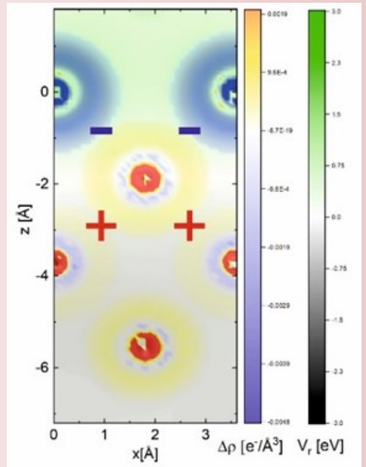


Fig. 2: Map of the difference in electron density $\Delta\rho$ and in the potential energy V_r induced by the Helmholtz potential. It is shown along the [100] direction (bulk coordinates) through the Br adsorbate. The '+' and '-' indicate the additional charge rearrangement

In addition, the dipole surface moment shifts into the metal electrode. A similar effect with an electric dipole in the metal surface was found with the same method on Pt(111).

These results show that *in situ* SRXRD studies combined with self-consistent DFT calculations can suitably assess the charge distribution and bonding mechanism of specific adsorbate at the electrochemical interface.

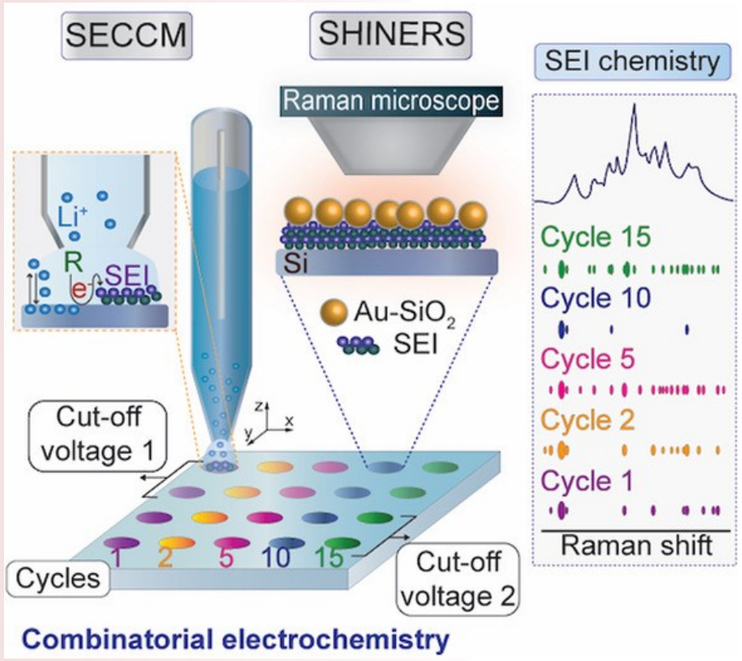
Battery research: Electrochemical and Raman screening of dynamic film formation on silicon electrodes

Laurence Hardwick

Laurence's group focusses on understanding real-time interface processes in batteries, a crucial step in improving energy storage solutions to meet net zero targets. The work has focused on developing cutting-edge technologies such advanced *in situ* Raman and infrared spectroscopic techniques that can probe the functionality of electrode interfaces at the nanoscale to inform material design. He is editor of the International Society of Electrochemistry Journal Electrochimica Acta (Elsevier) and was Conference Chair of the 2023 Royal Society of Chemistry Faraday Discussion conference on Metal-air Batteries.

Highlight: Observing battery chemistry at the nanoscale

Lithium-ion batteries are key for decarbonising energy and transportation systems. Silicon is promising as negative electrode in Li-ion cells due to the higher theoretical specific capacity compared with graphite. However, Si undergoes large volume expansion during lithiation leading to instability of the solid-electrolyte interphase (SEI) and mechanical failure. The SEI should ideally prevent continuous electrolyte decomposition, but cracking of the Si surface and the SEI breathing effect lead to a sustained loss of cyclable lithium leading to capacity fading and cell death. SEI composition and properties are affected by experimental formation conditions, but its characterisation is challenging as only a few techniques can provide meaningful chemical information. Thereby revealing how formation protocols influence the properties of the SEI on silicon electrodes is key to developing the next generation of Li-ion batteries. SEI understanding is, further limited by the low-throughput nature of conventional characterisation techniques. Herein, correlative scanning electrochemical cell microscopy (SECCM) and shell-isolated nanoparticles for enhanced Raman spectroscopy (SHINERS) are used for combinatorial screening of the SEI formation under a broad experimental space (20 sets of different conditions with several repeats). Working with colleagues at Warwick University and Prof. Alex Cowan in SIRE, the team revealed the heterogeneous nature and dynamics of the SEI electrochemical properties and chemical composition on Si electrodes, which evolve in a characteristic manner as a function of cycle number, coupled with instability towards the $LiPF_6$ salt. Correlative SECCM/SHINERS has the potential to screen thousands of candidate experiments on a variety of battery materials to accelerate the optimisation of SEI formation methods, a key bottleneck in battery manufacturing.



Scanning electrochemical cell microscopy (SECCM) enables combinatorial electrochemical assessment of a broad experimental space for solid-electrolyte interphase (SEI) formation on Si electrodes for Li-ion batteries, which is correlated to the heterogeneous and dynamic SEI chemistry through co-located shell-isolated nanoparticles for enhanced Raman spectroscopy (SHINERS).

Martín-Yerga et al. Angew. Chem., Int. Ed. 2022, 61, e202207184.

Useful materials from waste sulfur

Tom Hasell

Elemental sulfur is a waste by-product of the petrochemicals industry. It is produced in much larger quantities than it is used – leading to storage problems and vast stockpiles of sulfur being generated at oil refineries. Our group has been researching ways to turn this waste sulfur into useful materials with interesting properties. It can be turned into a polymer. Most polymers (plastics) are made from the limited petrochemical resources themselves–so making polymers instead from a by-product is more sustainable. Sulfur polymers also have some really interesting and unique properties that make them easier to recycle, and give them applications in heavy metal recovery, energy storage, infra-red transparent lenses, and antimicrobial materials.

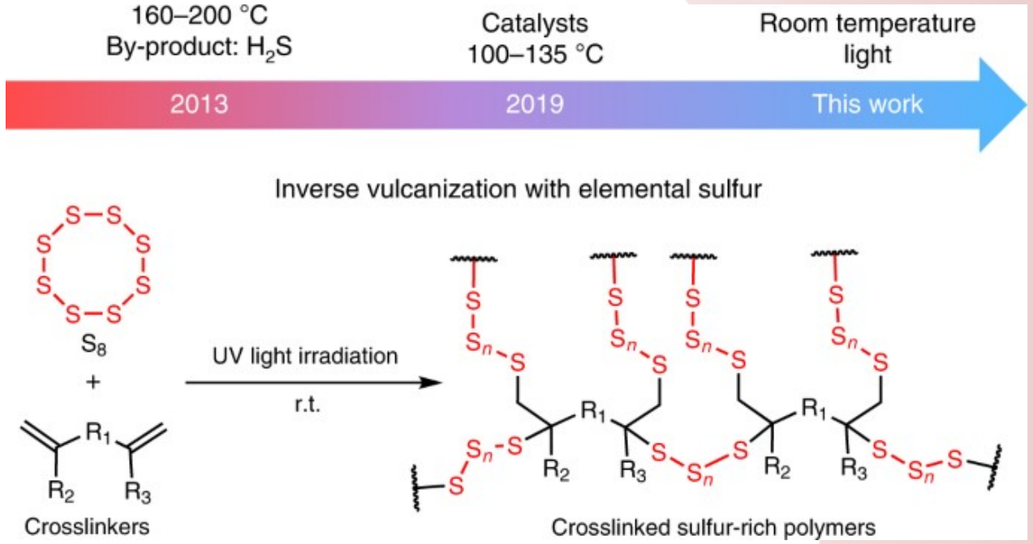
This year we congratulate PhD students graduating from the group, Sam Petcher, Bowen Zhang, Peiyao Yan, Haoran Wang, and Romy Dop, who join our previous graduates Doug Parker and Jess Smith. We also welcome new students Xi Deng and Pan Yang to join current students Veronica Hanna, Diana Cai, Liam Dodd, and Joe Dale.

Highlight: Photo-induced inverse vulcanisation

Elemental sulfur is usually comprised from eight membered rings of sulfur. As a material, it is a crumbly crystalline powder, that cannot be made into useful materials. When heated, the sulfur first melts, and then polymerises—forming a red solid material. However, in this pure form the polymer is unstable and will readily de-polymerise back to eight membered sulfur rings, even at room temperature. A process called inverse vulcanisation has been receiving much attention, as a way to make these sulfur polymers stable by copolymerising the sulfur with organic comonomers. These comonomers can be chosen from a range of commercial chemicals as well as industrial by-products and sustainable bioderived molecules—even used cooking oil.

However, the previous synthesis methods require the sulfur and co-monomer to be heated to high temperatures, causing some challenges. Not only the energy requirement, but also the temperatures required can limit the range of co-monomers that can be easily used, as the reaction temperature is above the boiling temperature of many. More significantly, there is also a risk of dangerous thermal runaway, and the production of toxic hydrogen sulfide gas as a by-product.

In a collaborative project with Northwest Normal University in Lanzhou, we were able to show for the first time that inverse vulcanisation could also be initiated by light, rather than heating. This provides an alternative, potentially safer and more sustainable route, especially for coatings and thin films, as well as broadening the range of co-monomers that are possible to react, and opening up new synthetic avenues. The work was published in *Nature Chemistry* 14, 1249-1257 (2022), as well as being highlighted in a News and Views article by Courtney Jenkins, a leading expert in inverse vulcanisation, in *Nature Synthesis*, 1, 835-836 (2022).



Hybrid nanomaterials: for renewable energy, nanoplasmonics and nanophotonics

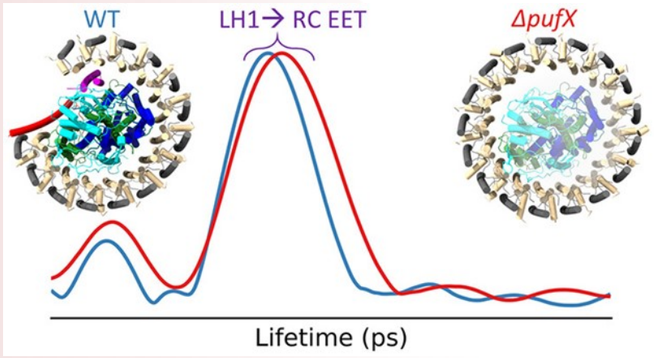
Frank Jaeckel

Hybrid nanomaterials combine different material classes (i.e. metals, semiconductors, organics) on the nanoscale. Nanomaterials themselves can display properties significantly different from their bulk counterparts due to quantum confinement effects. Hybrid nanomaterials on the other hand can exhibit novel or enhanced properties that neither of the components exhibits itself. We are interested in the preparation and fundamental photophysical characterisation of hybrid nanomaterials for applications in renewable energy, nanoplasmonics and nanophotonics. Hybrid metal-semiconductor nanomaterials can be used for photocatalytic hydrogen generation and other solar fuels as part of a green and sustainable energy supply. We are interested in developing novel hybrid nanomaterials for photocatalysis and in understanding their fundamental photophysics.

Highlight: Ultrafast transient absorption spectroscopy of excitation energy transfer in photosynthetic RC-LH1 supercomplexes

Converting solar energy into chemical fuels is performed on a large scale via photosynthesis in nature. Purple bacteria represent a model system in which the central functional unit for anoxygenic photosynthesis consist of light harvester (LH1) and reaction centre (RC) supercomplex. Wildtype RC-LH1 complexes form both monomers and dimers in cells, comprising LH1 α and β-subunits, RC H, L, and M subunits, as well as the PufX and PufY (the latter was also named protein-Y or protein-U) transmembrane (TM) polypeptides. Wildtype complexes can be modified by deleting individual components. This allows to unravel the role of individual components in the structure-function relationship of the supercomplexes. Such understanding will be useful for engineered artificial photosynthetic systems.

In collaboration with the Liu group at Liverpool (Institute of Systems, Molecular and Integrative Biology), we used ultrafast transient absorption spectroscopy in the Early Career Laser Laboratory at Liverpool to study excitation energy transfer in wildtype and modified supercomplexes. We found that the absence of PufX increases both the LH1 → RC excitation energy transfer lifetime and distribution due to the role of PufX in defining the interaction and orientation of the RC within the LH1 ring. While the absence of PufY leads to the conformational shift of several LH1 subunits toward the RC, it does not result in a marked change in the excitation energy transfer lifetime.



Representation of the changes in excitation energy transfer lifetime distribution from light harvesting complex to reaction centre when transmembrane polypeptide pufX is deleted from the wild-type super complex. A shift to longer wavelength and broadening can be observed demonstrating the central function of pufX in defining the relative orientation and interaction of light harvester and reaction centre in the supercomplex.

O Thwaites et al Unravelling the roles of integral polypeptides in excitation energy transfer of photosynthetic RC-LH1 supercomplexes J. Phys. Chem. B 2023, 127, 33, 7283 –7290.

Catalysis for green chemistry, recycling and energy

Tony Lopez-Sanchez

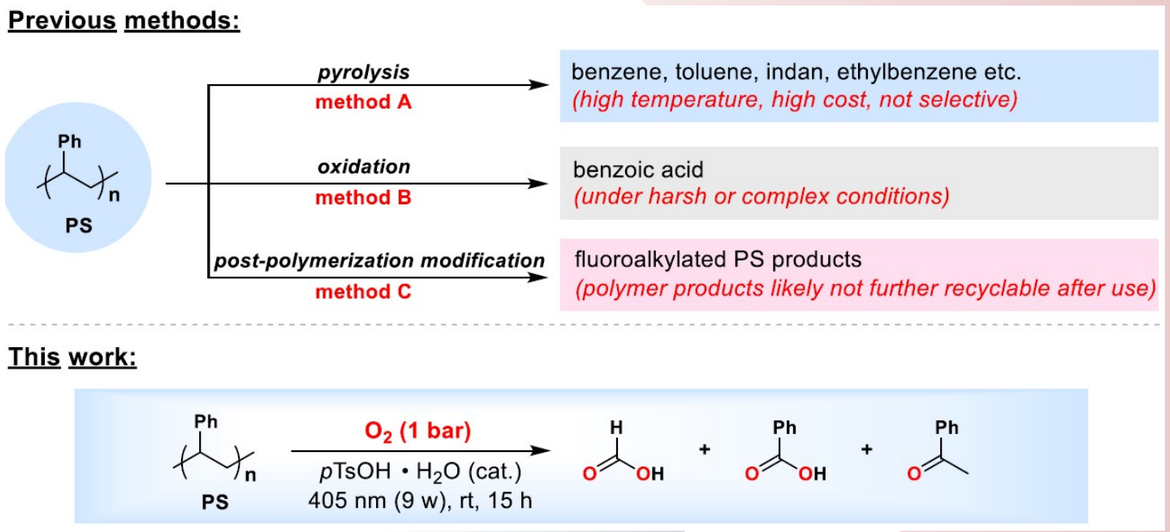
Our overall goal is to contribute to a more sustainable development by tackling some of the most challenging and exciting research problems that we face today, in particular in the application of Catalysis for green chemistry and energy. We are particularly interested in developing novel chemo- and biocatalysts and efficient routes to renewable chemicals from biomass, CO_2 utilisation, photocatalysis and the utilisation of heterogenous catalysts for energy-related reactions. We believe that some of these targets will require the development of new advanced materials and we collaborate with other colleagues in the development of such new materials such as nanostructured oxides, metal nanoparticles and porous polymers using high-throughput automated instruments whenever advantageous.

Highlight: Chemical recycling of polystyrene to valuable chemicals by aerobic digestion

Globally, 58% of discarded plastics end up in landfills or are incinerated. Mechanical recycling is preferable but those recycled plastics can only be used for downgraded applications. Hence chemical recycling—to create useful feedstock chemicals is highly attractive.

Polystyrene is one of the most important materials in the modern plastics industry, with tens of millions of tonnes being produced annually, amounting to 6% of the global plastic market share. However, existing chemical recycling routes have the disadvantages of high cost, lack of selectivity, or yield only highly stable fluoroalkylated products that cannot be recycled again.

Hence we focussed on new and alternative methods to chemically recycling polystyrene, notably direct oxidation using oxygen mediated via selective aerobic digestion. We found that triflic acid can catalyse selective oxidation of polystyrene under 1 atm of oxygen under irradiation from violet-blue light (405 nm). The isolable reaction products were formic acid, benzoic acid, and benzophenone. These are all valuable bulk chemicals having wider use in the chemicals industry. Moreover we demonstrated a process for flow degradation of polystyrene which provides support for its potential application on a wider scale.



Our new method for the chemical recycling of polystyrene has the advantages of being low cost, operates under mild conditions with a green oxidant, is highly selective and the products are all easily isolated and comprise useful bulk chemicals.

Thin film solar cell device development

Jon Major

Solar cells have the potential to generate power from a range of applications. Beyond the standard implementation as photovoltaic modules, solar cells can be integrated into buildings, vehicles, indoor devices or even used the basis for water splitting or CO_2 reduction. Each of these uses requires different considerations for the base property of the material and design of the cell structure. Our research focusses on the design, optimisation and device level physics of novel thin film solar cells, with particular focus on innovative processing techniques to improve efficiency and reduce cost.

Highlight: Multi-phase sputtered TiO_2-induced current-voltage distortion in Sb_2Se_3 solar cells

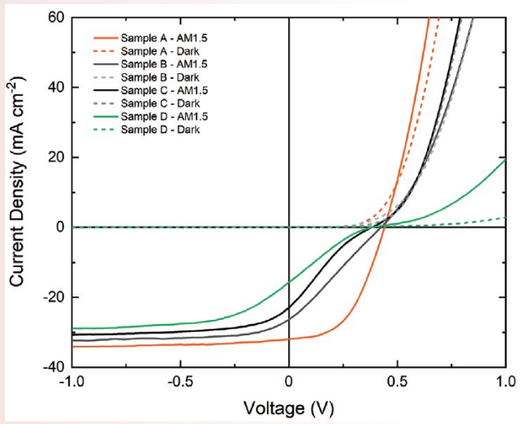
Antimony selenide (Sb_2Se_3) has rapidly achieved impressive results as a solar cell absorber layer, with the record performance currently standing at 10.6% PCE. Here we report work on changes to the device design – and the importance of materials control – which give insight into how to increase this performance to commercially viable levels.

The most popular partner layer for Sb_2Se_3 is n-CdS. However, this suffers from having a relatively low bandgap (blocking some of the light) and intermixes with Sb_2Se_3 at the hetero-interface. On the other hand, TiO_2 is an attractive alternative since it has a wide bandgap and does not intermix with the Sb_2Se_3. Despite this, it is less-widely researched, and there are also some reports of irreproducibility with it. Nevertheless, our own initial work with TiO_2 spin coated from titanium iso-propoxide gave reliable results and solar cell efficiencies around 7%. We therefore decided to explore sputter coating for TiO_2 on the basis that it is directly compatible with in-line industrial processing methodologies. Initial trials with sputtered TiO_2 (from a ceramic target in argon) gave inconsistent results, as shown in the figure: While some devices had ideal exponential current-voltage curves (orange curve), others had s-shapes (black curve) which indicate the presence of an unwanted electrical barrier which reduces efficiency. Moreover, both types of curve could result from using TiO_2 films sputtered under nominally identical conditions.

Our first line of investigation was to explore whether one of the two possible phases of TiO_2 (rutile or anatase) gave higher performance than the other. In the event, the materials situation was much more complex, with the surface and bulk phase compositions being different, and with there being mixed phases having differing degrees of crystallinity too. We evaluated the bulk phase composition using a combination of x-ray diffraction and Raman spectroscopy. It was found that the bulk comprised a mixture of disordered anatase and rutile phases. The surface composition was evaluated by taking advantage of the distinctly different valence band shapes of anatase and rutile in a combined XPS and DFT study. It was found that the surface comprised the rutile phase which was present as a coating on top of the mixed anatase/rutile phase bulk material.

Correlation of the phase character of the films with solar cell performance was then investigated by comparing devices made on anatase, rutile and mixed phase TiO_2 films (spin coating gives rutile, and control of the sputtering conditions was found to give either rutile or the mixed phase). It was found that both the anatase and rutile films gave good quality current-voltage curves while the s-shaped curves only arose for the mixed-phase samples. Ultimately, we found that reactive sputtering of TiO_2 with oxygen gave the single-phase films required for high photovoltaic performance.

CH Don et al, Multi-phase sputtered TiO_2-induced current–voltage distortion in Sb_2Se_3 solar cells, Adv. Mater. Interfaces 2023, 10, 2300238



Current-voltage curves for solar cells having exponential character (orange) and deleterious s-shaped character (black).

Semiconductor devices for renewable energy

Asim Mumtaz

I am a member of the solar energy materials and solar cells group. My interests are in semiconductor devices, particularly solar cells and power semiconductor devices. In terms of solar cells, I have been involved in projects relating to tandem solar cells, which have included crystalline III-V semiconductors and perovskite solar cells. I also have an interest in modelling and fabrication of high-performance power devices employing wide band gap semiconductors such as silicon carbide and gallium nitride. Such power devices are essential for energy conversion applications — for example inverters used in renewable energy systems. I have also undertaken a project on electrodes for lithium ion cells driving towards improved energy capacity and durability. More recently I have worked on devices for devices for hydrogen evolution, as explored further in the highlight report below

Highlight: Interface-engineered CdTe photocathode for photoelectrochemical hydrogen generation

Photoelectrochemical hydrogen generation from water splitting has clear attraction for generating a clean fuel with no damage to the environment. The key part of a PEC water splitting cell is the photoelectrode, which must absorb sunlight efficiently to generate electron-hole pairs while being resistant to corrosion and supporting a catalyst. This is a challenging set of requirements – and moreover, the catalyst is most often noble metal platinum, which increases the cost.

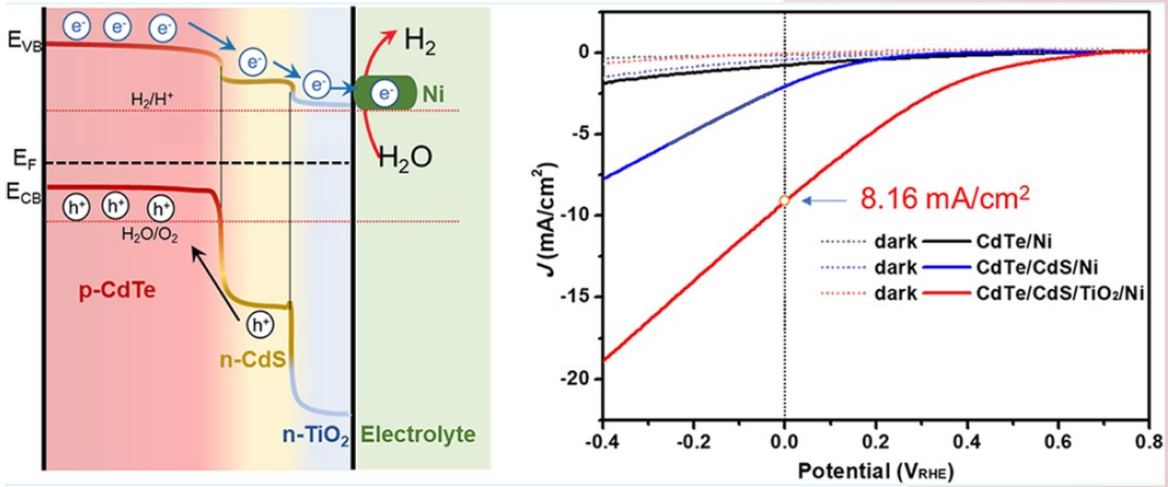
In this work we explored different heterostructure combinations with CdTe and also nickel as a low-cost catalyst. The full device structure is shown in the left-hand panel below. Each layer has its particular function: CdTe is a strong solar absorber making optimal use of the solar spectrum to generate electron-hole pairs. The n-type CdS forms a heterostructure with it to enhance charge extraction. Both are protected against corrosion by the TiO_2 overlayer. Finally, vacuum-evaporated Ni nanoparticles provide the catalytic activity for the actual water splitting. The current voltage response of the heterostructures (right-hand panel) shows that the combination of the whole set achieves the highest performance.

This work provides new insights for designing noble-metal free photocathodes for solar hydrogen production.

J-X Jian et al, Interface-engineered Ni-coated CdTe heterojunction photocathode for enhanced photochemical hydrogen evolution. ACS Appl. Mater. Interfaces 2023, 15, 21057-21065

News: Asim moves to York University

Asim has recently moved to York where he has taken up a Senior Lectureship in the School of Physics, Engineering and Technology. He joined us in 2017 as an academic and Deputy Director of the EPSRC Centre for Doctoral Training in New and Sustainable Photovoltaics. Always popular with students and staff alike, Asim quickly established a reputation for making things run smoothly. He left a particular legacy of by bringing new industrial connections to the CDT and used his extensive network of contacts to bring new ideas into the CDT's events. All the SIRE staff and former CDT students warmly congratulate Asim on his new position and wish him every success.



Left: the CdTe heterostructure photoelectrode. Right: the photoelectric performance was maximised by the three layers' enhancing charge extraction, corrosion resistance and catalytic activity.

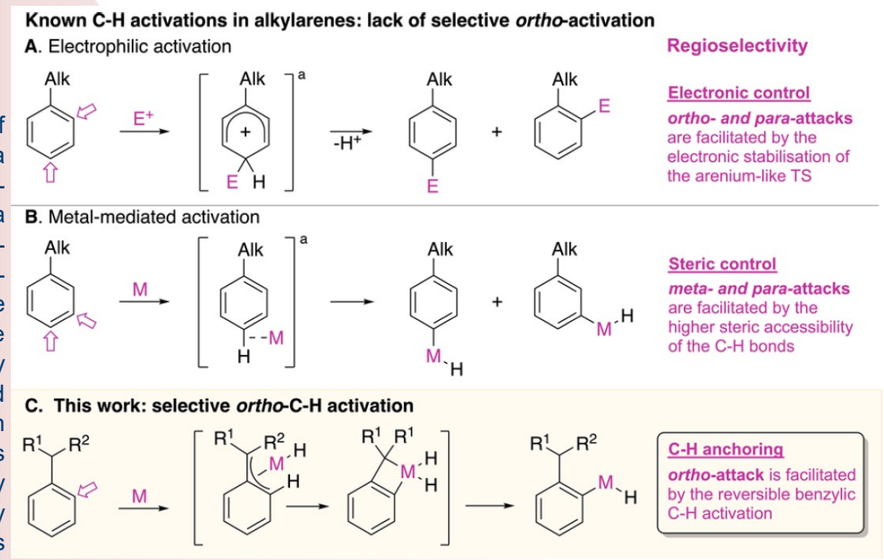
Homogeneous catalysis and organometallic chemistry

Alexey G. Sergeev

We focus on improving existing catalytic reactions and discovering new ones for the synthesis of value-added chemicals and fuels from hydrocarbon natural resources at mild temperatures and with minimum side products. In particular, we investigate the key steps underpinning these reactions, that is, activation of the most abundant, yet relatively inert, C-H, C-C and C-O bonds by well-defined soluble metal complexes. The goal is to identify key principles enabling the high selectivity and activity in these fundamental steps and translate these findings into synthetically useful catalytic reactions for making functionalised molecules with a broad range of applications. To achieve this goal, we study both mechanisms and synthetic applications of these processes using a combination of experimental methods (NMR, GC, GC-MS, HR-MS and XRD), and theoretical computations (DFT) in collaboration with our colleagues from University of Liverpool and University College of Dublin.

Highlight: Selective *ortho*-C-H activation in arenes

Site-selective activation of aromatic C−H bonds is a challenging step that is important for the synthesis of a range of functionalized aromatic molecules, from pharmaceuticals to polymers. The established way to achieve the required regiospecificity is to use functionalised groups to direct the reaction to *ortho*-, *meta*- or *para*- sites as shown in figure A (by electronic control) and B (by steric control). However, it is a much more appealing prospect to activate non-functionalised arenes e.g. with alkane substituents, particularly as they are readily available from petrochemical feedstocks. To date this has been challenging since alkanes have limited site-directing capacity with ortho- isomers being particularly difficult to synthesize in high yield.



C-H activations in alkylarenes. (A) and (B) Known methods (only para-intermediates shown). (C) Our new approach - selective iridium-mediated ortho-C-H activation.

In this work we demonstrated high regiospecific activation of *ortho*-C-H bonds in alkylarenes using iridium complexes, Cp*Ir(η^4-alkylarene), which bear a non-polar, 'spring-loaded' alkylarene ligand with enhanced reactivity. We also explored how the selectivity of *ortho*-C-H oxidative addition depends on the identity of the alkyl substituent on the alkyl ring. The observed order of *ortho*- regiospecificity was *sec*-alkyl > *n*-alkyl >> methyl, i.e. opposite to that expected for classical electrophilic substitution.

Explanation of this demanded a careful determination of the reaction mechanism by employing a model deuterated arene (*p*-diisopropylbenzene) to allow NMR studies. This was coupled with a DFT evaluation of the possible intermediates. It was found that the *ortho*-C-H activation is kinetically preferred over the *meta*- and *para*-C-H activation because of the specific directing effect of an alkyl group (Fig. C .

Translation of this stoichiometric reactivity into catalytic *ortho*-C−H functionalizations may open new avenues for the selective synthesis of value-added chemicals from unactivated aromatic hydrocarbons.

APY Chan et al, Selective ortho-CH activation in arenes without functional groups, J. Am. Chem. Soc. 2022, 144, 11564-11568

Active interfaces and coatings

Dmitry Shchukin

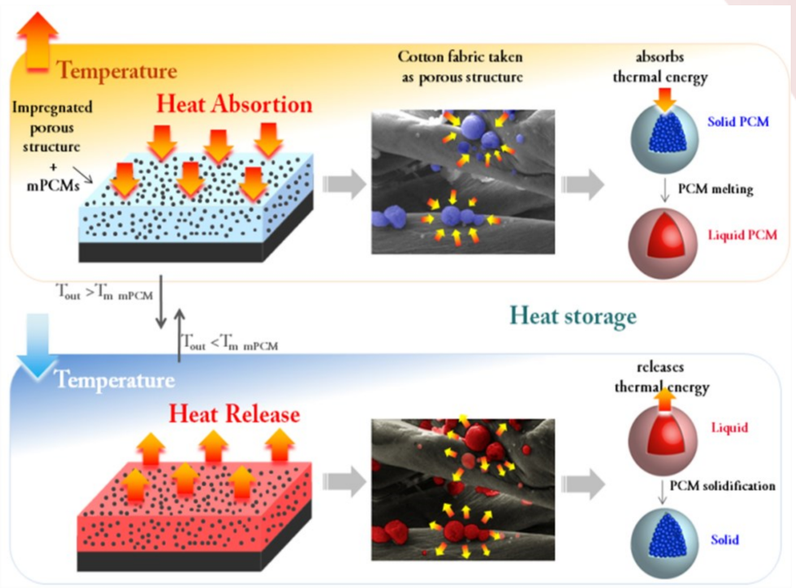
The group is strong in the encapsulation of various active materials into the polymer or mesoporous nanocapsules with multifunctional shell, which is responsive to both local (changes of pH, ionic strength) and external (light, magnetic field, temperature) impacts, controlling the release/uptake of the active species. The group is focused on the encapsulation of phase change materials (PCMs) for thermal energy storage with application in thermo-regulating coatings, packages and textiles. Another direction of the Shchukin's group is the development of new synthetic approaches for complex nanomaterials (two and three phase mixed oxides, hydroxides, metal nanoalloys) either in confined nanocapsule volume or at cavitation interface applying ultrasonic treatment as a tool for input of "green" energy into the reaction system. The group has around 70 publications in this area.

Highlight: Self-regulating thermo-textiles

Nanoencapsulation is one of the most promising solutions to increase the efficiency of both organic and inorganic phase change materials (PCMs). It promotes high specific surface area, prevents loss of encapsulated material, controls heat exchange across the capsule shell and initiates congruent melting/crystallisation due to the small core size. Energy nanocapsules can find new applications in thermal energy storage, such as cascaded multi-temperature systems, additives to thermal paints or other building materials, packaging and textiles.

We loaded microcapsules with n-docosane with activity in the range of 36-45°C - and impregnated cotton fabrics with them. Just 8 wt% of PCM provided 11°C of temperature buffering during heating. On cooling, they gave 6°C temperature increase for over 100 on/off cycles of heating. Ageing the fabrics for 1500 days at room temperature *increased* the effect: The temperature buffering during the heating cycle increased to 14°C and the temperature increase effect reached 9°C during cooling. Both effects remained stable for > 100 heating/cooling cycles.

Impregnated structures showed thermal stability up to 190°C and high heat capacity. The observed heat capacity for fabrics impregnated with 8 wt% of mPCMs was 6.3 $J.g^{-1}$ of latent heat which provided 11°C of temperature buffering during heating as compared to non-impregnated fabrics, while the one with 34 wt% of mPCMs had 26.3 $J.g^{-1}$ of latent heat and exhibited 12°C temperature buffering. FTIR spectra showed no change in the chemical morphology after dynamic heat storage measurements confirming their structural stability.



Scheme illustrating thermal energy uptake and release process for porous textile structures impregnated with microcapsules loaded with phase change materials when the environment temperature increases and drops over the phase change temperature of the encapsulated PCM.

Widespread use of PCMs in energy storage has the capacity for high impact in areas such as reduction in energy demand, reduced waste heat and improved efficiency for concentrated solar power plants. New methodology for capsule production needs to be developed further using high-throughput manufacturing methods, such as complex emulsions, layer-by-layer assembly, microfluidics and industrial-scale sonication. These methods will lead to simple fabrication of PCM nanocapsules, reducing costs and increasing viability.

Those working on the project were postdocs Drs Michael Graham and Paula Felix de Castro, supported by an ERC grant.

Semiconductor physics for renewable energy devices

Tim Veal

The Veal group works on semiconductor physics with the aim of improving renewable energy materials and devices, including solar cells, themoelectrics, photocatalytic devices and transparent conductors.

In particular, Veal has an interest in near-surface charge accumulation effects that introduce band bending that can have a significant influence of electronic device performance. These studies have extended to include nitrides, antinomides, oxides and chalcogenides, including the 2D molybdenum di-chalocogenides.

Veal collaborates extensively with both materials experimentalists and density functional theorists for the investigation of new and emerging materials, including the understanding of doping and electronic compensation effects in semiconductors. This approach has also been used to propose and demonstrate new doping routes in tin oxide, which is an industrially important conducting transparent oxide used in commercial photovoltaics.

Highlight: GeSe photovoltaics—doping, interfacial layers and devices

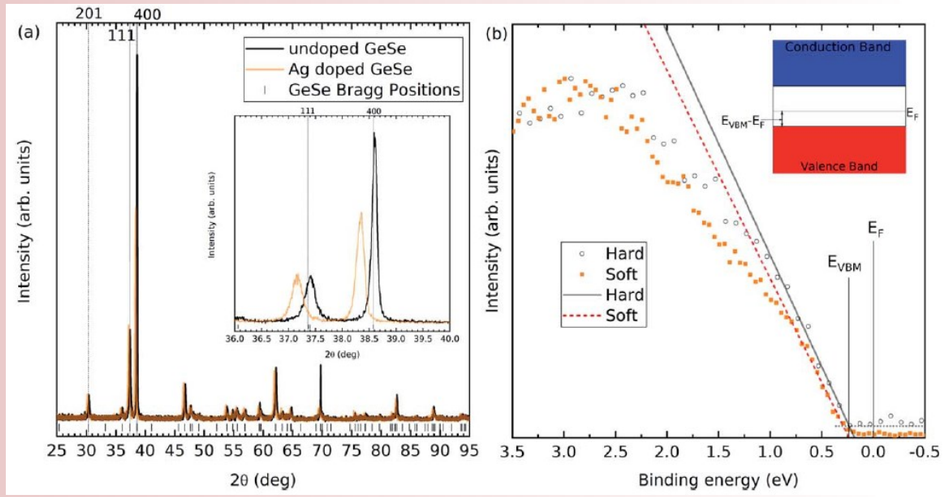
Germanium selenide (GeSe) is a promising photovoltaic (PV) absorber material due to its optical properties1 and its stereochemically-active Ge 4s lone pairs. A direct band gap of 1.30 eV and absorption coefficient $>10^4$ cm^{-1} suggest a high theoretical efficiency from the detailed balance limit.

One of the reasons methylammonium lead iodide (MAPI) has seen such success is linked to the Pb $6s^2$ lone pairs, which are thought to play a role in some of its desirable PV properties. Having antibonding states in the VBM should lead to shallow states, the formation of electrically passive-grain boundaries, and a strong defect tolerance. The cation s-orbitals also result in band edges with greater dispersion, leading to reduced carrier effective mass and increased carrier mobility, which are desirable for PV applications.

Due to these properties, GeSe is under investigation as an absorber material in PV devices. Despite reports of the effect of varying the device design and partner layers, there has yet been no study of the effects of deliberate impurity doping of GeSe to give p-type conductivity for inclusion in a controlled p-n junction.

Therefore, this paper investigates two key areas for the development of GeSe as a PV material. Firstly, bulk crystalline Ag-doped GeSe source material was synthesized, with inductively coupled plasma optical emission spectroscopy (ICP-OES) confirming the incorporation of Ag, giving carrier concentrations up to ~2 x 10^{16} cm^{-1}. XRD confirmed the material to be single-phase, with a slight increase in lattice parameter. Variable energy hard X-ray photoelectron spectroscopy (HAXPES) measurement of the Fermi level position confirmed the material to be p-type, with slight downward surface band bending. Secondly device trials on the FTO/CdS/Sb_2Se_3/GeSe structure showed the Sb_2Se_3 layer to be beneficial. However, for these preliminary devices, doping the GeSe did not improve their efficiency and further development will be required to take advantage of the controlled doping.

MJ Smiles et al GeSe photovoltaics: doping, interfacial layer and devices, Faraday Discuss., 2022, 239, 250



Left: XRD of Ag-doped GeSe showing that there are no second phases, but a slight increase in lattice parameter.

Right: HAXPES measurement of the Fermi level position confirms the p-type character of GeSe:Ag

Single-Molecule electronic devices

Andrea Vezzoli

Andrea's group specialises in the synthesis of molecular wires, their fabrication into single-molecule junctions — electronic devices made by a molecule sandwiched between atomically sharp nanoelectrodes — and their characterisation. We are particularly interested in devices that show mechano/piezoresistivity — changes in charge-transport efficiency as the device is compressed and/or stretched — and single-molecule electroluminescence phenomena. An important avenue the group is exploring now is the use of plasmonically-active electrodes to study in detail light-matter interaction at the nanoscale, with the aim of improving efficiency and drive these devices into applications in quantum

Highlight: Mechanoresistive molecular junctions

The concept of a *single* molecule as active component in electronic devices has been around since the 1970s, but only recent advancements have made it an experimental reality. In the last 20 years, many devices mimicking traditional silicon electronics behaviour have been developed, with desirable properties such as transistors, diodes and resistors been replicated at immensely smaller length-scales.

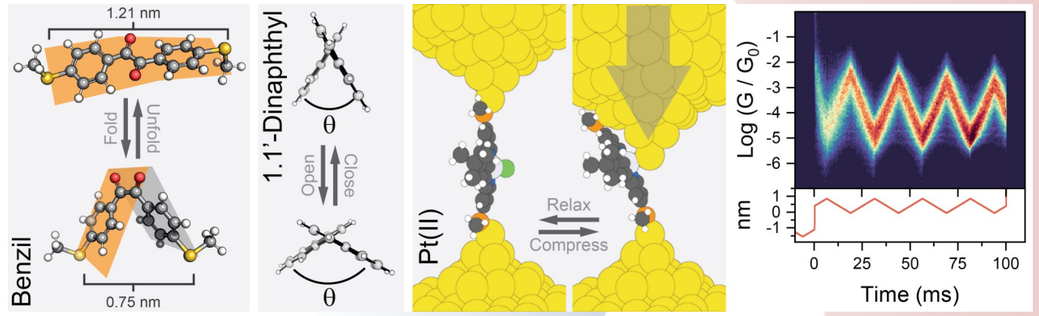
Another subset of single-molecule devices that have garnered significant attention are those displaying mechano– or piezoresistive behaviour. These devices are subject to changes in their charge transport efficiency upon mechanical stimulus, the latter being generally compression/stretching of the molecular wire obtained by moving the electrodes closer together or farther apart. They have been proposed in the literature as single-molecule potentiometers or, more accurately as they are two-terminal devices, single-molecule rheostats, but there is great promise for their applications as nanoelectromechanical systems (NEMS) and as analytical tools to probe metal–molecule interfaces.

In research funded by EPSRC and by the Royal Society, we have consistently pushed the envelope for sensitivity and reliability of such devices. Along with researchers Chuanli Wu, Amit Sil, Chiara Spano, and Xiaohang Qiao, we have studied mechanoresistive phenomena arising in the core of the molecular wire, exploiting conformational flexibility of structural moieties such as benzil or 1,1'-dinaphthyl, or by introducing organometallic fragment that interact with the electrode through intermetallic bonds — the structures of interest are reported below.

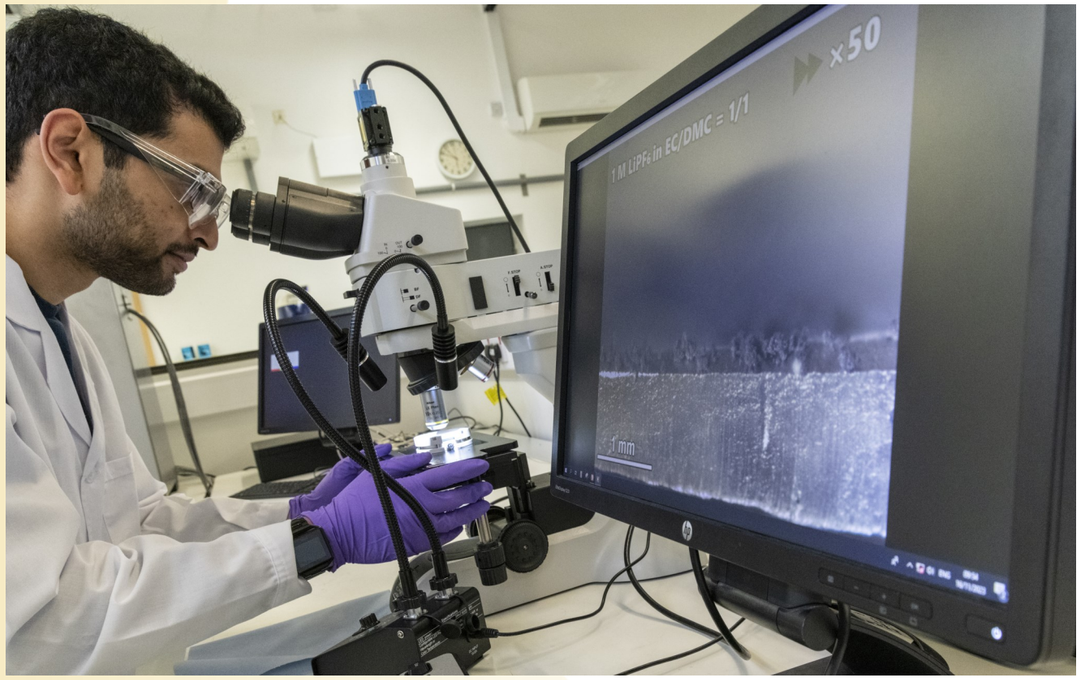
In the case of benzil derivatives, mechanoresistivity is imparted by the switch from a thermodynamically stable but poorly conductive "*anti*" structure to a *"syn"* conformation that, while being higher in energy and thermodynamically unstable grants higher transport.

In the case of 1,1'-dinaphthyl derivatives, on the other hand, we exploited quantum interference phenomena unique to the nanoscale world. As the dinaphthyl core is compressed, charge reorganisation in the molecules introduces interference features, modulating charge transport with exquisite magnitude.

As last example, we have developed the first organometallic mechanoresistive device by exploiting the electronic structure of a Pt(II) cyclometalated complex. The Pt(II) centre lies in a square planar configuration, leaving the empty *d* orbitals sterically free. Compression of the devices bring the metallic electrode in contact with the Pt(II) centre, and the resulting intermetallic bond generates a high-conductance pathway.



Structures and mechanism of molecular piezoresistive devices, along with example modulation curve for the 1,1'-dinaphthyl derivative. Large conductance modulation exceeding 2 orders of magnitude can be achieved with just 0.9 nm compression/relaxation cycles.



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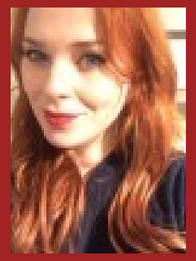
PhD Graduates in 2022/23



Natalie Bavis
Utilising atomic layer deposition (ALD) to develop efficient hematite-based photoanodes for photocatalytic water- splitting
Supervisor: Alex Cowan

Jack Beane
Structural studies of the solid-liquid interface reactions a at the noble electrode surface
Supervisor: Yvonne Grunder

Zhenyu Chen
Rhodium catalysed transfer hydrogenation and transamination
Supervisor: Alexey Sergeev

Nicole Fleck
The role of surfaces, interfaces and oxides in antimony selenide photovoltaics
Supervisors: Jon Major, Frank Jaeckel

Benjamin Greeves
Self-assembled perylene bisimides for water splitting devices
Supervisor: Alex Cowan

Adrian Hannah
Synthesis and characterization of thin film coatings for accelerators
Supervisor: Vin Dhanak

Scott Christy
The synthesis of novel bio-derived cyclic organic carbonates via the alcoholysis of urea with sugar alcohols
Supervisor: Tony Lopez-Sanchez

Romy Dop
Sulfur polymers as antibacterial particles and surfaces
Supervisor: Tom Hasell

Benjamin Duff
Towards understanding of the local structure and li- ion dynamics in solid electrolyte candidates using solid-state NMR
Supervisor: Frederic Blanc

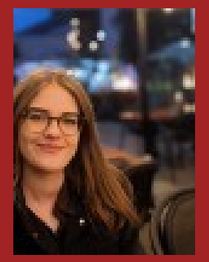
Joseph Horne
Plasmonic substrates and their applications in photocatalytic water splitting and molecular electronics
Supervisor: Frank Jaeckel

Leanne Jones
X-ray photoemission spectroscopy of the Mo, Re and W dichalcogenides
Supervisors: Vin Dhanak, Tim Veal

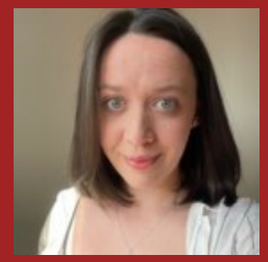
Jacob Leaver
Impacts of Se alloying and diffusion on optimal fabrication procedures for $CdSe_xTe_{1-x}$ solar cells
Supervisors: Jon Major, Ken Durose

Holly Edwards
Synthesis and characterisation of kesterite thin films and single crystals for photovoltaics
Supervisors: Vin Dhanak, Jon Major

Julia Fernandez Vidal
Shining light on interfacial electrochemical reactions
Supervisor: Laurence Hardwick



Monika Lisauskaite
Target deconvolution in anti-wolbachia and antimalarial drug development
Supervisor: Frederic Blanc



Sarah Livesley
Electrophilic activation of 1-1-1 propellane towards the synthesis of substituted bicyclo 1-1-1 pentanes
Supervisor: Alex Cowan

PhD Graduates cont….

Yi-Ting Lu
Oxygen electrochemistry in divalent metal-air batteries
Supervisors: Laurence Hardwick and Chi-Chang Hu

Qurat Nadeem
Design and construction of metal oxides based hybrid nanocoatings for remediation of aquatic pollutants
Supervisor: Dmitry Shchukin

Omer Omar
High-throughput virtual screening of existing organic chromophores for materials discovery
Supervisor: Alexey Sergeev

Abbie Scholes
Synthesis, solution and solid state behaviour of substituted iso-trianglimines
Supervisor: Dmitry Shchukin

James Smith
The investigation of the PCMs nucleation mechanism in both bulk and confined environments
Supervisor: Dmitry Shchukin

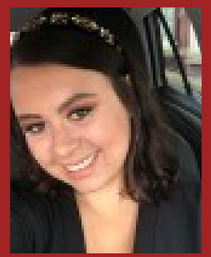
Luke Thomas
n-type CdTe for photovoltaic devices
Supervisors: Ken Durose, Jon Major

Dora García Osorio
Solar fuels production by photo-electrochemical CO_2 reduction
Supervisor: Alex Cowan

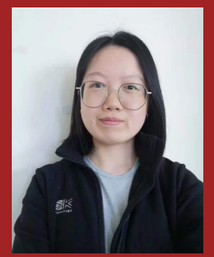
Andrea Pugliese
Molecular insights into pharmaceutical amorphous solid state nuclear magnetic resonance spectroscopy
Supervisor: Frederic Blanc

Kieran Routledge
Structurally and magnetically complex materials: a magneto-caloric, a multiferroic skyrmion host and a ferrimagnetic semiconductor
Supervisor: Jon Alaria

Katherine Tustain
Inorganic and hybrid analogues of Kagomé and triangular magnets
Supervisor: Jon Alaria



Rebekah Upton
Highly water repellent polymer-nanoparticle composite coatings: moving towards real world applications
Supervisor: Tom Hasell



Peiyao Yan
Mechanical properties and functional applications of high-sulfur polymers prepared by inverse vulcanization
Supervisor: Tom Hasell

Khezar Saeed
Mechanistic studies of solar fuel generation at electrode surfaces
Supervisors: Alex Cowan, Laurence Hardwick

Arne Sandschulte
Scale and bandwidth extension of power converter-based impedance spectroscopy
Supervisor: Laurence Hardwick

Haofan Yang
Organic nanoparticles for photocatalytic hydrogen evolution
Supervisor: Tom Hasell

Bowen Zhang
Synthesis and applications of high-sulfur polymers
Supervisor: Tom Hasell

Hongda Zhou
Integrated adaptive systems based on stimuli-responsive capsules
Supervisor: Dmitry Shchukin

Research Grants held in 2022 and 2023

A total of > £30m is currently held by SIRE investigators. New grants won in 2022/23 are highlighted with an asterisk.*

Australian Research Council

T Hasell Unusual trisulfide chemistry*	£232,668

Engineering & Physical Sciences Research Council

J Major, **K Durose** & **T Veal** Bandgap engineering for optimal antimony chalcogenide solar cells*	£700,973
T McDonald & **D Shchukin** Active mapping of biological substrates for crop care and personal care applications	£45,924
T Hasell Bridging the TRL gap to enable commercialisation of sorbent for mercury capture and precious metal recovery	£39,983
D Shchukin Enzymatic activity improvement using controlled deformation dynamic mixing technology*	£30,000
A Cowan Sum-frequency generation spectroscopy for studying coating chemistries in the glass industry*	£9,821
J Xiao & **J Lopez-Sanchez** Iron-catalysed oxygenation with O_2	£349,348
M Rosseinsky & **J Alaria** Chemical control of function beyond the unit cell for new electroceramic materials	£928,091
F Blanc Connect NMR UK: A national NMR network for the physical and life sciences	£382,000
F Blanc The UK high-field solid-state NMR national research facility	£2,650,000
A Cooper & **A Cowan** Autonomous mobile robot chemists	£902,085
A Cowan REDEEM-electrocat: Rethinking electrode design – emergent electronic and magnetic effects in electrocatalysis	£127,498
A Vezzoli Quantum-enhanced molecular piezoresistivity	£509,841
M Rosseinsky & **J Alaria** Digital navigation of chemical space for function	£8,699,373
A Cowan Zero-Chem: Zero gap bipolar membrane electrolyser for CO_2 reduction to chemicals & fuels	£308,419
M Rosseinsky & **A Cowan** Water dissociation interfaces for high current density bipolar membrane electrolysers*	£312,276
F Blanc NMR at 1.2 GHz: A world-leading UK facility to deliver advances in biology, chemistry, and materials science*	£17,000,000
A Cowan The Solar Chemicals Network*	£277,529
P Weightman & **V Dhanak** FLUENCE: Felix light for the UK: exploiting novel characteristics and expertise	£507,705
K Durose & **J Major** New designs for thin film solar cells	£509,722
W Van Der Hoek, I Sandall, **F Jaekel**, L O'Brien & **A Vezzoli** EPSRC core equipment award 2020	£594,430
A Mumtaz 2D materials for photovoltaic cells*	£3,014
C A Lucas & **Y Grunder** Xmas: The UK materials science facility at the ESRF	£3,515,607
M Rosseinsky and J Alaria Correlated metals as transparent conductive coating	£24,877
F Blanc UK Dynamic nuclear polarisation magic angle spinning NMR facility *	£4,600,000
J Major Capacitance spectroscopy led process innovations to improve Voc in CdTe thin film solar cells	£810,102
C A Lucas, **Y Grunder** & T Hase XMaS Capital equipment upgrade*	£434,678
D Shchukin Enzymatic activity improvement using controlled deformation dynamic mixing technology	£30,000
D Shchukin Active mapping of biological substrates for crop care and personal care applications	£49,674

European Commission

A Cowan SEAFUEL*	£269,486
L Hardwick BIGMAP (Battery Interface Genome – Materials Acceleration Platform) H 2020	£554,000

Henry Royce Institute

A Cowan & **L Hardwick** Materials for end-to-end hydrogen application	£326,026

Industrial and Charitable

Bristol-Myers Squibb Pharmaceuticals Ltd, **F Blanc** DTP Studentship - Industry top-up	£80,000
Croda, T McDonald & **D Shchukin** Active mapping of biological substrates for crop care and personal care applications	£10,000
IDRIC, **A Cowan** CapCon - conversion of captured carbon dioxide*	£98,321
Johnson Matthey PLC, **F Blanc** Deciphering reaction mechanism(s) of biomass upgrading over zeolitic materials via advanced NMR*	£135,000
Johnson Matthey PLC, **L Hardwick** Using SHINERS technology to solve challenging interfacial problems in catalytic and battery applications	£58,860
Kidney Research Northwest, D Neill & **T Hazell** Use of inverse vulcanized sulfur polymers for prevention of catheter-associated urinary tract infections*	£197,996
NSG (UK) Ltd, co-funded by EPSRC M Rosseinsky & **J Alaria** Correlated metal oxides on glass as transparent conductors *	£37,281
Impact acceleration account (with NSG), M Rosseinsky & **J Alaria**	£94,357
Pilkington Group Limited (UK), **T Veal**, **V Dhanak** & **J Major** Studentship - industry top-up	£10,000
SEMEFAB, **A Mumtaz** Novel devices using wide band gap semiconductors	£5,000
Uberbinder Limited, **T Hasell** Contract research for Uberbinder*	£59,431
Lubrizol, **L Hardwick** Ionic Liquid and redox mediator electrolyte blends for long-life lithium -air batteries	£90,000

The Faraday Institution

L Hardwick CATMAT: Next generation lithium-ion cathode materials*	£590,101
N Browning & **A Cowan** Quantitative imaging of multi-scale dynamic phenomena at electrochemical interfaces	£410,078

Higher Education Innovation Fund

D Shchukin Thermo-regulating magnetic covers for autonomic zero-CO_2 heating of domestic and industrial areas	£31,486

Innovate UK

D Shchukin Thermo-regulating magnetic coverings for storing and releasing lost heat	£287,725

Leverhulme Trust

A Cowan Gel-based photoelectrodes for clean fuels	£125,987
F Blanc Dynamic nuclear polarisation from paramagnetic metal ions	£263,000
A Sergeev SELAROMA: Selective C-H functionalisations in aromatic hydrocarbons*	£362,854

Natural Environment Research Council

A Lyons, **T Hazell** & **F Blanc** Post-consumer resin - understanding the quality-performance linkage for packaging	£897,765

Research England

L Hardwick PRR Fund - Cell level demonstration of MnO_2/FeO_x asymmetric electrochemical graphene based capacitor	£26,235
D Shchukin PRR Fund - Thermo-regulating magnetic covers for autonomic zero-CO_2 heating of domestic and industrial areas.	£31,486
M Rosseinsky & **J Alaria** New transparent conductors* (co-funded by NSG Ltd	£67,474
A Cowan Green Hydrogen electrode formulation and catalyst discovery*	£29,786
A Cowan Sustainable ethylene production: a joint UoL – INEOS pilot study of decarbonisation technology*	£40,350
L Hardwick Automated assembly of 3-electrode lithium-ion pouch cells*	£15,036

Royal Academy of Engineering

A Mumtaz Novel devices using wide band gap semiconductors	£38,481

Royal Society

T Hasell Carbonised sulfur polymers for gold extraction	£92,087
D Shchukin Thermal management of perovskite solar cells based on layer-by-layer assembled liquid metal nanoparticles	£11,940
D Shchukin Thermal management of perovskite solar cells based on layer-by-layer assembled liquid metal nanoparticles	£11,940
A Vezzoli Single-entity electronics and photonics of chemically wired nanocrystals	£1,149,367
T Hasell Sulfur polymers for optical and antimicrobial applications	£685,086
A Vezzoli Molecular engineering in quantum thermoelectrics	£16,800
Y Grunder Charge distribution at the electrochemical interface	£696,327
Y Grunder Elucidating the relationship of Interfacial charge distribution and structural behaviour and stability of bimetallic electro-catalysts	£38,821
J Alaria Advanced functional materials for waste heat harvesting and green computing a bridge between thermoelectricity and spin-electronics	£12,000
A Sergeev Selective ortho-functionalisation of alkylarenes without directing groups	£12,000

Royal Society of Chemistry

A Sergeev Selective ortho-functionalisation of alkylarenes without directing groups*	
F Blanc Advancing the understanding of disorder and dynamics in oxides using ^{17}O NMR*	£4,000

UK Research and Innovation

A Cowan NIC3E: National interdisciplinary centre for circular chemical economy	£853,759

Univ. Liverpool Faculty Impact Fund

D Shchukin Antibacterial magnetic covers for prevention of biofilm formation inside buildings	£12,200


Jon Alaria


Frédéric Blanc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Vin Dhanak

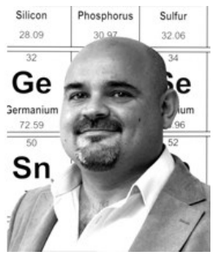

Ken Durose


Yvonne Grunder


Tom Hasell


Laurence Hardwick


Frank Jaeckel



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