



UNIVERSITY OF
LIVERPOOL

Stephenson Institute for
Renewable Energy

Stephenson Institute Annual Report 2015

LIFE CHANGING
World Shaping

The Stephenson Institute for Renewable Energy

Content

03 – Director's welcome

04 – News, events and activities

11 – Selected research projects

20 – Publications by SIRE members

22 – Research funding

23 – Staff directory

Director's welcome

As a specialist energy materials research institute, the Stephenson Institute for Renewable Energy (SIRE) focuses on the physics and chemistry that will transform the future of energy generation, storage, transmission and energy efficiency. During our lifetimes we can all expect to see major changes in the availability, price and supply of energy, and we believe as a scientific group that the best way to deal with that change is to create new approaches.

2015 has been an excellent year for SIRE's 13 academics, 20 postdocs and 60 postgraduate students and this annual report celebrates their successes. Firstly, congratulations are due to Frédéric Blanc who has won a Science and Technology Facilities Council (STFC) Early Career Award, and Dmitry Shchukin who has won a European Research Council Consolidator Grant. These prestigious awards both recognise the excellence of individuals in research and help provide an environment for them to flourish. Jon Major's work on solar cell processing was again in the spotlight this year when he and his colleagues won the Institution for Chemical Engineering Global Award for Energy – which is especially important since it recognises an interdisciplinary contribution. I am particularly pleased to congratulate SIRE postgraduates Arturas Adomkevicius, Tom Galloway, Annette Pressman and Tzu-Ho (Henry) Wu who have all won prizes for posters at major conferences – in Henry's case, two prizes!

The Institute's involvement in major programmes continues to be strong, with the EU-SIRBATT battery programme, the SUPERGEN SuperSolar Hub and the EPSRC Centre for Doctoral Training in New and Sustainable Photovoltaics all being successful and mature operations. You will

find more details within. Also our seminar programme this year has been excellent, and I thank the visitors and speakers for their insights and also the organisers, Yvonne Gründer and Gilberto Teobaldi.

This report also includes a snapshot of projects in what has been a terrific year for research in SIRE. It has been a particularly exciting time for magnetism, with there being two *Nature* and one *Science* paper among our total output of more than sixty papers. You will find more detail on the creation of magnetism at interfaces and multiferroics for memory storage in the articles by Jonathan Alaria and Gilberto Teobaldi (see pages 12 and 14). Our research stories are truly wide ranging, with activity on supercapacitors and ionic conductors; photocatalytic hydrogen generation; sustainable chemical feedstock; catalytic bond cleavage; capsules for energy-rich materials; novel materials and surface studies; optical design for hybrid perovskite solar cells – and of course the new results on magnetic effects.

SIRE's members do a lot more that we can put in this short brochure though. If you'd like to hear more or perhaps collaborate, please do get in touch. Thanks for looking at our annual report!



Ken Durose

**Professor Ken Durose,
Director, SIRE**

News, events and activities

Awards

Jon Major, Rob Treharne, Laurie Phillips and Ken Durose

ICHEME Global Award for Energy 2015 for their project 'Safer and cheaper solar cell processing'.

Congratulations to:

Dmitry Shchukin

For winning a European Research Council (ERC) Consolidator Grant.

Frédéric Blanc

For winning a Science & Technology Facilities Council (STFC) Early Career Award.

Arturas Adomkevicius

For winning 'Best Poster' at the International Society of Electrochemistry Symposium 5: Novel insights to Electrochemical Capacitors and the Taiwanese Electrochemistry Society 2015 with his poster 'Synthesis and Characterisation of Sodium ion Pre-intercalated Manganese Oxide for High Performance Asymmetric Supercapacitors'.

Tom Galloway

For winning the prize for the Best Poster at the STFC Early Career Researchers Conference: Surface Enhanced Raman Spectroscopy 2015 for his poster 'The Study of Oxygen Electrochemistry in Aqueous and Non-Aqueous Electrolytes'.

Tzu-Ho (Henry) Wu

For winning the Poster Award at the International Society of Electrochemistry Symposium 17: Novel in Situ in Operando Methods with his poster 'Cation Effect on Ni(OH)₂ Phase Transformation, and for winning the prize for the Best Poster at Electrochem NW 2015 for his poster 'In Situ Raman Microscopy Studies on Electrochemically Activated Manganese Oxide Pseudocapacitors'.

Annette Pressman

For winning Best Poster at the 11th Photovoltaic Science and Technology Conference April 2015 for her poster 'On the Mechanism of Chloride Activation of CdTe Solar Cells'.

Gilberto Teobaldi

For being appointed to an Invited Professorship at the Laboratory of Solid State Physics, Université Paris-Sud in Orsay, France in February 2016, and to an External Associate Professorship at the Beijing Computational Science Research Centre, Beijing, China from January 2016 to December 2018.

SIRE Seminar Series 2015

All staff in SIRE would like to extend their thanks to seminar speakers who have visited us in 2015.

Date	Name	Affiliation	Title
17.2.2015	Professor Henning Sirringhaus	Cavendish Laboratory, University of Cambridge	Charge and spin transport of high mobility conjugated polymers
21.4.2015	Professor Harry E Hoster	Department of Chemistry, Lancaster University	Electrocatalysis and Surface Science – lessons learned in model studies at single crystals
5.5.2015	Professor Karen Wilson	European Bioenergy Research Institute, Aston University	Designing heterogeneous catalysts for biorefining
15.10.2015	Dr Ning Liu	Department of Physics, University of Limerick	Manipulating the optical properties of semiconductor nanostructures for super resolution and integrated photonics applications
3.11. 2015	Dr Alex Chin	Cavendish Laboratory, University of Cambridge	Quantum mechanical effects in biological light harvesting and their potential use in future photovoltaic devices
8.12.2015	Dr Roberto Ferrero	Department of Electrical Engineering and Electronics, University of Liverpool	Challenges in battery and fuel cell diagnostics: From lab tests to electric vehicles (and other applications)

Our seminars are open to all and further details of the current programme may be found at: www.liverpool.ac.uk/renewable-energy/events/

Institution of Chemical Engineers Global Award for Energy Winners 2015

Jon Major, Rob Treharne, Laurie Phillips and Ken Durose

A team of physicists from SIRE have won the prestigious Institution of Chemical Engineers (IChemE) Global Award for Energy 2015 for their project 'Safer and cheaper solar cell processing'.

The method, published in *Nature* in 2014, replaces an expensive toxic chemical with a safe one, which turns out to be the principal ingredient of bath salts. It promises to make the manufacture of thin film chalcogenide solar cells cheaper by simplifying the process engineering – and attracted widespread media attention when it was published.

The team received the award at a high-profile ceremony held in Birmingham in November which attracted nominees from academia and industry from all over the world.

Dr Jon Major, lead author on the programme said: "We are pleased to win this award as it reflects the work in SIRE to enable new forms of power generation and it highlights the increasingly cross-disciplinary nature of our work. It is really special to have a paper in *Nature* and then have it recognised for its impact. For a physics based team, it's quite something to have won an award in chemical engineering and we're very pleased that the new process is seen important for real practice."



"We are pleased to win this award as it reflects the work in SIRE to enable new forms of power generation and it highlights the increasingly cross-disciplinary nature of our work."

University of Liverpool India fellowship programme 2014/15

V Dhanak

In 2014/15, in collaboration with Dr Vin Dhanak of SIRE, Professor Amit Chakrobarty from the National Institute of Technology Durgapur, India came to the University on a six month fellowship programme which was split into two parts, each part consisting of three months.

Professor Chakrobarty's first visit was spent measuring photoemission from various copper doped zinc oxide and sulphide materials related to photovoltaics of interest to SIRE generally. He also started collaborations with other members of SIRE, notably Dr Frank Jaekel and Dr Laurence Hardwick.

In between his visits the first international conference on 'Emerging Materials: Characterisation and Application (EMCA-2014)' was organised in Kolkata, India in which SIREs Director, Professor Ken Durose gave a plenary lecture.

On his second visit, data which had been taken previously was data analysed and manuscripts were written up for publication. One of the papers has now been published (J. Appl. Pol. Sci., 132 (2015) 42766) and another is being prepared.

This collaboration between SIRE and Professor Chakrobarty will continue through exchange and research grants through the Newton fund.



This collaboration between SIRE and Professor Chakrobarty will continue through exchange and research grants through the Newton fund.





SIRBATT Management, Work Package Leaders and EC Expert at the Mid-Term Review Meeting

SIRBATT: Stable Interfaces for Rechargeable Batteries

The SIRBATT (Stable Interfaces for Rechargeable Batteries) Project is coordinated by Dr Laurence Hardwick from the Department of Chemistry at the Stephenson Institute for Renewable Energy.

In June 2015 the European Commission's (EC) expert evaluator met with the Work Package Leaders for a mid-term review meeting in Liverpool. The meeting was considered to be extremely successful and as a result the EC have now presented their report on SIRBATT's progress.

This report considered that all work was on task and that "the success of

SIRBATT is expected to make a large impact". The project had progressed well and "was advancing the state-of-the-art in several key areas".

Project management at the University of Liverpool were praised for dissemination and the timely submission of quality reporting achieved through regular partner updates and strict monitoring of progress and deliverables. The EC stated that "the synergy between all partners is well established and the workflow is harmonised with excellent integrity"; the balance of knowledge between partners from academia and industry was particularly highlighted. Dr Gilberto Teobaldi,

from the Stephenson Institute, leads Work Package 3 on the modelling and simulation of the electrode interface and has recently published two papers relating to this work, with further papers under review.

The European Commission's report was discussed at the project's board meeting in Bilbao, Spain on 28 September 2015. During the meeting it was noted that the project had further strengthened; with several new papers accepted to quality scientific journals and made available through open access.

Current publications and full information on the project can be found at: www.sirbatt.eu.



EPSRC SUPERGEN 'Supersolar' Hub for Photovoltaics Research

Ken Durose

SUPERGEN is EPSRC's (Engineering and Physical Sciences Research Council) main framework for delivering energy research programmes in the UK. Introduced in 2003, SUPERGEN transformed the delivery of national research initiatives by providing the support for teaming, developing a critical mass and providing continuity of funding for nurturing talent and leadership in energy research. From 2011 onwards the emphasis was put on 'Hubs' that would create national networks of energy researchers, connecting a wide portfolio of research and additional funding to the centrally supported projects. Presently the six Hubs are Marine, H₂FC (hydrogen and fuel cells), SuperSolar, Bioenergy, Energy Storage and Wind.

The Durose research group has been a key part of the solar photovoltaics SUPERGEN programme since its outset in 2004, and is the only continuous member of the founding group. SuperSolar's core team comprises Bath, Cambridge, Liverpool, Loughborough, Oxford, Sheffield and Southampton universities.

SuperSolar's research programmes embrace a wide range of solar energy materials and solar cells projects, including new solar

absorber materials - where hybrid perovskites have been in the news (there is more detail under 'Selected research projects'), advanced transparent conductors, materials and device physics modelling and experimental studies of the limiting aspects of the performance of state of the art devices. There is industrial connectivity with, for example, the design of tandem PV devices and new processing methods for manufacturing- including both new chemical routes and physical interconnections in modules by means of one-side laser scribing.

SuperSolar also plays a large part in supporting the UK PV research community. Its network is free to join and gives members access to financial support for:

- Academic and industrial secondments (including to and from the UK)
- Support for postdocs to travel
- Funded student places at UK conferences and workshops.

The network is free to join and more information can be found at: www.connect.innovateuk.org/web/supersolar-hub



Hubs that would create national networks of energy researchers, connecting a wide portfolio of research and additional funding to the centrally supported projects.



SIRBATT: 'Understanding Lithium Battery Interfaces' workshop

On the 29 September 2015, more than 60 battery scientists attended SIRBATT's first workshop 'Understanding Lithium Battery Interfaces' in Bilbao, Spain.

Kristina Edström, from Uppsala University, gave the keynote talk on 'Interfaces and Interphases in Silicon Anodes for Li-ion batteries'. Five guest speakers included Ivan Lucas (UPMC University, Paris); Eric Berg (Paul Scherrer Institut, Switzerland) and Gunther Wittstock (Carl von Ossietzky University of Oldenburg, Germany). Two of the other three successful projects with SIRBATT's EC call were presented with Grietus Mulder (InfluENCE) and Lucile Quazaguel (BACCARA) giving an outline

and preliminary results from their work. The keynote speaker, Kristina Edström, also represented the Hi-C project.

Peter Hall from the University of Sheffield gave a talk entitled 'When interfaces go wrong: Challenges in the remote monitoring and grid connected LTO batteries'. SIRBATT work was well disseminated with talks from partners Universidade de Aveiro (Portugal), Università Degli Studi di Camerino (Italy), Karlsruher Institut fuer Technologie (Germany) and Centre National de la Recherche Scientifique (France).

Industry partners from the SIRBATT network presented their experience of energy storage

with talks from Allan Paterson (Johnson Matthey, UK) and Andres Gomez Navarro (Iberdrola, Spain).

A poster prize (sponsored by Johnson Matthey) was awarded to Christine Brinkmann from the Fraunhofer Institute for Silicate Research (Germany) for her poster 'Effect of Lithium ex situ passivation in Lithium-polymer symmetric cells'.

SIRE was well represented with Ivan Scivetti giving a talk on his work within the project and four posters on display from members of the Hardwick Group.



The EPSRC Centre for Doctoral Training in New and Sustainable Photovoltaics (CDT-PV)

R Treharne

Following its very successful first year the Centre for Doctoral Training in New and Sustainable PV (CDT-PV) has continued with its high quality doctoral training curriculum that embraces physics, chemistry, engineering and electronics. The taught part of the PhD programme provides specific training in thin-film deposition, optics and photonics, polymer synthesis and processing of advanced materials, device characterisation, computational materials science and systems design, optimisation and reliability.

In November 2015, the Stephenson Institute for Renewable Energy hosted the annual induction event for CDT-PVs second cohort of students. It was an excellent opportunity for a new cohort of 12 doctoral students to interact with the SIRE academic and student teams and to experience at, a very early stage of their academic careers, the high level of research activity and capability that exists within SIRE. A significant contribution to the CDT-PV training curriculum was made by Professor Ken Durose, Dr Jon Major, Dr Tim Veal, Dr Vin Dhanak and Dr Rob Treharne who delivered a series of lectures, workshops and lab demonstrations to the

new cohort over a two week period.

Beyond SIRE, additional training is being delivered by over 20 highly qualified supervisors from six internationally leading PV groups across the UK that collectively cut across the thin-film, wafer, dye, perovskite, OPV and systems technologies within the field. Full use of each group's research infrastructures provide students with access to an extensive range of highly sophisticated, and in some cases, unique equipment and resources. Students will retain access to many of these resources beyond their training year and the second years are now primed to work collaboratively with their cohort of peers for the remainder of their CDT-PV projects. The project selection mechanism instigated by CDT-PV has ensured that the main PhD projects investigated by our students are truly cutting edge research problems that will undoubtedly generate work of high impact internationally.

In addition to training on fundamental science and practical techniques related directly to their technical research projects, the students have also completed training that has developed a wider understanding of renewables (including UK energy policy), business skills and scientific entrepreneurship. The regular focus on PV research within the context of these additional aspects has fuelled student enthusiasm for their own research initiatives and has instilled in them the need for innovation-driven growth and leadership to secure the future expansion and success of their field.

The centre has successfully instigated a cohort based training model. A key success of this has been the high level of 'student to student' interactions and the highly constructive feedback received from the students concerning their training experiences. As a collective, students frequently perform an analysis of their development needs throughout their first year training. This is used by CDT-PV coordinators to make changes and incorporate additional resources for training 'on-the-fly' throughout the training. As a result the CDT-PV curriculum has been optimised ahead of its delivery to our second cohort. The effectiveness of the cohort model has been further



demonstrated with the induction of our second of CDT-PV students by the first cohort who presented their collective research and training experiences at our showcase event at Liverpool in November 2015.

Our first cohort has, to date, participated in strong end-user engagement with several of industry partners, including Pilkington NSG, Ossilla and Oxford PV, who have provided contributions to workshops and experimental skills training throughout the year. The centre is now focused on increasing industry participation further and securing relevant work placements for existing studentships and direct financial contributions to upcoming projects from our existing and additional industry partners.

For further information visit: www.cdt-pv.org



Microscopy and analysis training



CDT researcher Silvia Mariotti



Selected research projects

Electronic characterization of MgZnO thin film transistors and TCOs

V R Dhanak

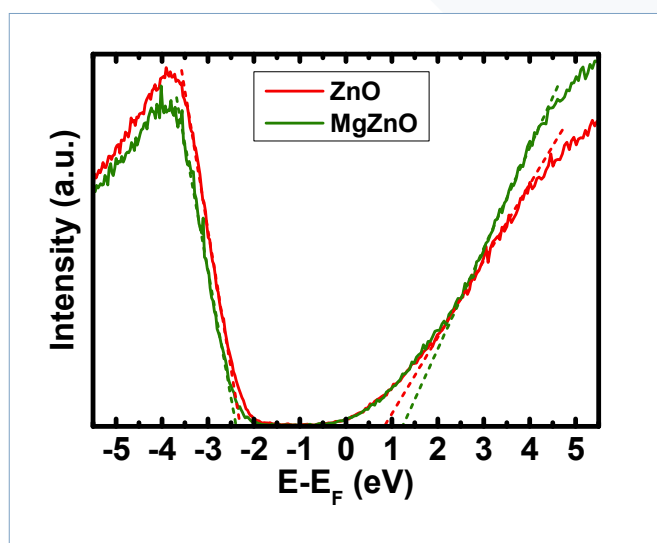
Oxide semiconductors such as zinc oxide have attracted a great amount of attention due to their attractive properties for the transparent (TCO) electronics industry. The current leading ZnO alloy indium-gallium-zinc-oxide is attractive for various applications such as active matrix displays. The advantages are high electron mobility, optical transparency owing to their wide band gaps, uniformity, and low processing temperature. However, degradation of electrical properties due to temperature, bias, humidity and light illumination are issues not well understood. Moreover, indium is a rare element in IGZO and is known to suffer from price fluctuations and hence limiting its potential to dominate the TCO industry. Currently much research effort is directed at finding alternative dopants for ZnO, such as F, Li, Mo and Mg, in order to improve the electrical characteristics of thin film transistors (TFT).

Recently we have used photoemission and inverse photoemission to characterise Mg-doped ZnO TFTs. These techniques allow probing the filled as well as empty density of states on either side of the Fermi level (see Figure). Furthermore, the valence band offset (VBO) for the MgZnO/SiO₂ and ZnO/SiO₂ interfaces was determined using monochromated XPS. The results showed that there was no significant change to the valence band edge for both the MgZnO/SiO₂ and ZnO/SiO₂ interfaces, confirming that the VBM position did not change with the addition of Mg. The conduction band minimum, however, was found to increase from 0.83 eV for ZnO to 1.2 eV for MgZnO films. As the surface band gap can be extracted through the difference of the two determined band positions, one can confirm the band gap widening with the addition of Mg. The parameters extracted from our measurements were used to construct a band diagram, and extract realistic fitting parameters from the measurements for analysing the transport mechanism and modeling the TFT [1]. This work is part of a long-term collaboration with the department of electrical and electronic engineering.

Another important quantity for characterizing TCOs is work function, an important parameter for charge-exchange because it represents the energetic requirements for adding or removing an electron to or from a solid. However, the surface electronic properties, and in particular work function of TCOs have not received much attention and the precise value is often not known, ranging from 4.4 – 5 eV. Commonly it is quoted as 4.4 eV, despite efficient operation of organic devices requiring the work function to be close to 5 eV. We have been using XPS to measure secondary electron cutoff to determine the absolute work function of fluorine doped tin oxide (FTO) in collaboration with NSG Pilkington glass. Our results indicate that it is possible to achieve the desired high work function value for FTO glass by in situ vacuum cleaning procedures. This is an on-going project with Pilkington Glass [2].

[1] A Shaw, T J Whittles, I Z Mitrovic, J D Jin, J S Wrench, D Hesp, V R Dhanak, P R Chalker and S Hall, *Physical and Electrical Characterization of Mg-Doped ZnO Thin-Film Transistors*, IEEE Solid State Device Research Conference, (2015) 206.

[2] D Hesp, T J Whittles, T Veal, V R Dhanak and P Warren, *unpublished*.



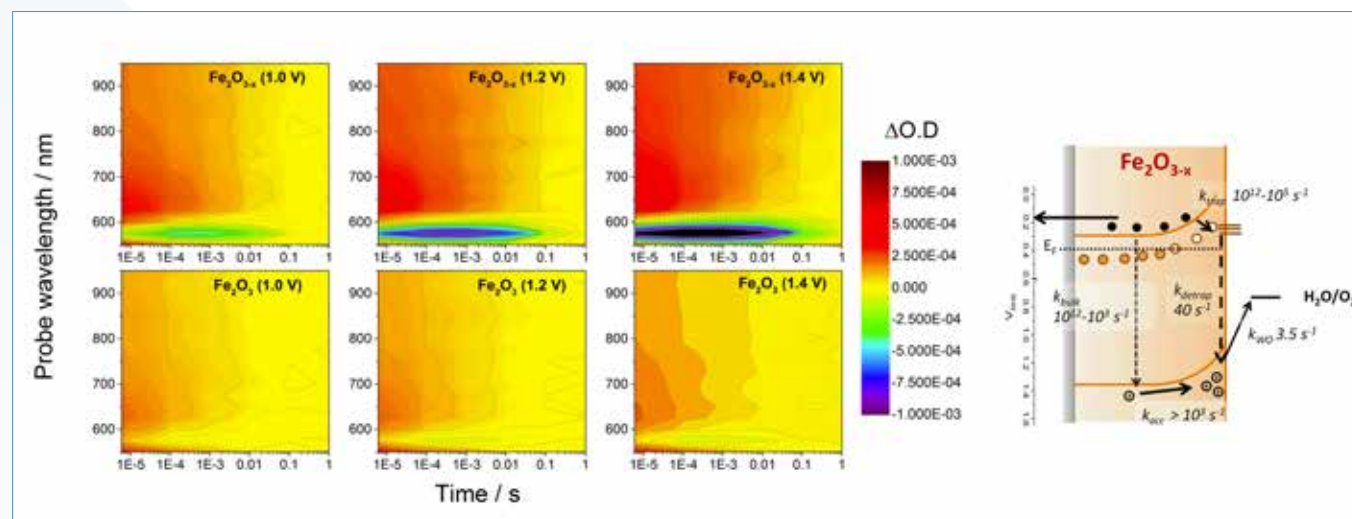
Conduction and Valence band edges obtained from IPES and XPS respectively for the ZnO and MgZnO thin films.

Oxygen deficient $\alpha\text{-Fe}_2\text{O}_3$ photoelectrodes: A balance between enhanced electrical properties and trap-mediated losses

A Cowan

Light driven water splitting provides a route to sustainably producing hydrogen using only sunlight and water as the inputs. Hematite ($\alpha\text{-Fe}_2\text{O}_3$) is amongst the most promising materials for use in a photoelectrochemical water splitting device. Hematite photoanodes are low cost, stable and have a theoretical maximum solar to hydrogen fuel conversion efficiency of $\sim 15\%$. However to date the best materials can only achieve $\sim 1\text{-}2\%$. The deliberate incorporation of oxygen vacancies to make $\alpha\text{-Fe}_2\text{O}_{3-x}$ greatly improves activity of otherwise un-doped films however prior to this study the details of how this occurs were debated.

In this project we utilised transient optical measurements to follow short lived photoelectrons and holes in hematite electrodes allowing for a thorough understanding of the structure/function relationship. In light of these results and in partnership with colleagues in the School of Engineering at the University of Liverpool (Dr R Potter) and the University of California Santa Cruz (Prof Y Li) we were then able to identify and demonstrate a simple material modification to further enhance the activity of $\alpha\text{-Fe}_2\text{O}_{3-x}$.



Transient spectroscopy (left) can be used to study the charge carrier dynamics in water splitting hematite photoelectrodes. Using this data we are able to construct a simplified energy diagram and kinetic model for the key steps in $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_{3-x}$, allowing us to identify and remedy the primary loss pathways. Figure adapted from Chem. Sci., 2015, 2015, 6, 4009-4016

Multiferroic oxides

J Alaria

The miniaturisation of memory devices based on current controlled states is reaching its physical limitation and are power hungry. The possibility to create voltage controlled and non-volatile memory devices using new type of materials where both switchable electrical polarisation and magnetic moment coexist has so far been limited by the difficulty to design multiferroic materials where both ferroic orders are retained at room temperature. A multidisciplinary team at the University of Liverpool have demonstrated the possibility to engineer new classes of multiferroic materials with transition above room temperature. The first concept published in Science is to couple octahedral tilting and shear in Fe based layered perovskite to achieve high temperature polarity and magnetism. If magnetic hysteresis was observed, the difficulty to switch the polarisation in an improper

ferroelectric impeded to observe polarisation hysteresis. A second concept was developed in parallel and published in Nature and consists in using magnetic percolation in a ferroelectric compound at a morphotropic phase boundary.

P Mandal, M J Pitcher, J Alaria, H Niu, P Borisov, P Stamenov, J B Claridge and M J Rosseinsky, *Designing Switchable Polarization and Magnetization at Room Temperature in an Oxide*, Nature 525 (2015) 363.

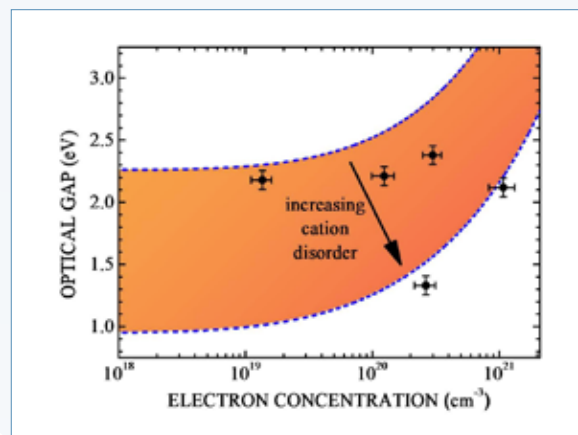
M J Pitcher, P Mandal, M S Dyer, J Alaria, P Borisov, H Niu, J B Claridge and M J Rosseinsky, *Tilt Engineering of Spontaneous Polarization and Magnetization above 300 K in a Bulk Layered Perovskite*, Science 347 (2015) 420.

Novel nitride photovoltaic absorber tuned via cation disorder

T Veal

Tim Veal and Wojciech Linhart of the Stephenson Institute have demonstrated a new material, zinc tin nitride, the band gap of which can be 'tuned' by varying the degree of cation disorder by altering the growth conditions. This work, in collaboration with researchers from Western Michigan and Binghamton universities and University College London, paves the way for this earth abundant material to be used in future solar cell technologies, either in single junction thin film devices or forming the wider band gap absorber in tandem cells to enhance the performance of mature silicon-based technology.

This novel nitride semiconductor is shown to have a band gap that can be varied from 1 to 2 eV, by reducing the degree of cation disorder by increasing the metal nitrogen flux ratio and increasing the substrate temperature during growth. This means the alloying with other elements, commonly used to optimise the band gap, may not be necessary. Zinc tin nitride is derived from gallium nitride by cation mutation in an analogous way to how more common solar cell materials copper indium diselenide and copper zinc tin sulphide are derived from zinc selenide. As zinc tin nitride contains only earth abundant elements, it avoids some of the drawbacks of conventional thin film solar cell materials such as CdTe and CIGS which employ the scarce and/or price volatile elements tellurium and indium. Zinc tin nitride, therefore, holds promise as an earth abundant semiconductor for solar cells and other optoelectronics. Further work to develop



The calculated dependence of absorption edge on free electron density for the two extreme cases of cation ordered and fully cation disordered zinc tin nitride (ZnSnN₂). Optical absorption edge versus free electron density data points are also shown for some ZnSnN₂ films.

intentional n- and p-type doping is required. This method of varying the band gap by tuning the degree of cation disorder is applicable to other heterovalent ternary semiconductors.

T D Veal, N Feldberg, N F Quackenbush, W M Linhart, D O Scanlon, L F J Piper, and S M Surbin, *Band Gap Dependence on Cation Disorder in ZnSnN₂ Solar Absorber*, *Advanced Energy Materials* 5, (2015)

Long lifetime hole traps at grain boundaries in CdTe thin-film photovoltaics

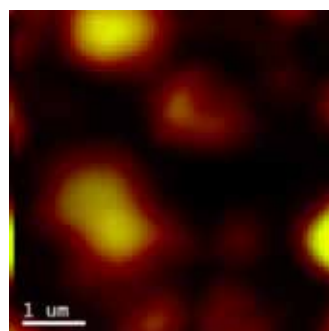
J Major

Cadmium telluride (CdTe) thin film solar cells are now one of the lowest cost forms of photovoltaic (PV) power generation and module efficiency has now surpassed that of the traditional multicrystalline silicon equivalent. CdTe solar cells now account for around 7% of the PV market with over 10GW of modules installed worldwide. However, despite this success there are still fundamental limitations to the technology that is restricting further development. In order to overcome these limitations a greater level of materials understanding is required to identify how they may be improved.

As CdTe is a polycrystalline film, one primary limitation of CdTe solar cells is believed to be the grain boundaries within the material. These boundaries are known to introduce defects and to capture impurities, causing electrons to recombine within the material and power to be lost. It is notoriously difficult to characterise these grain boundaries accurately however, owing to their small size and the difficulty in separating their behaviour from that of the grain bulk. Functional electron microscopy techniques such as cathodoluminescence offer a powerful route to both analyse and visualise the behaviour of grain boundaries.

Work published in Physical Review Letters focused on using a novel time resolved form of cathodoluminescence to characterise individual grain boundaries. From this it was demonstrated not only that excitons were quenched at grain boundaries but also that hopping conduction occurred across grain boundaries at low temperatures. This work provides vital new insight into the functionality of this key solar cell material.

B G Mendis, D Gachet, J D Major, and K Durose, *Long Lifetime Hole Traps at Grain Boundaries in CdTe Thin-Film Photovoltaics*, *Physical Review Letters*, 115, 218701 (2015).



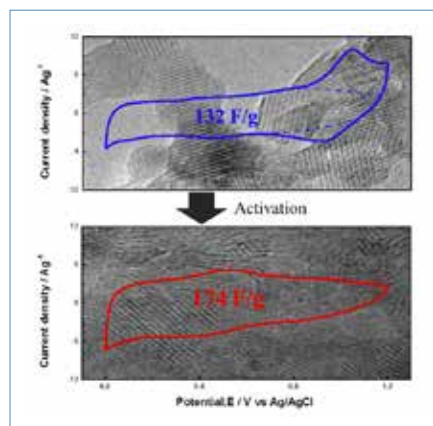
Time resolved cathodoluminescence spectrum of a CdTe solar cell. Bright areas show the CdTe grains while the dark areas show the change in recombination at the grain boundaries.

Electrochemistry and in-situ spectroscopy of advanced supercapacitor materials

L J Hardwick

Electrochemical supercapacitors have been widely investigated due to their high charge/discharge efficiency, high-rate charge storage and delivery, as well as long cycle life. Recently, researchers have investigated approaches to increase the specific energy stored in supercapacitors in order to apply to numerous energy storage applications, such as hybrid electric vehicles, starting assistance to fuel cells, and power sources of electronics and cordless electric tools. According to the charge storage mechanism, the non-faradaic electrical double-layer capacitors (EDLCs) are based on charge separation (ie arrangement of ions/polar molecules) at the electrode/solution interface. The pseudocapacitance originates from the Faradaic redox reactions of electroactive species within electrode materials.

Manganese oxides can undergo an electrochemical activation step that leads to greater capacitances, of which the structural change and mechanism remains poorly understood. Our work has shown that electrochemically activated MnO_x , from one-pot synthesised hausmannite- Mn_3O_4 , exhibits a capacitive performance of 174 Fg^{-1} , which is superior to reported values of comparable materials. Activation from primarily hausmannite- Mn_3O_4 to predominantly localised birnessite- MnO_2 by potential cycling is verified by both *in situ* and *ex situ* Raman microscopy, X-ray photoelectron spectroscopy and transmission electron microscopy. Due to the structural disordering of electrochemically activated birnessite- MnO_2 and residual Mn_3O_4 , the charge storage is attributable to the redox reaction between Mn(III) and Mn(IV) at outer surface active sites, rather than cations and/or



Manganese oxides can undergo an electrochemical activation step that leads to greater capacitances, of which the structural change and mechanism remains poorly understood

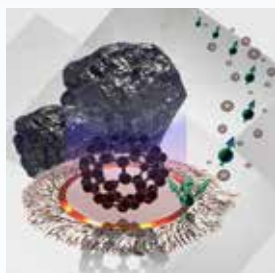
protons intercalation into layer structures. The improved capacitive performance relates to the synergistic effect of well-dispersed MnO_2 and Mn_3O_4 nanoscale domains present within the activated material. Overall we show that the integrated nanoscale structuring of different phases of manganese oxides offers superior properties compared to bulk parent materials, and as such offers an avenue of future supercapacitor materials development.

T H Wu, D Hesp, V Dhanak, C Collins, F Braga, L J Hardwick, C C Hu, *Charge Storage Mechanism of Activated Manganese Oxide Composites for Pseudocapacitors* J Mater Chem A, 3 (2015) 12786-12795

Beating the stoner criterion using molecular interfaces – making ferromagnets where there were none

G Teobaldi

Since the introduction of the first commercial direct-drive ferromagnetic generator (DDFMG), greatly improving the mechanical stability and reliability of MegaWatt (MW) turbines for wind and tidal energy generation, the uptake of this new technology in wind and tide farm has been hampered by the substantial amount of ferromagnetic material required for the generator (roughly 2 tons of Nd-Fe-B ferromagnet for a 3.5 MW turbine).



Concerns about global availability and distribution of Nd have prompted growing interest in the development of novel lightweight room-temperature ferromagnets to potentially substitute Nd-Fe-B in DDFMG turbines, opening up for a more sustainable design. Unfortunately, generation of room temperature ferromagnetism from inexpensive, low-toxicity, non-magnetic materials such as molecular semiconductors and light metals has long remained an unsolved challenge.

Here, it is demonstrated that it is possible to alter the electronic states of non-ferromagnetic materials, such as diamagnetic copper and

paramagnetic manganese, and make them ferromagnetic at room temperature. This effect, detected by both magnetometry and low-energy muon spin spectroscopy, is achieved via interfaces between metallic thin films and fullerene C_{60} molecular layers. The emergent ferromagnetic state exists over several layers of the metal before being quenched at large sample thicknesses by the material's bulk properties. Density Functional Theory simulations suggest a mechanism based on magnetic hardening of the metal atoms, owing to electron transfer. This mechanism might allow for the exploitation of molecular coupling to create ferromagnets using abundant, non-toxic components such as light transition-metals and organic semiconductors, with new opportunities for the design of power, electronic or computing devices.

Artistic representation of the onset of magnetic spin-ordering at the interface between non-magnetic cheap substrates such as metal manganese (or copper) and fullerene C_{60} molecules. Picture courtesy of Fatma Al Ma'Mari, Timothy Moorsom, and Oscar Cespedes (Department of Physics, University of Leeds).

F Al Ma'Mari, T Moorsom, G Teobaldi, W Deacon, T Prokscha, H Luetkens, S Lee, G Sterbinsky, D Arena, M Flokstra, M Ali, M Wheeler, G Burnell, B Hickey and Oscar Cespedes, *Beating the Stoner Criterion Using Molecular Interfaces*. Nature, 524, 69-73 (2015).

Computational identification and experimental realisation of lithium vacancy introduction into the olivine LiMgPO_4

F Blanc

There has been considerable recent attention to the development of fast solid-state Li^+ ion conductors, largely driven by their proposed use as electrolytes in all solid-state Li^+ ion batteries that are safer to operate than conventional Li^+ ion batteries containing flammable organic liquid electrolytes. However, the most challenging issue associated with solid-state Li electrolytes remains the low bulk Li^+ ion conductivity at room temperature. The identification of new families of Li^+ ion conductors and the development of methodologies that enable this is thus an important problem. One approach is to consider electronically insulating analogues of known Li electrode compounds (eg olivine LiFePO_4), which must support sufficient Li^+ ion diffusion to allow Li intercalation and deintercalation.

Calculation of the energetics of aliovalent substitution into the related olivine LiMgPO_4 suggests that replacement of Mg^{2+} by In^{3+} is the most effective way to introduce lithium vacancies (see Figure a) and thus generate Li^+ ion conductivity. Experimental synthesis accesses materials with up to 17% Li vacancy content. An order of magnitude increase in the high temperature hopping rates probed by ^7Li Nuclear Magnetic Resonance (NMR) (see Figure b), and over two orders of magnitude increase in the room temperature Li^+ ion conductivity measured by impedance spectroscopy is observed on introduction of In^{3+} ions and Li vacancies. NMR spectroscopy and calculations reveal that the energy barrier to site-to-site hopping is 0.3 eV – 0.5 eV, comparable with best-in-class non-oxide systems (eg argyrodite), but the data shows that longer range transport is less facile with activation energies in the range of 0.7 – 1 eV. Calculations suggest that this is because the Li vacancies are strongly bound to the In^{3+} dopants, suggesting that high Li mobilities in oxides are accessible but high conductivities require strategies to separate defect from dopant.

L Enciso-Maldonado, M S Dyer, M D Jones, M Li, J L Payne, M J Pitcher, M K Omir, J B Claridge, F Blanc, M J Rosseinsky, *Computational Identification and Experimental Realisation of Lithium Vacancy Introduction into the Olivine LiMgPO_4* , Chem. Mater. 27(6), 2074 (2015).

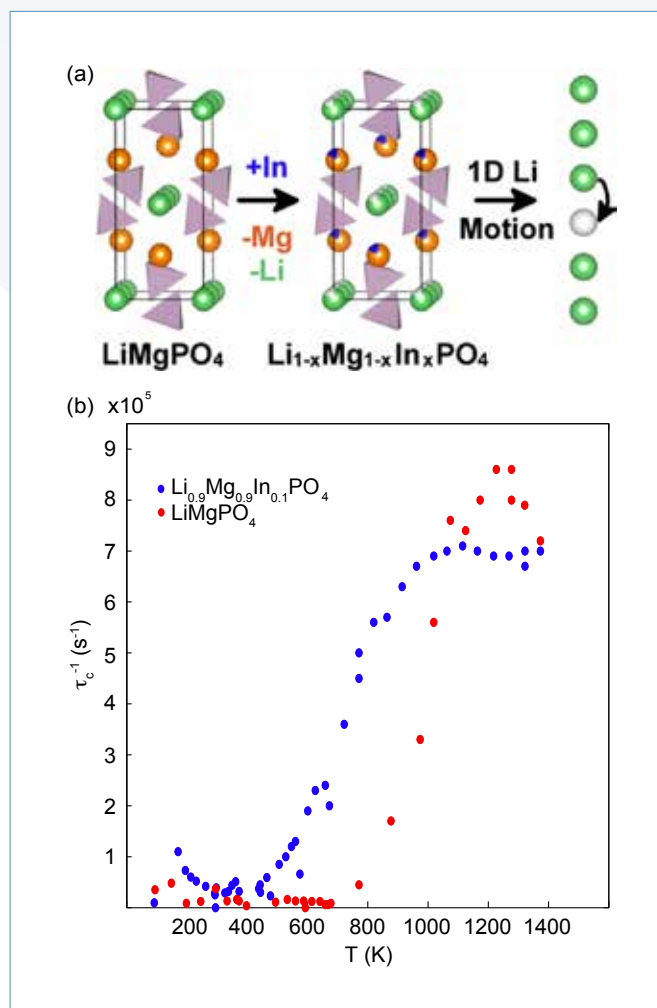


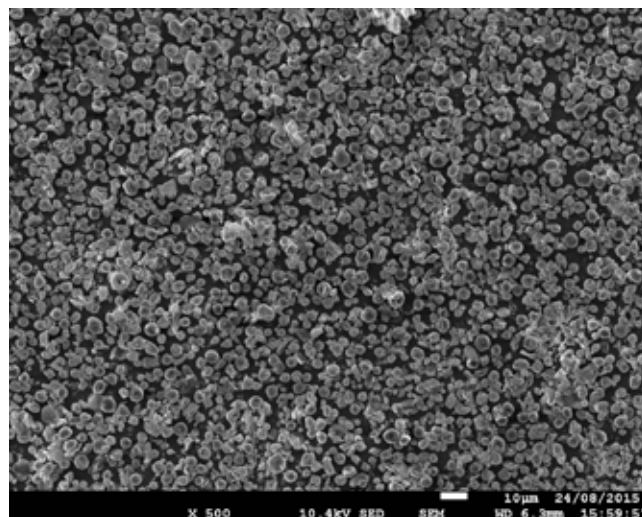
Figure (a) Representation of In doping into the LiMgPO_4 olivine structure and 1D Li motion.

Figure (b). Plot of the Li jump rates obtained from Lithium-7 Nuclear Magnetic Resonance spectroscopy as a function of temperature. Reprinted with permission from L Enciso-Maldonado et al. Chem. Mater. 27(6), 2074-2091 (2015). Copyright 2015 American Chemical Society.

Encapsulation of energy-enriched materials

D Shchukin

The main vision of the project is the development of nanoencapsulation technologies based on switchable nanoscale barriers for novel generation of controlled energy storage and delivery systems. These systems will be based on the 'smart' nanocontainers loaded with the energy-enriched active components: materials for thermal energy (both latent and based on chemical reactions) storage and substances for bioenergy (ATP or its components) storage for synthetic biology platforms. First novelty of the proposed project is the protection of the nanoscaled energy-enriched materials against environment during storage and controlled release of the encapsulated energy on demand only using both inherent properties of nanocontainer shell or biomimetic nanovalves introduced as shell components. Another main objective of the project is to study the structure and surface-to-volume properties of the energy enriched materials dispersed and encapsulated on nanoscale. The questions of stability of energy nanomaterials, influence of the nanocontainer shell on their energy capacity, homogeneity and operation lifetime will be investigated. Polymer organic nanocapsules with hollow interior and mesoporous carbon nanoparticles are chosen in the project as main types of the nanocontainer scaffolds for energy-enriched materials due to their high loading capacity and potential to design their shells to attain them controlled permeability properties. At the end of the project, developed novel energy storage and delivery systems will be combined within one network having several mechanisms for release and uptake of energy, which can be activated depending on type and intensity of the external impact (demand). The potential applications of such multienergy storage systems will be tested by industrial companies supporting the project.



Energy storage microcapsules loaded with *n*-docosane.

P F De Castro, D G Shchukin, *New Polyurethane/Docosane Microcapsules as Phase-Change Materials for Thermal Energy Storage*, *Chemistry – A European Journal* Vol. 21, 11174 (2015)

Dual band gap photocatalytic cells for hydrogen generation

F Jaeckel

Solar hydrogen is expected to play a major role in a future sustainable energy mix. A key challenge is the low cost and efficient generation of hydrogen from water. Colloidal, catalyst-decorated semiconductor nanocrystals are considered one option for photocatalytic hydrogen generation and offer a potentially cheap and flexible route. In particular, their widely tuneable optical and electronic properties are a potential advantage.

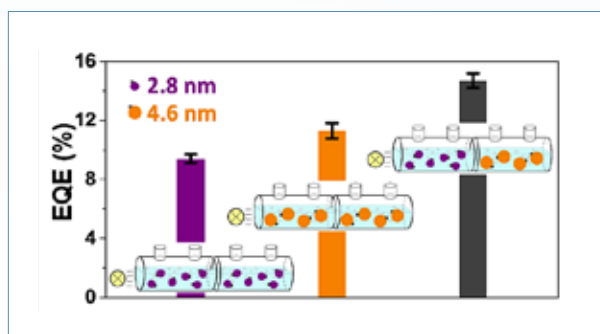
In this work we show that quantum confinement in Pt-decorated CdS nanospheres can be used to tune the internal quantum efficiency for hydrogen generation. This is explained by the fact that stronger quantum

confinement in smaller nanocrystals increases the energetic driving force for photoelectron transfer from CdS to Pt due to the larger band gap in the smaller nanocrystals. At the same time, the larger band gap shifts the optical absorption of the smaller nanocrystals further into the blue spectral range. This allows construction of a dual band gap photocatalytic cell (see figure), in which, similar to a tandem solar cell, small nanocrystals in the front of the cell convert higher energy photons with larger efficiency into hydrogen, while larger nanocrystals in the back of the cell convert the remaining photons that are not absorbed by the smaller nanocrystals.

This approach increases the overall efficiency with which incident photons are used. This proof-of-principle demonstration is an important step towards true tandem photocatalytic cells in which the two compartments would be electrically or electronically connected.

External quantum efficiencies for photocatalytic hydrogen generation using dual cells with either the same size or different size nanocrystals. Combining different size nanocrystals results in a more efficient use of the incoming photons. Reproduced with permission from Li et al. *Nanoscale* 7, 16606 (2015). Copyright Royal Society of Chemistry.

W Li, G O'Dowd, T J Whittles, D Hesp, Y Gründer, V R Dhanak, F Jaeckel, *Colloidal Dual-Band Gap Cell for Photocatalytic Hydrogen Generation*, *Nanoscale* 7, 16606 (2015).



Screening of mono- and bi-functional catalysts for the one-pot conversion of cellobiose into sorbitol

J A Lopez-Sanchez

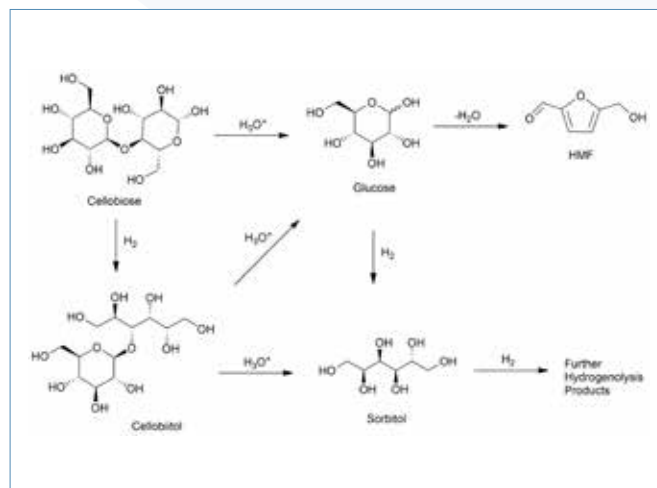
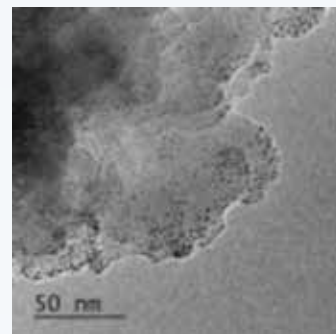
The uncertainty regarding the future supply of oil, the increasing energy demand per capita and the need for reducing the environmental impact of processes and products has been the driving force behind the development of a new industry based on renewables. In this present scenario, the efficient use of lignocellulosic biomass and its conversion in high value products has become one of biggest challenges for both the academia and industry.

In the past ten years, a lot of work has been done in optimizing conditions for hydrothermal hydrolysis of both cellulose and hemicellulose. However, even with these optimized conditions a broad distribution of by-products is obtained. On the other hand, the hydrogenation of sugars is already a well-established industrial process, but the severe reaction conditions along with the possibility of producing sugar alcohols from different feedstocks undoubtedly offer room for improvement. In this context, the one-pot conversion of polysaccharides into sugar alcohols is a very interesting route as the sugar monomers (glucose and xylose) are hydrogenated to more stable products (sorbitol and xylitol), producing higher valuable products and minimizing the formation of by-products in the hydrolysis step.

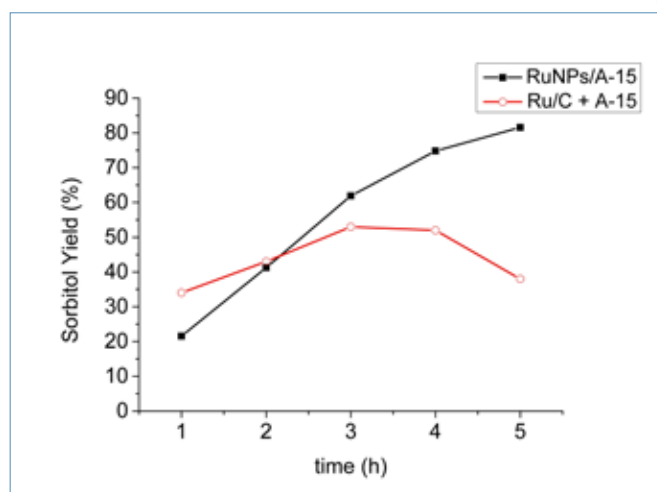
In collaboration with Professor Eduardo Falabella Sousa-Aguar in UFRJ (Brazil), we have developed a bifunctional catalyst, product of the impregnation of Amberlyst 15 with pre-formed ruthenium nanoparticles (3% RuNPs/A15), that is very active in the one pot conversion of cellobiose into sorbitol, at 40 bar of hydrogen pressure in water, affording a yield of sorbitol higher than 80% in 5 h. This value is much higher than the yield obtained when a physical mixture of the solid acid A15 and the hydrogenation catalyst Ru/C is used, indicating that the bifunctionality of the catalyst plays a major role in the one pot conversion of cellobiose into sorbitol. We have also evaluated the performance of different acid functionalized SBA-15 materials for the hydrolysis of cellobiose and concluded that all these materials suffer from severe leaching. This fact is often neglected in similar studies for the conversion of biomass employing acid functionalized silica-type material. A15 is much more stable under the same conditions, thus being more adequate for the preparation of the bifunctional catalyst for the direct one-pot conversion of cellobiose to sorbitol.

J M A R Almeida, L Da Vià, P Demma Carà, Y Carvalho, P N Romano, J A O Peña, L Smith, E F Sousa-Aguar and J A Lopez-Sanchez. *Screening of mono- and bi-functional catalysts for the one-pot conversion of cellobiose into sorbitol*. *Catalysis Today*, in press (2016).

Transmission electron microscopy for the 3% RuNPs/A15 catalyst.



Global reaction scheme for the hydrogenation of cellobiose to sorbitol along with the undesired glucose dehydration side reaction.



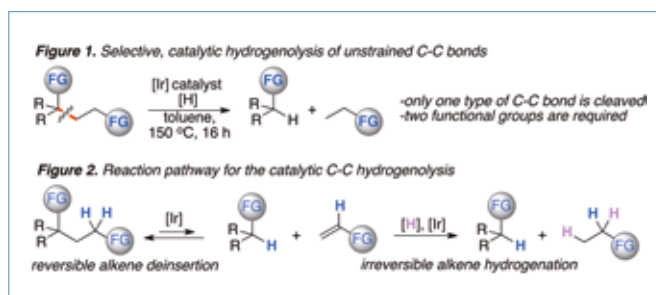
One pot hydrogenolysis of cellobiose into sorbitol: sorbitol yield % for 3% RuNPs/A15 and the physical mixture of 5% Ru/C + A15.

Selective, catalytic cleavage of unstrained carbon-carbon bonds: Insight into the catalytic cycle

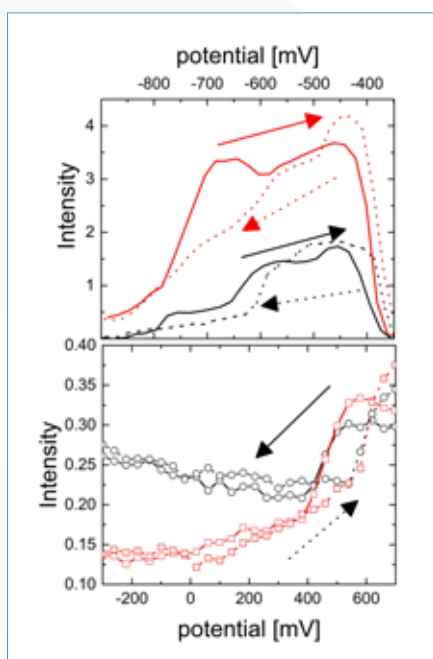
A Sergeev

Catalytic activation of unstrained aliphatic carbon-carbon bonds underpins many industrial processes for generation of chemicals and fuels from hydrocarbon resources. Current catalysts for these processes operate at high temperatures (>300 °C) and cause unselective cleavage of all types of C-C bonds yielding complex mixture of products. To develop more energy efficient and clean technologies for these transformations, more selective and active catalysts are needed. Design of such catalysts requires detailed understanding of mechanisms of catalytic C-C bond cleavage, which is currently deficient.

This project aims to fill this gap and focuses on mechanistic studies of a rare catalytic process that involves selective reductive cleavage of C-C bonds in functionalised aliphatic compounds (see Figure). This process occurs in the presence of well-defined iridium complexes that cleave only one type of C-C bonds in the substrate. Our preliminary results revealed that essential for this unique selectivity is the presence



of two functional groups in the starting compounds. Further studies indicated that this catalytic process takes place through reversible deinsertion of an alkene from the C-H bond with subsequent irreversible hydrogenation of the alkene to give products of formal hydrogenolysis of the C-C bond (Figure 2). This reaction pathway can be realised through two different mechanisms. We aim to distinguish these mechanisms through kinetic and stoichiometric studies that involve observation and characterisation of reaction intermediates by NMR, MS and XRD methods. Obtained results will provide important information on how selectivity of C-C bond cleavage can be controlled and will help develop more active and stable catalysts for C-C bond functionalisations of industrial importance.



The difference in the ordering effect of the Ag (a) and Cu (b) UPD layer can be seen in the potential dependent intensity at a surface sensitive position (Ag) and the intensity arising from the ordered adlayer (Cu) at high (red) and low temperature (black). In the case of copper the higher intensity observed at high temperature points towards an additional ordered phase.

Temperature effects on the atomic structure and kinetics in single crystal electrochemistry

Y Gründer

In many practical applications relevant electrochemical processes often occur at non-ambient temperatures, however, little is known about the effect of temperature on the atomic structure at the electrochemical interface. We have studied the influence of temperature on the atomic structure at the electrochemical interface using in situ surface x-ray diffraction (SXRD) during the formation of metal monolayers on an Au (111) electrode.

For the under-potential deposition (UPD) systems, the surface diffusion of the depositing metal adatoms is significantly reduced at low temperatures which results in the frustration of ordered structures in the case of Cu UPD, occurring on a Br-modified surface, and in the formation of a disordered Ag monolayer during Ag UPD. In contrast at higher temperatures both Cu and Ag UPD result in ordered, smooth thin film structures. X-ray voltammetry (see Figure) shows the difference in the kinetic ordering. For the Cu UPD system a higher ordering at high temperatures due to the formation of a phase which is frustrated at lower temperature is observed. The Ag UPD system differs in the ordering kinetics at different temperatures which is not due to frustration.

The results indicate that temperature changes affect the mass transport and diffusion of metal adatoms on the electrode surface.

We believe that these results open up new opportunities to establish correlations between temperature, structure, and surface reactivity that will be important for the future development of efficient energy conversion systems. For example, the stability of the metal catalysts used in low temperature hydrogen fuel cells is crucial to the longevity of operation and knowledge of the surface atomic structure, for example in bimetallic systems, would be invaluable.

Optical design for hybrid perovskite photovoltaics

K Durose

Hybrid perovskites are the biggest news in photovoltaics in a generation. Methylammonium lead iodide (MAPI) comprises both organic and inorganic ions in a perovskite lattice. The excitement has been caused by MAPI's rapid gains in solar conversion efficiency, despite being such a new material. In just three years it has achieved 15–20% efficiency - a rate of increase that outstrips any other material in history by a factor of x10-20.

The earliest MAPI-based devices were based on porous TiO_2 – reflecting the material's PV origins in a variation of the dye sensitised solar cell. Going forward though, it is attractive to make simpler planar multilayer devices instead. Here in Liverpool we have been making MAPI layers and their derivatives for some years, but rather than dive straight into an experimental study, we decided to create the data necessary for optical design.

To achieve maximum efficiency, a solar cell must be designed to absorb most light in the active layer, in this case MAPI. To minimise light loss in the other layers by reflection and absorption (see Figure), their thickness and composition must be optimised. Calculation of this may be done using the 'transfer matrix method' that takes into account reflection, absorption and phase effects in thin film multilayers. The source data required for this is the dispersion relations for each layer, and in the case of MAPI, we needed to determine this from scratch. Our papers (with lead author Laurie Phillips, see below) give this data as a publicly accessible data file for others to use in modelling too. The papers also give details of the spectroscopic variable angle ellipsometry and modelling used to determine the data (ie the oscillator model - Tauc-Lorenz, critical point parabolic band and harmonic).

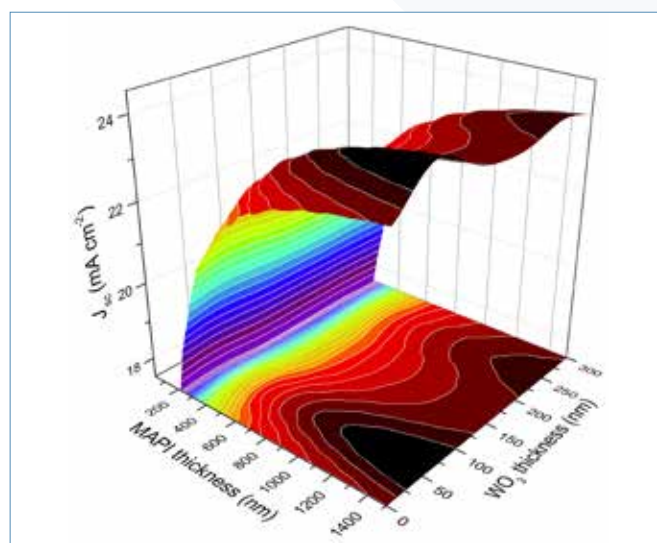
Having the dispersion data allowed us to make a liberal study of the composition and thicknesses of window layers that would give highest optical coupling to the MAPI absorber layer. We included both new and standard materials including CdS, CdZnS, TiO_2 , WO_3 and Ta_2O_5 . There were some surprising results: the well-known materials were not always the best. While parasitic absorption in CdS killed the short circuit current, simply opening the band gap with (CdZn)S still did not bring the performance to the highest levels. Moreover, the performance of the TiO_2 (the best known window for MAPI) was found to be quite sensitive to its thickness, with just ± 10 nm making a 5% difference in current collection. This means that control in industrial processes would be critical. However, WO_3 , a relative newcomer, achieved slightly higher current collection, and is not so sensitive to thickness variations. ZnO also performed well, although with lower peak current collection.

Overall, this work has created a publicly available data set of dispersion relations for MAPI that will inform both our experiments going forward and the designs and experiments of others.

Variation of the maximum current density (J_{sc}) for a MAPI solar cell using WO_3 as a window layer, as determined by our optical model. We show the current as a function of the thickness of both the MAPI and the window. There is an interference 'sweet spot' for the most effective thickness of WO_3 , and it is broader than for other materials tested. This makes WO_3 easier to handle in practice when some degree of thickness variation is inevitable.

L J Phillips, A M Rashed, R E Treharne, J Kay, P Yates, I Z Mitrovic, A Weerakkody, S Hall, K Durose. *Maximizing the optical performance of planar $\text{CH}_3\text{NH}_3\text{PbI}_3$ hybrid perovskite heterojunction stacks*. *Solar Energy Materials and Solar Cells* 147, (2016) p 327–333

L J Phillips, A M Rashed, R E Treharne, J Kay, P Yates, I Z Mitrovic, A Weerakkody, S Hall, K Durose. *Dispersion relation data for methylammonium lead triiodide perovskite deposited on a silicon wafer with a two-step vapour-phase reaction process*. *Data in Brief* 5(2015) 926–928



Reproduced with permission from L J Phillips et al *Solar Energy Materials and Solar Cells* 147 (2016) 327.

Publications by SIRE members in 2015

Catalysis and transformation

M Forster, R J Potter, Y Ling, Y Yang, D R Klug, Y Li and A J Cowan, *Oxygen deficient alpha-Fe₂O₃ photoelectrodes: a balance between enhanced electrical properties and trap-mediated losses*, Chemical Science **6** (2015) 4009.

W Li, G O'Dowd, T J Whittles, D Hesp, Y Gründer, V R Dhanak and F Jaekel, *Colloidal dual-band gap cell for photocatalytic hydrogen generation*, Nanoscale **7** (2015) 16606.

J A Lopez-Sanchez, C Morisse, J M Winfield, B Krumm, T M Klapoetke and D Lennon, *The preparation of a residue-free, alumina-supported gold catalyst by decomposition of an azido-gold(III) complex and an evaluation of the effectiveness of the catalyst for the hydrogenation of Propyne*, Z. Anorg. Allg. Chem. **641** (2015) 694.

G Neri, J J Walsh, C Wilson, A Reynal, J Y C. Lim, X Li, A J P White, N J Long, J R Durrant and A J Cowan, *A functionalised nickel cyclam catalyst for CO₂ reduction: electrocatalysis, semiconductor surface immobilisation and light-driven electron transfer*, Physical Chemistry Chemical Physics **17** (2015) 1562.

E Remiezowicz, J Spooren, E Bay, A J Cowan et al., *Capture agents, conversion mechanisms, biotransformations and biomimetics: general discussion*, Faraday Discuss. (2015), **183**, 463–487

J J Walsh, C L Smith, G Neri, G F S Whitehead, C M Robertson and A J Cowan, *Improving the efficiency of electrochemical CO₂ reduction using immobilized manganese complexes*, Faraday Discuss. (2015) **183**, 147–160.

Charge storage, batteries and capacitors

A Birrozzi, M Copley, J von Zamory, M Pasqualini, S Calcaterra, F Nobili, A Di Cicco, H Rajantie, M Briceno, E Bilbe, L Cabo-Fernandez, L J Hardwick, D Bresser and S Passerini, *Scaling up "nano" Li₄Ti₅O₁₂ for high-power lithium-ion anodes using large scale flame spray pyrolysis*, J Electrochem. Soc **162** (2015) A2331.

C Sole, N E Drewett, F Liu, A M Abdelkader, I A Kinloch and L J Hardwick, *The role of re-aggregation on the performance of electrochemically exfoliated many-layer graphene for Li-ion batteries*, J Electroanal. Chem **753** (2015) 35.

T H Wu, D Hesp, V Dhanak, C Collins, F Braga, L J Hardwick and C C Hu, *Charge storage mechanism of activated manganese oxide composites for pseudocapacitors*, Journal of Materials Chemistry A **3** (2015) 12786.

Electrochemistry

Y Gründer, N M Markovic, P Thompson and C A Lucas, *Temperature effects on the atomic structure and kinetics in single crystal electrochemistry*, Surf. Sci. **631** (2015) 123.

Y Gründer, Q M Ramasse and R A W Dryfe, *A facile electrochemical route to the preparation of uniform and monoatomic copper shells for gold nanoparticles*, PCCP **17** (2015) 5565.

P Weightman, P Harrison, C A Lucas, Y Gründer and C I Smith, *The reflection anisotropy spectroscopy of the Au(110) surface structures in liquid environments*, Journal of Physics: Condensed Matter **27** (2015) 475005.

Electronic and magnetic materials

M Althobaiti, S Mather, N Sedghi, V R Dhanak, I Z Mitrovic, S Hall and P R Chalker, *Hafnia and alumina on sulphur passivated germanium*, Vacuum **122** (2015) 306.

B Kisan, P Saravanan, S Layek, H C Verma, D Hesp, V Dhanak, S Krishnamurthy and A Perumal, *Effect of annealing on the magnetic properties of ball milled NiO powders*, J Magn. Magn Mater. **384** (2015) 296.

Q Lu, Y Mu, J W Roberts, M Althobaiti, V R Dhanak, J Wu, C Zhao, C Zhou Zhao, Q Zhang, L Yang, I Z Mitrovic, S Taylor and P R Chalker, *Electrical Properties and Interfacial Studies of HfTi_{1-x}O₂ High Permittivity Gate Insulators Deposited on Germanium Substrates*, Materials **8** (2015) 8169–8182

P Mandal, M J Pitcher, J Alaria, H Niu, P Borisov, P Stamenov, J B Claridge and M J Rosseinsky, *Designing switchable polarization and magnetization at room temperature in an oxide*, Nature **525** (2015) 363.

V Meriga, S Valligatla, S Sundaresan, C Cahill, V R Dhanak and A K Chakraborty, *Optical, electrical, and electrochemical properties of graphene based water soluble polyaniline composites*, J Appl Polym Sci **132** (2015).

I Z Mitrovic, S Hall, M Althobaiti, D Hesp, V R Dhanak, A Santoni, A D Weerakkody, N Sedghi, P R Chalker, C Henkel, E D Litta, P E Hellstrom, M Ostling, H Tan and S Schamm-Chardon, *Atomic-layer deposited thulium oxide as a passivation layer on germanium*, J Appl. Phys. **117** (2015).

M J Pitcher, P Mandal, M S Dyer, J Alaria, P Borisov, H Niu, J B Claridge and M J Rosseinsky, *Tilt engineering of spontaneous polarization and magnetization above 300K in a bulk layered perovskite*, Science **347** (2015) 420

Heat storage materials and microcapsules

P Felix De Castro and D G Shchukin, *New polyurethane/docosane microcapsules as phase-change materials for thermal energy storage*, Chemistry (Weinheim an der Bergstrasse, Germany) **21** (2015) 11174.

S Gao, X Wei, H Liu, K Geng, H Wang, H Moehwald, and D G Shchukin: *Transformation of worst weed into N-, S-, and P-tridoped carbon nanorings as metal-free electrocatalysts for the oxygen reduction reaction*, J Mater Chem. A, **3**, (2015) 23376.

A Latnikova, D Grigoriev, H Moehwald and D Shchukin, *Microgel containers for self-healing polymeric materials: Morphology prediction and mechanism of formation*, Polymer **73** (2015) 183.

B Parakhonskiy and D Shchukin, *Polypyrrole Microcontainers: Electrochemical Synthesis and Characterization*, Langmuir **31** (2015) 9214.

D V Voronin, D Grigoriev, H Mohwald, D G Shchukin, D A Gorin, *Non-uniform growth of composite layer-by-layer assembled coatings via three-dimensional expansion of hydrophobic magnetite nanoparticles*, ACS Applied Materials & Interfaces **7** (2015) 28353.

H Wang, Z Xu, M J Fink, D Shchukin and B S Mitchell, *Functionalized silicon nanoparticles from reactive cavitation erosion of silicon wafers*, Chem. Commun. **51** (2015) 1465.

Z Zheng, X Huang, M Schenderlein, H Moehwald, G K Xu and D G Shchukin, *Bioinspired nanovalves with selective permeability and pH sensitivity*, *Nanoscale* **7** (2015) 2409.

Z Zheng, M Schenderlein, S Huang, N Brownbill, F Blanc, and D Shchukin. *Influence of functionalization of nanocontainers on self-healing anticorrosive coatings*, *ACS Applied Materials & Interfaces* **7** (2015) 22756.

Solar energy materials and solar cells

E A Anyebe, M K Rajpalke, T D Veal, C J Jin, Z M Wang and Q D Zhuang, *Surfactant effect of antimony addition to the morphology of self-catalyzed $\text{InAs}_{1-x}\text{Sb}_x$ (x) nanowires*, *Nano Research* **8** (2015) 1309.

E A Anyebe, A M Sanchez, S Hindmarsh, X Chen, J Shao, M K Rajpalke, T D Veal, B J Robinson, O Kolosoy, F Anderson, R Sundaram, Z M Wang, V Falko and Q Zhuang, *Realization of vertically aligned, ultrahigh aspect ratio InAsSb nanowires on graphite*, *Nano Lett.* **15** (2015) 4348.

D S Bhachu, D O Scanlon, G Sankar, T D Veal, R G Egdell, G Cibin, A J Dent, C E Knapp, C J Carmalt and I P Parkin, *Origin of high mobility in molybdenum-doped indium oxide*, *Chem. Mater.* **27** (2015) 2788.

Y G Fedorenko, J D Major, A Pressman, L J Phillips and K Durose, *Modification of electron states in CdTe absorber due to a buffer layer in CdTe/CdS solar cells*, *J Appl. Phys.* **118** (2015).

S Herodotou, R E Treharne, K Durose, G J Tatlock and R J Potter, *The effects of Zr doping on the optical, electrical and microstructural properties of thin ZnO films deposited by atomic layer deposition*, *Materials* **2015**, 8(10), 7230–7240; doi:10.3390/ma8105369

G Kartopu, L J Phillips, V Barrioz, S J C Irvine, S D Hodgson, E Tejedor, D Dupin, A J Clayton, S L Rugen-Hankey and K Durose *Progression of metalorganic chemical vapour-deposited CdTe thin-film PV devices towards modules*. *Prog. Photovolt: Res. Appl.* (2015) DOI: 10.1002/pip.2668

J D Major, L Bowen, R E Treharne, L J Phillips and K Durose, *NH_4Cl alternative to the CdCl_2 treatment step for CdTe thin-film solar cells*, *IEEE Journal of Photovoltaics* **5** (2015) 386.

J D Major, R Tena-Zaera, E Azaceta, K Durose, *ZnO nanowire radial CdTe solar cells*, *Proceedings of the 42nd IEEE Photovoltaics Specialists Conference 2015* doi 10.1109/PVSC.2015.7356440

J D Major, M K Al Turkestani, K Durose, *Structural and electrical characterisation of MgCl_2 -treated CdTe solar cells*, *Proceedings of the 42nd IEEE Photovoltaics Specialists Conference 2015*, doi:10.1109/PVSC.2015.7356363

B G Mendis, D Gachet, J D Major, K Durose, *Long lifetime hole traps at grain boundaries in CdTe thin-film photovoltaics*, *Phys. Rev. Lett.* **115** (2015) 218701.

L J Phillips, A M. Rashed, R E Treharne, J Kay, P Yates, I Z Mitrovic, A Weerakkody, S Hall, K Durose. *Maximizing the optical performance of planar $\text{CH}_3\text{NH}_3\text{PbI}_3$ hybrid perovskite heterojunction stacks*. *Solar Energy Materials and Solar Cells* **147**, (2016) p 327–333

L J Phillips, A M Rashed, R E Treharne, J Kay, P Yates, I Z Mitrovic, A Weerakkody, S Hall, K Durose. *Dispersion relation data for methylammonium lead triiodide perovskite deposited on a silicon wafer with a two-step vapour-phase reaction process*. *Data in Brief* **5**(2015)926–928

M K Rajpalke, W M Linhart, K M Yu, T S Jones, M J Ashwin and T D Veal, *Bi flux-dependent MBE growth of GaSbBi alloys*, *J Cryst. Growth* **425** (2015) 241.

N Segercrantz, I Makkonen, J Slotte, J Kujala, T D Veal, M J Ashwin and F Tuomisto, *Increased p-type conductivity in $\text{GaN}_x\text{Sb}_{1-x}$: experimental and theoretical aspects*, *J. Appl. Phys.* **118** (2015).

K Sinapis, G Papageorgiou, K Durose, M van den Donker, W Folkerts, *Outdoor degradation of CdTe modules at open circuit and at maximum power point*. *Proceedings of the 42nd IEEE Photovoltaics Specialists Conference 2015*.doi 10.1109/PVSC.2015.7355628

A A Taylor, J D Major, G Kartopud, D Lamb, J Duenowe, R G Dhere, X Maeder, S J C Irvine, K Durose and B G Mendis, *A comparative study of microstructural stability and sulphur diffusion in CdS/CdTe photovoltaic devices*, *Sol. Energy Mater. Sol. Cells* **141** (2015) 341.

T D Veal, N Feldberg, N F Quackenbush, W M Linhart, D O Scanlon, L F J Piper, and S M Surbin, *Band gap dependence on cation disorder in ZnSnN_2 solar absorber*, *Advanced Energy Materials*, **5**, (2015) 501462.

A D Weerakkody, N Sedghi, I Z Mitrovic, H van Zalinge, I N Nouredine, S Hall, J S Wrench, P R Chalker, L J Phillips, R Treharne and K Durose, *Enhanced low voltage nonlinearity in resonant tunneling metal-insulator-insulator-metal nanostructures*, *Microelectron. Eng.* **147** (2015) 298.

B L Williams, J D Major, L Bowen, W Keuning, M Creatore and K Durose, *A comparative study of the effects of nontoxic chloride treatments on CdTe solar cell microstructure and stoichiometry*, *Advanced Energy Materials* **5** (2015) 554.

Q D Zhuang, E A Anyebe, R Chen, H Liu, A M Sanchez, M K Rajpalke, T D Veal, Z M Wang, Y Z Huang and H D Sun, *Sb-Induced Phase Control of InAsSb Nanowires Grown by Molecular Beam Epitaxy*, *Nano Lett.* **15** (2015) 1109.

Solid state NMR and spectroscopy

E F Baxter, T D Bennet, C Mellon-Draznieks, C Gervais, F Blanc and A K Cheetham. *Combined experimental and computational NMR study of crystalline and amorphous zeolitic imidazolate frameworks*. *Physical Chemistry Chemical Physics*, (**17**). pp. (2015) 25191–25196.

R Dervisoglu, D S Middlemiss, F Blanc, Y L Lee, D Morgan and C P Grey, *Joint experimental and computational ^{17}O and ^1H solid state NMR study of $\text{Ba}_2\text{In}_2\text{O}_4(\text{OH})_2$ structure and dynamics*. *Chemistry of Materials*, (**27**). (2015) pp. 3861–3873.

M T Dunstan, J M Griffin, F Blanc, M Leskes, and C P Grey. *Ion dynamics in Li_2CO_3 studied by solid-state NMR and first-principles calculations*. *Journal of Physical Chemistry C*.119 (**43**), (2015) pp 2 4255–24264.

L Enciso Maldonado, M Dyer, M Jones, M Ming, J Payne, M Pitcher, M Omir, J Claridge, F Blanc and M Rosseinsky *Computational identification and experimental realisation of lithium vacancy introduction into the olivine LiMgPO_4* . *Chemistry of Materials* **27** (**6**), (2015) pp 2074–2091.

Publications (Continued)

K Gunwoo, J M Griffin, F Blanc, S M Haile and C P Grey *Characterization of the dynamics in the protonic conductor CsH₂PO₄ by 17O solid-state NMR spectroscopy and first-principles calculations: correlating phosphate and protonic motion*. Journal of the American Chemical Society, **(137)**, pp. (2015) 3867-3876

M Meng, X P Wu, S Sujuan, L Zhao, L Li, L Shen, Y Gao, N Xue, X Guo, W Huang, Z Gan, F Blanc, Z Yu, X Ke, D Xiaokang, X Q Gong, C P Grey, and L Peng *Identification of different oxygen species in oxide nanostructure with 17O solid-state NMR spectroscopy*. Science Advances, 1. 1(1), (2015) e1400133.

Theoretical studies

F Al Ma'Mari, T Moorsom, G Teobaldi, W Deacon, T Prokscha, H Luetkens, S Lee, G E Sterbinsky, D A Arena, D A MacLaren, M Flokstra, M Ali, M C Wheeler, G Burnell, B J Hickey and O Cespedes, *Beating the stoner criterion using molecular interfaces*, Nature **524** (2015) 69.

S L Koch, B J Morgan, S Passerini and G Teobaldi, *Density functional theory screening of gas-treatment strategies for stabilization of high energy-density lithium metal anodes*, J. Power Sources **296** (2015) 150.

G Mandi, G Teobaldi and K Palotas, *What is the orientation of the tip in a scanning tunneling microscope?*, Prog. Surf. Sci. **90** (2015) 223.

E Poli, J D Elliott, N D M. Hine, A A Mostofi and G Teobaldi, *Large-scale density functional theory simulation of inorganic nanotubes: a case study on imogolite nanotubes*, Mater. Res. Innovations **19** (2015) S272.

I Scivetti and G Teobaldi, *(Sub)surface-promoted disproportionation and absolute band alignment in high-power LiMn₂O₄ Cathodes*, Journal of Physical Chemistry C **119** (2015) 21358.

Patents

"Solar cell manufacturing method" P210325GB J D Major, R E Treharne, L M Phillips and K Durose

"Novel porous materials" GB1521640.1 B. Li, J A Lopez-Sanchez and A I Cooper

Theses

PhD: I McLeod; *'Epitaxial growth of lead and bismuth on silver and silver rich alloys'*

PhD: Emiliano Poli, *Challenges in the simulation of large-scale, medium exposed, inorganic nanotubes*

PhD: Luigi Da Vià, *Photocatalytic oxidation of glucose andc Using TiO₂ supported bimetallic nanoparticles: a systematic study*.

PhD: David Hesp: *'Surface Characterisation of Contact Materials for Thin Film CdTe Solar Cells'*

Research funding held in 2015

SIRE holds more than £ 15,000,000 in active grant income.
New grants added in 2015 are marked with an asterisk:

Engineering and Physical Sciences Research Council



*F Blanc, Dynamic Nuclear Polarization Solid-state Nuclear Magnetic Resonance Spectroscopy of Insensitive Nuclear Spins, **£76,000**

A Cooper, L Hardwick, Porous Organic Crystals: From Prediction to Synthesis and Function, **£488,824**

*A Cowan, Spectroscopy Driven Design of an Efficient Photocatalyst for CO₂ Reduction, **£885,064**

*K Durose, Overcoming the Grain Size Limit to Voc in Sustainable Photovoltaics, **£510,591**

K Durose, Improved Understanding, Development and Optimisation of Perovskite-based Solar Cells, **£800,500**

K Durose, CDT Equipment Grant: New and Sustainable Photovoltaics, **£280,000**

K Durose, EPSRC Centre for Doctoral Training in New and Sustainable PV, **£5,300,000**

K Durose, SUPERSOLAR Hub Extension, **£150,000**

L Hardwick, Role of Electro-catalysts in the Electrochemistry of Oxygen in Non-Aqueous Electrolytes, **£354,296**

L Hardwick, Practical Lithium Air Batteries **£95,087**

L Hardwick, Electrochemical Energy Storage with Graphene-Enabled Materials, **£642,208**

T Lopez-Sanchez, Renewable Chemicals from Sustainable Feedstocks via HT methods, **£1,859,979**

*T Lopez-Sanchez, Novel Bio-renewable polyester resins, Impact Acceleration Account, **£74,862**

*T Lopez-Sanchez, Bio-renewable Formulation Information and Knowledge Management System, **£25,392**

*R Nichols, S Higgins, F Jaekel, Single-Molecule Plasmo-electronics, **£444,776**

*M J Rosseinsky, A Cowan, J Claridge et al. Flexible Routes to Liquid Fuels from CO₂, **£1,806,265**

G Teobaldi, In-silico development of the Potential of Doped Metal-oxide nanotubes as Novel Photo-catalysts for Energy Applications, **£577,003**

*G Teobaldi, Support for the UKCP Consortium, **£14,442**

*T Veal, Donor Design for Maximum Mobility Transparent Conducting Oxides, **£509,178**

Science and Technology Facilities Council –

*F Blanc, 2015 SFTC Early Career Award Grant, **£3,000**

The University of Nottingham

*F Blanc, Collaborative Advanced Materials Research Priority Grant, **£3,000**

European Commission

L Hardwick, FP7 608502 SIRBATT: Stable Interfaces for Rechargeable Batteries, **£1,045,833**

*D Shchukin, NanoBarrier, **£480,000**

*D Shchukin, Byefouling, **£160,000**

*D Shchukin, Sono Engineering, **£180,000**

ERC

*D Shchukin, Energizing smart coatings and textiles, ~**£1,600,000**

The Royal Society

Y Grunder, Alternative Solvents for Electrochemical Processes, **£428,176**

Y Grunder, Electrochemistry in non-aqueous solvents **£134,337**

*L Hardwick, Electrochemistry and in situ Spectroscopy of Asymmetric Supercapacitors, **£12,000**

Royal Society of Chemistry

*A Sergeev, Selective reduction of arenes to alkanes by assisted tandem catalysis, **£14,807**

*G Teobaldi, Advanced new linear-scaling constrained density-functional theory approaches, **£11,995**

Beijing Computational Science Research Centre

G Teobaldi, Novel subspace-corrected linear-scaling constrained density-functional theory approaches to modelling photo-electro-chemical interfaces, **£120,000**



Staff directory

Name	Email address	Telephone	Area of interest
Alaria, Dr Jonathan	alariaj@liverpool.ac.uk	+44 (0)151 794 3366	Oxides, magnetic and thermoelectrics
Blanc, Dr Frédéric	fblanc@liverpool.ac.uk	+44 (0)151 794 3511	NMR spectroscopy
Cowan, Dr Alexander	acowan@liverpool.ac.uk	+44 (0)151 794 3481	Electro- and photo-catalytic conversion
Dhanak, Dr Vin	v.r.dhanak@liverpool.ac.uk	+44 (0)151 795 0534/1	Electronic structure of advanced materials
Durose, Professor Ken	ken.durose@liverpool.ac.uk	+44 (0)151 795 9048	PV materials and devices
Grunder, Dr Yvonne	yvonne.grunder@liverpool.ac.uk	+44 (0)151 795 2156	Fundamental electrochemistry
Hardwick, Dr Laurence	hardwick@liverpool.ac.uk	+44 (0)151 794 3493	Batteries
Jaeckel, Dr Frank	fjaeckel@liverpool.ac.uk	+44 (0)151 795 2283	Nanocatalysis
Lopez-Sanchez, Dr Tony	j.lopez-sanchez@liverpool.ac.uk	+44 (0)151 794 3535	Bio chemicals and catalytic conversion
Major, Dr Jon	jonmajor@liverpool.ac.uk	+44 (0)151 795 9049	Solar PV
Sergeev, Dr Alexey	sergeev@liverpool.ac.uk	+44 (0)151 794 2665	Novel catalytic transformations
Shchukin, Professor Dmitry	shchukin@liverpool.ac.uk	+44 (0)151 795 2304	Nanoencapsulation
Teobaldi, Dr Gilberto	g.Teobaldi@liverpool.ac.uk	+44 (0)151 795 8136	Theoretical chemistry
Treharne, Dr Robert	treharn@liverpool.ac.uk	+44(0)151 795 8125	Centre for Doctoral Training
Veal, Dr Tim	timveal@liverpool.ac.uk	+44 (0)151 794 3872	Semiconductor physics



Contact

To find out more about our research, our vacancies and postgraduate opportunities contact:

Stephenson Institute for Renewable Energy
The University of Liverpool
Chadwick Building
Peach Street
Liverpool L69 7ZF

T: +44 (0)151 794 9489
E: carlaj@liverpool.ac.uk

www.liverpool.ac.uk/stephenson-institute

