

Stephenson Institute for Renewable Energy

## Stephenson Institute Annual Report 2014

LIFE CHANGING World Shaping

# The Stephenson Institute for Renewable Energy

## Content

- 03 Director's welcome
- 04 News, events and activities
- 09 Selected research projects
- 16 Publications by SIRE members
- 18 Patents
- 18 Theses
- 18 New funding
- 19 Staff directory

## Annual Report 2014

Welcome to our first Annual Report! The Stephenson Institute for Renewable Energy (SIRE) is different from most renewable energy institutes in that we focus on the chemical, materials and physical sides of energy science: Our work is directed at the 'high tech' end of the energy world. It includes batteries, catalytic conversion of bio-feedstocks, photochemical conversion/catalysis, photovoltaic materials and devices, heat storage materials, new and sustainable materials and thermoelectrics, plus underpinning theory and spectroscopy activities.

SIRE is complementary to the wider energy theme at the University of Liverpool. This includes the engineering, planning and delivery aspects of wind, wave and tidal generation as well as distribution, social, environmental and economic aspects of energy. More information may be found at: <u>www.liverpool.ac.uk/research/</u> research-themes/sustainable-energy/.

At the core of SIRE there are 13 academic staff who are collectively responsible for 50 PhD students and 20 postdoctoral researchers. Together we hold a total of £23m of active research grants, £5 million of which is from industry directly. In 2014 we published more than 80 papers in peer-reviewed journals. SIRE is a powerful group, with a strong dynamic early career profile. Its members naturally collaborate with the Departments of Engineering, Electrical Engineering, Physics, Chemistry and others here in Liverpool to produce the best research. They also enjoy collaborations throughout the UK and internationally, making SIRE an increasingly recognised institute for top-quality research.

2014 has been an exceptional year for us. Some highlight events include the launch of the Engineering and Physical Sciences Research Council (EPSRC) Centre for Doctoral Training in New and Sustainable Photovoltaics, together with battery and fuel cell meetings here in Liverpool. Our research highlights include work on CO<sub>2</sub> reduction, batteries and energy storage materials, photovoltaics, thermophotovoltaics, fuel cell materials and fundamental work on multiferroics, magnetic interfaces and surfaces.

The year also saw SIRE's founding Director, Werner Hofer, leave us for new pastures. We wish him all the best in his new role as Dean of Research and Innovation in the Faculty of Science, Agriculture, and Engineering of Newcastle University.

Finally, I hope that you will find some stimulating science in our report. Should you wish to hear more or collaborate with us, please do get in touch.



Ken Dorore.

Prof Ken Durose, Director, SIRE

## News, events and activities



#### Awards

#### 1. Y. Gründer

Joachim Walter Schultze Prize (Arbeitsgemeinschaft Elektrochemischer Forschungsinstitutionen (AGEF e.V.) 2014)

#### 2. L.J. Hardwick

'Outstanding Early Career Researcher' 2013/2014 from the University of Liverpool

#### 3. J. Major

Presented with a SOLAR UK Young Researcher Award for his work on 'A low cost non-toxic MgCl<sub>2</sub> post-growth activation step for CdTe solar cells'

#### **Editorial Membership**

#### 4. F. Blanc

F Blanc became a member of the editorial board of *Scientific Reports* 

#### Launch Event: Centre for Doctoral Training in New and Sustainable Photovoltaics, November 2014

This year saw the Stephenson Institute launch the new EPSRC Centre for Doctoral Training in New and Sustainable Photovoltaics (CDT-PV). The Centre will train a total of 65 PhD students with the participation of seven leading UK universities and 11 companies. To coincide with the launch, the first cohort of 14 new PhD students from the seven universities were in Liverpool for the first training event. Here they received training on the background physics and chemistry related to PV for their research projects - and the students benefited from the highly relevant contributions of Stephenson Institute staff members: Professor K Durose, Dr T. Veal, Dr V. Dhanak, Dr J. Major and Dr R. Treharne.

Our 50 guests included the project's industry partners who visited the Institute to discuss the potential for future collaborative work with the student cohort. Such interactions permit the CDT students to develop an excellent network of contacts within the field of PV at a very early stage of their careers. The Centre's partners include: Echerkon, Eight19, Loughborough Surface Analysis Ltd, Osilla, Oxford PV, Power Vision, McCamley Middle East, M-Solv, NSG, Silicon CPV and Taylor Hobson.

The objective of the Centre – led by the University of Liverpool in partnership with the universities of Bath, Sheffield, Loughborough, Southampton, Oxford, and Cambridge – is to train highly-skilled PhD students capable of transforming state-of-the art research and development across the sustainable energy and PV sectors. This will in turn aid the country to achieve its renewable energy obligations, and will generate jobs in both the PV and related technology sectors.

The funding for this CDT is part of an overall sum of £350 million, invested by the government and EPSRC, which represents the UK's largest ever commitment to postgraduate training in engineering and physical sciences. Within this CDT, funding is coupled with industry support which will allow the Centre's research outputs to have a direct impact on the skills and knowledge base of the energy sector.

The Centre Director is Professor Ken Durose, the Academic Director is Professor Alison Walker (University of Bath) and the Academic Manager is Dr Rob Treharne. Further information may be found at: <u>www.liverpool.</u> <u>ac.uk/new-and-sustainable-photovoltaics/</u>



Members of the first CDT-PV cohort speaking with Dr. Max Bernheirt from Osilla Ltd, one of the Centre's industry partners

Professor Ken Durose speaking at the CDT-PV Kick-Off event at the Foresight Centre, November 2014





#### Electrochem NW conference

Dr Laurence Hardwick from the Department of Chemistry hosted the Electrochem NW 2014 at the Stephenson Institute for Renewable Energy on 23 June 2014 with some 80 delegates attending. The event was sponsored by the International Society of Electrochemistry and the Royal Society of Chemistry. Electrochem NW is the premier annual meeting of electrochemists working within the northwest of the UK and provides an opportunity to hear of the diverse research taking place in electrochemistry. There was a mix of talks from both academics and industry with a keynote from Professor Karl Ryder from the University of Leicester on Electrochemistry in deep eutectic solvents; metals processing to energy storage. The University of Liverpool was well represented with talks given by Professor Mathias Brust, Dr James Walsh and postgraduates Gary Harlow and Andrea Vezzoli. Representing the Stable Interfaces for Rechargeable Batteries(SIRBATT) project, which is coordinated by Dr Hardwick, Stephan Koch from the Karlsruhe Institute of Technology, Germany, presented research currently being undertaken within the network.

Several trade stands were on display at the Stephenson Institute together with submitted posters. SciMed Scientific and Medical Products Ltd provided a £100 prize for the best poster which was awarded to lain Aldous and Tom Galloway of SIRE ('In Situ Spectroscopic Studies of the Electrochemistry of Dioxygen in Non-Aqueous Li-Oxygen Battery Electrolytes') and Metrohm Autolab UK awarded £100 to Stephan Koch from the Karlsruhe Institute of Technology for the best talk ('In situ investigation of lithium dendrite growth'). Additional sponsorship was received from Acal Energy, Alvatek, and EC-Lab.



### SIRBATT: First Sino-European workshop on the understanding of interfaces in rechargeable batteries

In December 2010 a Joint Statement was signed between the European Commission's Directorate-General for Research and Innovation and the Chinese Ministry of Science and Technology to boost research cooperation on renewable and energy efficient technologies, with special focus on participation of SMEs where appropriate. At a later stage Energy Storage – in particular battery interfaces – was identified as a first area of common interest.

The SIRBATT project (Stable Interfaces for Rechargeable Batteries) based within the Department of Chemistry and the Stephenson Institute for Renewable Energy, was one of four related projects selected by the EC to take part in the first Sino-European Workshop which took place in Tianjin, China on 20th and 21st May 2014. The workshop allowed for the establishment of personal contacts between project partners on both sides. Its main objectives, at this early stage, were to identify issues of common interest for possible future cooperation and to agree to EU-China knowledge exchange.

Dr Gilberto Teobaldi attended this event on behalf of the SIRBATT Consortium's Work Package 3 and presented his research on modelling and simulation of the electrode interface.

Other partners involved in this particular area of SIRBATT research are Universita Degli Studi di Camerino (Italy), Centro de Investigacion Cooperativade Energias Alternativas Fundacion (Spain), Johnson Matthey PLC (UK) and Centre National de la Recherche Scientifique (France).







#### SIRBATT research review meeting, Liverpool 24 and 25 February 2014

The University of Liverpool welcomed representatives from all SIRBATT partners to their first six-monthly, face-to-face, research review meeting. Arrival was Sunday 23 February with a full day meeting at the Hope Street Hotel, Liverpool on Monday 24th. The meeting covered all aspects of our research with each Work Package Leader presenting the progress within their group followed by an opportunity for questions and discussion. In addition there were a number of selected guest speakers who talked on specialist topics within our area of research:

'AC-impedance study of interfacial kinetics in metal/ graphite composite anodes for Li-ion batteries' Francesco Nobili, University of Camerino

'Initial SERS and SHINERS studies on Lithium-Ion Battery Electrolyte' Laura Cabo-Fernandez, University of Liverpool

'First-principles study of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>(111), Li<sub>7</sub>Ti<sub>5</sub>O<sub>12</sub>(111), and a-Li<sub>2</sub>TiO<sub>3</sub>(111) and (100) surfaces for Li-ion battery' Javier Carrasco, CIC energiGUNE

'Subspace corrected functionals for batte electrode interfaces' Gilberto Teobaldi, University of Liverpool



Day two included a tour of the Stephenson Institute for Renewable Energy (SIRE), where the SIRBATT Project is based. The partners had the opportunity to see first-hand the wide ange of energy-related research activities within SIRE that focus on developing clean and sustainable energy technologies.

There was an optional excursion of a 'Shiverpool' ghost tour walk of the local area followed by dinner at the Alma de Cuba Restaurant for those arriving in time on Sunday evening.

The University of Liverpool welcomed representatives from all SIR BATT partners to their first six-monthly, face-to-face, research review meeting.

## Second UK solar fuels symposium, University of Liverpool, 14 January 2014

#### Following on from the success of the first UK solar to fuels meeting, held at the RSC's Burlington House in 2013, the Stephenson Institute and the UK Solar Fuels Network hosted the second UK solar fuels symposium in January 2014.

Solar fuels research focuses on the development of new technologies and materials that uses sunlight to make fuels from abundant resources such as water and carbon-dioxide and this is a rapidly growing area of research both in the UK and world-wide.

For the Liverpool meeting more than 120 registrations from delegates in academia, industry and policy were received leading to the event being sold out some weeks in advance. Following an initial introduction and welcome to Liverpool from the joint meeting chairs, Dr Alex Cowan (Liverpool) and Professor Anthony Harriman (Newcastle), a fascinating range of invited and contributed talks from researchers across the UK were heard. Leading figures in the field including Professor Robin Perutz (York), Professor Fraser Armstrong (Oxford) and Professor Mercedes Maroto-Valer (Heriot Watt) delivered well received insights into a range of topics including light driven CO<sub>2</sub> reduction to fuels, the principles of molecular electrocatalysts for fuel generation and the engineering challenges of developing effective solar to fuels devices.

The meeting also offered a chance for early career researchers to present their work, both through posters and in the form of the excellent contributed talks including those from Dr Fezile Lakadamyali of the University of Cambridge on Dye Sensitized Hydrogen production and Mrs Dávidné Nagy of the University of Edinburgh on composite water splitting materials. The field of solar fuels research brings together a wide range of researchers from across several research areas and it was pleasing to see the, at times extremely lively, interactions between groups during discussion sessions. Following the close of the meeting delegates were given the chance to tour the Stephenson Institute for Renewable Energy.



... a fascinating range of invited and contributed talks from researchers across the UK were heard

## Selected research projects

#### Templated quasicrystalline molecular ordering of archetypal solar cell materials V.R. Dhanak

In this work we used scanning tunnelling microscopy (STM) to demonstrate, two examples of templated growth of quasicrystalline molecular layers of C<sub>60</sub> and pentacene, which are archetypical molecules for organic solar cell devices. C<sub>60</sub> on face-centered icosahedral Al-Cu-Fe and Pn (pentacene) on simple icosahedral Ag-In-Yb form extended quasicrystalline networks with well-defined nucleation sites. The rod-shaped Pn molecules exhibit ordering through their orientations as well as their locations.

Several depositions of  $C_{\rm 60}$  on Al-Cu-Fe were conducted, with the substrate temperature during deposition ranging from 773 K to 973 K. For C<sub>60</sub>/Al-Cu-Fe, shown below in panel a of the figure and in detail in panel b, all molecules occupy quasiperiodic sites. The molecules can be split into two categories: those which appear bright (B) and those which appear  $\dim$  (D). The tenfold symmetry of the B-molecules is clearly visualized in the autocorrelation of molecule locations in panel d of the figure. The molecules adopt positions and orientations on the surface consistent with the guasicrystalline ordering of the substrate. C<sub>60</sub> adsorbs atop sufficiently-separated Fe atoms on icosahedral AI-Cu-Fe to form a unique quasicrystalline lattice whereas further C60 molecules decorate remaining surface Fe atoms in a quasi-degenerate fashion. In the case of pentacene, the molecules adsorb at tenfold-symmetric points around surfacebisected rhombic triacontahedral clusters in icosahedral Ag-In-Yb. These systems constitute the first demonstrations of quasicrystalline molecular ordering on a template. While these studies do not constitute quasicrystalline self-assembly, they point to the possibility of using templated molecular systems to produce larger scale systems with the isotropic photonic band gap demonstrated for metamaterial quasicrystals.



J.A. Smerdon, K.M. Young, M. Lowe, S.S. Hars, T.P. Yadav, D. Hesp, V.R. Dhanak, A.P. Tsai, H.R. Sharma, R. McGrath, *Templated Quasicrystalline Molecular Ordering*, Nano Lett. **14** (2014) 1184.

Quasicrystalline  $C_{60}$  layer on icosahedral Al-Cu-Fe. (a) 50 nm x 50 nm STM image of  $C_{60}$  molecules decorating the Al-Cu-Fe. The molecules indicated are examples of the B and D molecules described in the text. (b) The detail of (a) indicated with a patch of a Penrose P1 tiling superimposed. (c) A saturated quasicrystalline lattice of  $C_{60}$  atop a 10 nm square patch of Al-Cu-Fe (Al grey, Cu brown, Fe red). Magenta molecules decorate a unique lattice, as there are no nearby Fe atoms to provide competing alternative adsorption sites. Blue molecules decorate subsurface centers. (d) The positions of the bright molecules extracted with the associated autocorrelation pattern, showing tenfold symmetry of the layer. Reprinted with permission from J. A. Smerdon et al., Nano Lett., 14 (2014) 2431, Copyright 2014 American Chemical Society.



Room temperature optical absorption spectra from GaSbBi alloys as a function of Bi content between 1.6 and 9.6% with low temperature photoluminescence from a film containing 9.6% Bi inset. This illustrates that these alloys have band gaps in the range applicable to all thermophotovoltaic applications. Reproduced from M.K. Rajpalke et al., J. Appl. Phys. 116 (2014) 043511, Copyright 2014, Authors, Creative Commons Attribution 3.0 Unported License.

## Novel semiconductor alloys for thermophotovoltaics **T. Veal**

Thermophotovoltaics (TPV) is the use of photovoltaic cells to generate electricity from the photons emitted by a heat source. It offers great potential for recovery of waste heat from diverse sources including industrial furnaces used in glass, cement and steel manufacture and also domestic heating systems. Gallium antimonide is the basis of most current TPV systems, but its band gap is too high to be optimum for many applications. As a result, we have developed gallium antimonide bismide (GaSbBi) alloys which have narrower band gaps that are better suited to maximal efficiency TPV. Our research includes exploring molecular beam epitaxy for controlled Bi incorporation in GaSbBi and probing the optical and band structure properties. Bi incorporation of up to 10% of the anion lattice sites has been achieved, enabling the band gap of GaSbBi alloys to be varied between 0.72 and 0.40 eV, the range required for TPV applications.

M.K. Rajpalke, W.M. Linhart, M. Birkett, K.M. Yu, J. Alaria, J. Kopaczek, R. Kudrawiec, T.S. Jones, M.J. Ashwin, T.D. Veal, *High Bi content GaSbBi alloys*, J. Appl. Phys. **116** (2014) 043511.

# Understanding reaction pathways in alkali metal-air batteries for high energy storage **L.J. Hardwick**

The global market for lithium-ion batteries is expected to increase to \$30 billion by 2017. Lithium-air or lithium-oxygen (Li-O<sub>2</sub>) batteries are an important technology for future energy storage because they have theoretical energy densities that are almost an order of magnitude greater than the state-of-the-art Li-ion battery. The energy storage needs of society in the long-term are likely to demand batteries for both stationary power storage to collect unwanted energy generated from solar and wind farms and batteries to power electric vehicles. The success of these technologies underpins the UK's need to move to a lower carbon and greener economy which is less reliant on carbon dioxide generating fossil fuels.

The development of Li-O<sub>2</sub> batteries is being hampered by lack of understanding of the complexity of products formed on the air-cathode during reduction and oxidation. Spectroscopy is critical for identification of products and the understanding of the chemistry at the interface of electrodes. Moreover advanced *in situ* spectroelectrochemical techniques help us to comprehend these complex interfaces whilst under full electrochemical control. The goal of our work is to enable the uptake of this technology by fully understanding the reduction and oxidation pathways taking place in Li-O<sub>2</sub> batteries.

Fundamental studies of dioxygen electrochemistry commonly require conductive supporting salts, such as tetraalkylammonium (TAA), to sustain redox processes in nonaqueous electrolytes. Electrochemical analysis of the formation and oxidation of superoxide on planar electrodes has shown a decrease in reversibility and lowering of the oxygen reduction rate constant when TAA cation alkyl chain length



Reorientation of tetra-alkyl ammonium ions at the electrode interface at ORR

is increased. Probing interfacial regions on Au using *in situ* surface enhanced Raman spectroscopy (SERS) provides evidence that this is caused by the changing adsorption characteristics of TAA cations under negative potentials (see the figure). These effects are heightened with longer alkyl chain lengths, therefore reducing the reversibility of superoxide formation and dioxygen evolution. From these observations it can be established that shorter chain TAA cations while retaining necessary conductive support: (1) enhance reversibility and rate of superoxide formation and oxidation and (2) for *in situ* SERS, have lower preference for adsorption, thus improving experimental detection of superoxide at the Au electrode interface.

I.M. Aldous, L.J. Hardwick, *Influence of Tetraalkylammonium Cation Chain Length on Gold and Glassy Carbon Electrode Interfaces for Alkali Metal-Oxygen Batteries*, J. Phys. Chem. Lett. **5** (2014) 3924.

The alternating layers of YFeO<sub>3</sub> (magenta block) and LaFeO<sub>3</sub> (cyan block) give the structure its unusual polarisation properties. Reproduced with permission from J. Alaria et al. Chem. Sci. 5 (2014) 1599. Copyright 2014 Royal Society of Chemistry.



#### Artificial growth of improper multiferroic thin films J. Alaria

Materials functionalities are often limited by their intrinsic physical properties. If it is possible to tune the properties using control of the structure and composition, coupling functionalities is technologically difficult. Based on the recent development in oxide superlattice growth in the University of Liverpool (Alaria et al. Chem. Sci. 2014) it is possible to explore a new class of material where both electrical polarisation and spontaneous magnetic moment coexist at room temperature. The project will focus on the layer by layer growth of oxide superlattice on single crystal wafers using pulsed laser deposition with the aim to produce materials with both switchable electrical polarisation and magnetic moment of a new type of low power consumption non-volatile memories for information storage and contribute to achieve green computing.

J. Alaria, P. Borisov, M.S. Dyer, T.D. Manning, S. Lepadatu, M.G. Cain, E.D. Mishina, N.E. Sherstyuk, N.A. Ilyin, J. Hadermann, D. Lederman, J.B. Claridge, M.J. Rosseinsky, *Engineered spatial inversion symmetry breaking in an oxide heterostructure built from isosymmetric room-temperature magnetically ordered components*, Chem. Sci. 5 (2014) 1599.

#### Dynamic Nuclear Polarization enhanced Solid State NMR Spectroscopy of Insensitive Nuclear Spins: Towards the Understanding of ProtonTrap Effects in Fast Proton Conductors for Fuel Cells

#### F. Blanc

Solid-state Nuclear Magnetic Resonance (ssNMR) spectroscopy is the most powerful technique for structure elucidation of solids. However, due to the low nuclear spin polarization at room temperature, ssNMR often suffers from a lack of sensitivity, preventing even wider use of the technique, despite the introduction and widespread implementation of cross polarization, magic angle spinning and high magnetic fields. The challenge of low sensitivity in NMR is exacerbated further for nuclei with low gyromagnetic ratio, g such as <sup>89</sup>Y.

In recent years, hyperpolarization methods (ie polarization of the nuclear spins beyond their intrinsic Boltzmann distribution) have blossomed and in particular Dynamic Nuclear Polarization (DNP) enhanced ssNMR spectroscopy has become a very powerful approach for enhancing the signal by multiple orders of magnitude,1-3 making use of a microwave-induced transfer of polarization from electron to nuclear spins at cryogenic temperatures.

Using this powerful approach, we have been able to detect <sup>89</sup>Y nuclear spins very quickly (see figure) and demonstrated the detection of the <sup>89</sup>Y and <sup>1</sup>H NMR signals from hydrated yttrium doped zirconate ceramics  $BaZr_{0.8}Y_{0.2}O_{2.9}(OH)_{0.1}$ , a technologically-important proton electrolytes for solid oxide fuel cells, in combination with DFT calculations, allows the local yttrium and proton environments present in these protonic conductors to be detected and assigned to different

hydrogen-bonded environments. In particular, these DNP enhanced ssNMR experiments demonstrate the existence of proton trap sites in this material and confirm our earlier work which postulated the existence of such site and investigate the diffusion of protons using a multidisciplinary approach centred around defect chemistry models, impedance spectroscopy and very high temperature <sup>1</sup>H ssNMR.

1. F. Blanc, L. Sperrin, D. Lee, R. Dervişoğlu, Y. Yamazaki, S.M. Haile, G. De Paëpe, C.P. Grey, *Dynamic Nuclear Polarization NMR of Low Gamma Nuclei: Structural Insights into Hydrated Yttrium-doped BaZrO<sub>3</sub>*, J. Phys. Chem. Lett. **5** (2014) 2431.

2. F. Blanc, L. Sperrin, D. A. Jefferson, S. Pawsey, M. Rosay, C.P. Grey, *Dynamic Nuclear Polarization Enhanced Natural Abundance* <sup>17</sup>O spectroscopy, J. Am. Chem. Soc. **135** (2013) 2975.

3. F. Blanc, S. Y. Chong, T.O. McDonald, D.J. Adams, S. Pawsey, M.A. Caporini, A.I. Cooper, *Dynamic Nuclear Polarization NMR Spectroscopy Allows High Throughput Characterization of Microporous Organic Polymers*, J. Am. Chem. Soc. **135** (2013) 15290.

4. Y. Yamazaki, F. Blanc, Y. Okuyama, L. Buannic, J.C. Lucio-Vega, C.P. Grey, S.M. Haile, *Proton Trapping in Yttrium-doped Barium Zirconate*, Nat. Mat. **12** (2013) 647.



Contour plot of the two-dimensional <sup>1</sup>H <sup>89</sup>Y CP MAS FSLG HETCOR spectrum of hydrated 20 % doped BaZrO<sub>3</sub> recorded at 9.4 T (exptl. time = 15 h). Top: <sup>1</sup>H <sup>89</sup>Y CP MAS spectra. Left: <sup>1</sup>H MAS spectrum of the sample obtained at ~105 K without polarizing agents or solvents. The experimental and DFT-calculated <sup>1</sup>H and <sup>89</sup>Y isotropic chemical shifts are indicated on the spectra. Insets show the optimized local structures about yttrium atoms (purple). Zirconium, oxygen and hydrogen atoms are in blue, red and white, respectively. Barium atoms have been omitted for clarity. Reprinted with permission from F. Blanc et al., J. Phys. Chem. Lett. 5 (2014) 2431, Copyright 2014 American Chemical Society.

#### Biomimetic nanovalves for storage and controlled release of small molecules in functional nanocontainers D. Shchukin

Biological systems with controlled release functionality, which are among the successful examples of creatures to survive in evolution, have attracted intensive investigation and been mimicked due to their broad spectrum of applications. So far, however, the biomimetic or bioinspired controlled release systems only performed effectively for cargo molecules with at least one dimension larger than 1 nm, such as drugs ( $\geq$  1 nm), enzyme, protein ( $\geq$  50 nm) and cell (~10-30 µm). A challenge remains in preventing the premature leakage and facilitating stimuliresponsive release of the entrapped cargo with a dimension around 5 Å or even smaller. Unfortunately, the well-known mechanisms for controlled release mainly depend on covering and opening the pores or switching between electrostatic repulsion and attraction, which would, in many cases, fail in pumping low molecular weight compounds.



Structure of the nanovalve system. (a) Schematic representation of components forming the nanovalve system and mechanism of selective permeability and pH sensitivity of it: premature leakage will be prevented by capturing the selectively detained cargo, for example benzotriazole, via strong complexation (log  $K_{\text{stab}} > 3$ ) between cargo molecules and unsheltered metal centers. The lower two cartoons are derived from crystal structure of CoCO<sub>3</sub> to highlight the complexation between cargo and nanovalve, as well as acid induced ① partial and gradual dissolution of valve structure and (2) dissociation of CO2+-cargo complex bonding. (b) HAADF-STEM and elemental mappings images of loaded MCM-41 nanoparticle with nanovalves at its surface. Silicon, carbon and cobalt element mapping are presented. Scale bar: HAADF-STEM 50 nm, elemental mapping 100 nm. (c) Premature leakage of Rhodamine B (purple), calcein (vellow), p-coumaric acid (green) and BTA (grey) from containers sealed by Co-Carbonate nanovalves.

Inspired by effective biological valve systems – nuclear pore complexes, which control the permeability with their three-dimensional structure and reversible complexation with cargo molecules, we have formed a novel sieving structure with controllable pore opening for small energy-enriched cargo molecules. Two theoretical models have been proposed for the first time and examined by the experimental and fitting results. The selective adsorption for small molecules and passive barrier for larger ones have been realized at the same time. We have chosen energy delivery and fast environment detection as promising applications because these two fields were often neglected by scientists working in controlled release field due to the limit in finding method to minimize the premature leakage of small functional molecules and scale up the product for commercial use. We believe the results of our project can provide more controlled release systems applicable in the fields outside biomedicine.

Z.L. Zheng, X. Huang, D. Shchukin, A *cost-effective pH-sensitive release system for* water source pH detection, Chem. Comm. **50** (2014) 13936.

T.N. Borodina, D.O. Grigoriev, M.A. Carillo, J. Hartmann, H. Moehwald, D.G. Shchukin, *Preparation of Multifunctional Polysaccharide Microcontainers for Lipophilic Bioactive Agents*, ACS Appl. Mat. & Interf. **6** (2014) 6570.





#### A low cost, non toxic alternative method for processing thin film solar cells J. Major

A SIRE project of a team around Drs Jon Major, Rob Treharne, Laurie Phillips and Prof Ken Durose has overturned a 30-year-old solar cell manufacturing protocol and promises to both slash the costs and improve safety in the industry. It was published in Nature and became the focus of a significant international press story.

As everyone knows, the big issue with solar PV is cost – although costs are tumbling the whole time as the industry expands, most sales globally still rely on government subsidies. Thin film competitors to the market leading silicon, are cheaper, but even the cheapest solar technology in the world, cadmium telluride, continually seeks factory and production efficiencies in order to stay ahead.

Right now the cadmium telluride market accounts for about 2GWp per annum, which at \$0.5 per Wp is a market of \$1,000,000,000 per annum. Even small savings in the industry scale up to a massive cash saving.

The innovation of thin film technology comes from making cheap and imperfect materials work with the same efficiency as more expensive and more perfect materials. The cadmium telluride used is a polycrystalline thin film. Normally we would expect a semiconductor with so many grain boundaries to be electrically dead and for the material to be useless. However, it has been known for 30 years or so that the grain boundaries can be chemically passivated. This is the basis of the entire industry.

The problem is that the crucial passivating chemical that works best is cadmium chloride, which is a water soluble toxic salt. It is the chlorine that does the job, but alternatives have been resisted for years for fear that they might introduce foreign impurities that harm the cell performance. The innovation, first suggested by Rob Treharne, was to use a magnesium chloride alternative. The idea was seized upon by cell maker Jon Major who quickly tried it out on real devices. Excellent solar cell device results came quickly, with the performance of cells from the new process rapidly equalling those from the traditional one. Over the next two years Jon investigated alternatives, screening the whole periodic table for suitable candidates but magnesium chloride did indeed prove to be the most suitable and was the subject of a Nature paper in 2014. Magnesium chloride finds uses in daily life as bath salts, is edible and is used for the coagulation of soya milk to make tofu. It's this that helped make the report a hit with the press. Jon gave a press conference at the European Science Open Forum conference in Copenhagen, and it was taken up by BBC TV News Science correspondent Palab Ghosh and a cameraman spent the day in SIRE with Jon, and his report was broadcast on BBC1 TV news in July. The item also made it to the BBC Radio 4 news, and its flagship science programme 'Inside Science'. The Independent carried the story as front page news, with its Editorial championing our message of taking solar PV out of the subsidy driven market by making genuine improvements to cost-effectiveness by science driven progress and improvements.

Overall the method has allowed us to create solar cells with the same 16% efficiency as with the traditional process – a result that has gained worldwide attention in the thin film solar community.

J.D. Major, R.E. Treharne, L.J. Phillips, K. Durose, *A low-cost non-toxic post-growth activation step for CdTe solar cells*, Nature **511** (2014) 334.



## Spin polarized electron transfer at ferromagnet/organics interfaces **G. Teobaldi**

Since the introduction in 2005 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 capture, the uptake of this new technology in wind and tide farms 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 light room-temperature ferromagnets to potentially substitute Nd-Fe-B in DDFMG turbines, opening up for a more scalable design. Unfortunately, generation of room temperature ferromagnetism from inexpensive, low-toxicity, non-magnetic materials such as molecular semiconductors and light metals is to date an unsolved challenge. Transfer of magnetization from a ferromagnetic substrate to an originally non-magnetic molecular material is one of the strategies currently explored to generate room-temperature magnetic ordering in light semi-conducting materials.

The contact between organic molecules and ferromagnetic metallic electrode contributes to or even determines the electronic and magnetic properties of the hybrid ferromagnet/organics interface. This is partly due to the charge transfer that takes place when two materials with different chemical potentials are put together. In the case of magnetic electrodes, the transfer can be accompanied by the transmission of a net spin polarization or spin doping. In nanocarbon systems, hybridization and spin doping can suppress the magnetic moment of a transition metal ferromagnet through the loss of majority spin electrons to the organic. Here, fullerene  $C_{60}$  is found to become ferromagnetic as a result of spin doping from cobalt with an induced moment of 1.2  $\mu$ B per cage while suppressing the moment of the ferromagnet by up to 21%. Polarized



The saturation magnetization, its suppression and coercivity enhancement for varying film thicknesses of C<sub>60</sub> deposited on (5 nm thick) Co-films. Reprinted with permission from T. Moorsom et al. Phys. Rev.B 90 (2014) 125311. Copyright 2014 American Physical Society.

neutron reflectivity, x-ray magnetic circular dichroism and density functional theory simulation reveal the presence of an anti-ferromagnetic coupling of the interfacial layers of cobalt and  $C_{60}$ , and weakly coupled induced magnetism propagating up to 200 nm into the bulk organic. It is thus shown that the deposition of molecules with high electron affinity can be used to induce zero-voltage spin injection. These novel findings should be useful to inform the design of novel hybrid magnetic interfaces based on light, non-toxic and abundant elements such as carbon.

T. Moorsom, M. Wheeler, T.M. Khan, F. Al Ma'Mari, C. Kinane, S. Langridge, D. Ciudad, A. Bedoya-Pinto, L. Hueso, G. Teobaldi, V.K. Lazarov, D. Gilks, G. Burnell, B.J. Hickey and O. Cespedes, *Spin-polarized electron transfer in ferromagnet/C*<sub>60</sub> *interfaces*, Phys. Rev.B **90** (2014) 125311.

### Catalytic CO<sub>2</sub> reduction to fuels **A. Cowan**

Our work explores the use of new catalysts for the reduction of carbon dioxide to useful fuels and feedstocks such as methanol and carbon monoxide. In this study we have developed new low cost electrocatalysts, materials that use electrical energy to drive the production of fuels from water and carbon dioxide, that are prepared using carbon nanotubes a polymeric membrane and a manganese complex. The electrocatalyst is able to maintain high current densities for CO<sub>2</sub> reduction and in water shows reasonable selectivity with mixtures of H<sub>2</sub> and CO being produced. Through potentiostatic control it is possible to control the H<sub>2</sub>:CO and ratios suitable for use as syngas in Fischer Tropsch chemistry (H<sub>2</sub>:CO ~ 2:1) are achieved. The ultimate goal of the groups work is to build new materials that incorporate the new electrocatalysts onto light absorbing semiconductors so that we are able to produce fuels using only sunlight, water and carbon dioxide as the inputs.

J.J. Walsh, G. Neri, C.L. Smith, A.J. Cowan, *Electrocatalytic CO₂reduction with a membrane supported manganese catalyst in aqueous solution*, Chem. Commun. **50** (2014) 12698.

Electrocatalytic reduction of  $CO_2$  in water to produce CO and  $H_2$ , a mixture otherwise known as syngas, was reported in 2014 using a low cost polymer immobilised catalyst.

#### Molybdenum carbide nanoparticles within carbon nanotubes as superior catalysts for γ-valerolactone production as biofuel J.A. Lopez-Sanchez

The use of waste biomass for the production of biofuels and high value-added chemicals is a key point towards the development of a sustainable economy. Indeed, biomass is the only renewable and sustainable source of organic molecules. In order to cope with the increasing demands in energy of the industrial and transport sectors, extensive research has been dedicated to improving the technologies which are able to transform biomass into value-added bio-derived compounds in a sustainable way. The conversion of residual biomass into platform molecules has attracted a great deal of attention because these platform molecules can be converted into an enormous variety of high value-added organic compounds. In particular, the production of  $\gamma$ -valerolactone (GVL) via the selective hydrogenation of levulinic acid (LA) (see scheme) is of high interest because of its applicability as a green solvent, a gasoline blender (can be mixed in any proportion to gasoline), and as a diesel precursor. In partnership with Victor Teixeira in UFRJ (Brazil) we have developed catalysts that can selectively produce y-valerolactone through levulinic acid hydrogenation at 30 bar of hydrogen pressure based on molybdenum carbide supported on activated carbon and on carbon nanotubes in a continuous reactor with water as the solvent. Particularly, when the carbide nanoparticles are positioned within the carbon nanotubes, conversions and selectivities above 90% were observed at 30 bar of H<sub>2</sub> and 200 °C using a continuous-flow trickle-bed reactor. The choice of carbon support had a large effect on the particle size, morphology and catalyst activity. When the Mo<sub>2</sub>C was prepared on carbon nanotubes most of the nanoparticles are encapsulated within the nanotubes and the Mo<sub>2</sub>C phase (see figure) and they display a higher activity (TOF) than ruthenium supported on activated carbon which is the standard for this reaction. In view of the sustainability and price limitations that noble metals have, the application of Mo<sub>2</sub>C for y-valerolactone production represents an excellent example of a necessary shift to more sustainable catalysts for the upgrade of bio-derived chemicals.

#### 1. J.A. Lopez-Sanchez, The Future of Feedstocks, Chem. World 3 (2014) 45.

2. M.A.M. Estevão Frigini Maia, T.E. Davies, J.A. Lopez-Sanchez, V. Teixeira da Silva, *Molybdenum carbide nanoparticles within carbon nanotubes as superior catalyst for*  $\gamma$ -*Valerolactone production via levulinic acid hydrogenation*, Green Chem. **16** (2014) 4092.





TEM micrographs of Mo₂C/ CNT at 150k× (a), 300k× (b) magnifications and the particle size distribution (c). Reproduced with permission from M.A.M. Estevão Frigini Maia et al. Green Chem. 16 (2014) 4092. Copyright 2014 Royal Society of Chemistry.





Reaction pathways for γ-valerolactone formation. Reproduced with permission from M.A.M. Estevão Frigini Maia et al. Green Chem. 16 (2014) 4092. Copyright 2014 Royal Society of Chemistry.

## Publications by SIRE members in 2014

J. Alaria, P. Borisov, M.S. Dyer, T. D. Manning, S. Lepadatu, M.G. Cain, E.D. Mishina, N.E. Sherstyuk, N.A. Ilyin, J. Hadermann, D. Lederman, J.B. Claridge, M.J. Rosseinsky, *Engineered spatial inversion symmetry breaking in an oxide heterostructure built from isosymmetric room-temperature magnetically ordered components*, Chem. Sci. **5** (2014) 1599.

I.M. Aldous, L.J. Hardwick, *Influence of Tetraalkylammonium Cation Chain Length on Gold and Glassy Carbon Electrode Interfaces for Alkali Metal–Oxygen Batteries*, J. Phys. Chem. Lett. **5** (2014) 3924.

J.S. Bair, Y. Schramm, A.G. Sergeev, E. Clot, O. Eisenstein, J.F. Hartwig *Linear-Selective Hydroarylation of Unactivated Terminal and Internal Olefins with Trifluoromethyl-Substituted Arenes.* J. Am. Chem. Soc. **136** (2014) 13098.

F. Blanc, L. Sperrin, D. Lee, R. Dervişoğlu, Y. Yamazaki, S.M. Haile, G. De Paëpe, C.P. Grey, *Dynamic Nuclear Polarization. NMR of Low Gamma Nuclei: Structural Insights into Hydrated Yttrium-doped BaZrO*<sub>3</sub>, J. Phys. Chem. Lett. **5** (2014) 2431.

K. Borisov, J. Alaria, J.M.D. Coey, P. Stamenov, *High field magnetotransport and point contact Andreev reflection measurements on CuCr<sub>2</sub>Se<sub>4</sub> and CuCr<sub>2</sub>Se<sub>3</sub>Br-Degenerate magnetic semiconductor single crystals, J. Appl. Phys. 115 (2014) 17C717.* 

T.N. Borodina, D.O. Grigoriev, M.A. Carillo, J. Hartmann, H. Moehwald, D.G. Shchukin, *Preparation of Multifunctional Polysaccharide Microcontainers for Lipophilic Bioactive Agents*, ACS Appl. Mat. & Interf. **6** (2014) 6570.

J. Buckeridge, D.O. Scanlon, T.D. Veal, M.J. Ashwin, A. Walsh, C.R.A. Catlow, *Incorporation and associated localized vibrational modes in GaSb*, Phys. Rev. B **89** (2014) 014107.

R. Ciriminna, P.D. Cara, J. A. Lopez-Sanchez, M. Pagliaro, *Catalysis via Sol-Gel Acid Silicas: An Important Chemical Technology for 2<sup>nd</sup> Generation Biorefineries*, ChemCatChem **6** (2014) 3053.

R. Ciriminna, M. Lomeli-Rodriguez, P.D. Cara, J.A. Lopez-Sanchez, M. Pagliaro, Limonene: a versatile chemical of the bioeconomy, Chem. Comm. **50** (2014) 15288.

R. Dawson, L.A. Stevens, O.S.A. Williams, W. Wang, B.O. Carter, S. Sutton, T.C. Drage, F. Blanc, D.J. Adams, A.I. Cooper, "*Dry Bases*": *Carbon Dioxide Capture using Alkaline Dry Water*, Energy & Environ. Sci. **7** (2014) 1786.

R. Dervisoglu, D.S. Middlemiss, F. Blanc, L.A. Holmes, Y.-L. Lee, D. Morgan, C.P. Grey, *Joint Experimental and Computational* <sup>17</sup>O Solid State NMR Study of Brownmillerite Ba<sub>2</sub>/n<sub>2</sub>O<sub>5</sub> (Part I), Phys. Chem. Chem. Phys. **16** (2014) 2597.

N. Dimitratos, J.A. Lopez-Sanchez, G.J. Hutchings, *Supported metal nanoparticles in liquid-phase oxidation reactions, In: D. Duprez, F. Cavani, Eds., Handbook of Advanced Methods and Processes in Oxidation Catalysis. From Laboratory to Industry,* London: World Scientific Publishing (2014) 631.

E.R. Draper, J.J. Walsh, T.O. McDonald, M.A. Zwijnenburg, P.J. Cameron, A.J. Cowan, D.J. Adams, *Air-stable photoconductive films formed from perylene bisimide gelators*, J. Mat. Chem. C **2** (2014) 5570.

R. Dryfe, G.Z. Chen, D. Bayer, M. Jonsson-Niedziolka, R. McCreery, J. Macpherson, H. Abruna, Y. Gogotsi, C.-C. Hu, F. Beguin, L. Hardwick, J. Foord, M. Duca, E. Howe, K. Holt, M. Alvarez-Guerra, P.R. Unwin, T. Rabbow, M. Shaffer, J.-S. Lee, E. Frackowiak, F. Qiu, B. Dyatkin, P.A. Ash, K. Stevenson, D. Guldi, P. Bergonzo, *The many faces of carbon in electrochemistry: general discussion*, Faraday Discussions. **172** (2014) 117.

N. Feldberg, J.D. Aldous, P.A. Stampe, R.J. Kennedy, T.D. Veal, S.M. Durbin, *Growth of ZnSnN*<sub>2</sub> by *Molecular Beam Epitaxy*, J. Electr. Mater. **43** (2014) 884.

M.M. Forde, R.D. Armstrong, R. McVicker, P.P. Wells, N. Dimitratos, Q. He, L. Lu, R.L. Jenkins, C. Hammond, J.A. Lopez-Sanchez, C.J. Kiely, G.J. Hutchings, *Light alkane oxidation using catalysts prepared by chemical vapour impregnation: tuning alcohol selectivity through catalyst pre-treatment*, Chem. Sci. **5** (2014) 3603.

M. Forde, L. Kesavan, M.I. bin Saiman, Q. He, N. Dimitratos, J.A. Lopez-Sanchez, R.L. Jenkins, S.H. Taylor, C.J. Kiely, G.J. Hutchings, *High Activity Redox Catalysts Synthesized by Chemical Vapor Impregnation*, ACS Nano **8** (2014) 957.

Y. Gogotsi, D. Guldi, R. McCreery, C.-C. Hu, C. Merlet, F. Beguin, L. Hardwick,
E. Frackowiak, J. Macpherson, A. Forse, G.Z. Chen, K. Holt, R. Dryfe, H. Kurig,
S. Sharma, P.R. Unwin, T. Rabbow, W. Yu, F. Qiu, F. Juarez, C. Sole, B. Dyatkin,
K. Stevenson, Y. Cao, N. Cousens A. Noofeli , *Carbon electrodes for energy storage:* general discussion, Faraday Discussions. **172** (2014) 239.

F. Golks, Y. Gruender, J. Stettner, K. Krug, J. Zegenhagen, O.M. Magnussen *In situ* surface *x-ray diffraction studies of homoepitaxial growth on Cu(001) from aqueous acidic electrolyte*, Surf. Sci. **631** (2014) 112.

D. Grigoriev, D. Akcakayiran, M. Schenderlein, D. Shchukin, *Protective Organic Coatings with Anticorrosive and Other Feedback-Active Features: Micro- and Nanocontainers-Based Approach*, Corrosion **70** (2014) 446.

Y. Gruender, A. Druenkler, F. Golks, G. Wijts, J. Stettner, J. Zegenhagen, O.M. Magnussen, *Cu(111) in chloride containing acidic electrolytes: Coadsorption of an oxygenated species*, J. Electroanal. Chem. **712** (2014) 74.

Y. Gruender, N.M. Markovic, P. Thompson, C.A. Lucas, *Temperature effects* on the atomic structure and kinetics in single crystal electrochemistry, Surf. Sc. **631** (2014) 123.

Y.S. Han, D. Shchukin, J. Schneider, H. Mohwald, *Fluorescence indicative pH drop in sonication*, Coll. Surf. A-Physicochem. Engin. Asp. **445** (2014) 30.

V.D. Hodoroaba, D. Akcakayiran, D.O. Grigoriev, D.G. Shchukin, *Characterization of micro- and nanocapsules for self-healing anti-corrosion coatings by high-resolution SEM with coupled transmission mode and EDX*, Analyst **139** (2014) 2004.

M. Iftekhar, N.E. Drewett, A.R. Armstrong, D. Hesp, F. Braga, S. Ahmed, L.J. Hardwick, *Characterization of Aluminum Doped Lithium-Manganese Rich Composites for Higher Rate Lithium-Ion Cathodes*, J. Electrochem. Soc., **161** (2014) A2109.

A.P. Katsoulidis, K. Sung Park, D. Antypov, C. Martí-Gastaldo, G.J. Miller, J.E. Warren, C.M. Robertson, F. Blanc, G. Darling, N. Berry, J.A. Purton, D.J. Adams, M.J. Rosseinsky, *Guest Adaptable and Water Stable Peptide Based Porous Materials by Imidazolate Sidechain Control*, Angew. Chem. Int. Ed. **125** (2014) 1.

M.O. King, I.M. McLeod, D. Hesp, V.R. Dhanak, A. Tadich, L. Thomsen, B.C.C. Cowie, D.A. MacLaren, M. Kadodwala , *The templated growth of a chiral transition metal chalcogenide*, Surf. Sci. **629** (2014) 94.

B. Kisan, P.C. Shyni, S. Layek, H.C. Verma, D. Hesp, V. Dhanak, S. Krishnamurthy A. Perumal, *Finite Size Effects in Magnetic and Optical Properties of Antiferromagnetic NiO Nanoparticles*, IEEE Trans. Magn. **50** (2014) 2300704.

B. Kiss, C. Didier, T. Johnson, T.D. Manning, M.S. Dyer, A.J. Cowan, J.B. Claridge, J.R. Darwent, M.J. Rosseinsky, *Photocatalytic Water Oxidation by a Pyrochlore Oxide upon Irradiation with Visible Light: Rhodium Substitution Into Yttrium Titanate*, Angew. Chem. Int. Ed. **53** (2014) 14480.

J. Kopaczek, R. Kudrawiec, W. Linhart, M. Rajpalke, T. Jones, M. Ashwin, T. Veal, Low- and high-energy photoluminescence from  $GaSb_{t,x}Bi_{x}$  with 0 < x < 0.042, Appl. Phys. Expr. **7** (2014) 111202. J. Kopaczek, R. Kudrawiec, M.P. Polak, P. Scharoch, M. Birkett, T.D. Veal, K. Wang, Y. Gu, Q. Gong, S. Wang, *Contactless electroreflectance and theoretical studies of band gap and spin-orbit splitting in*  $InP_{t,x}B_{ix}$  *dilute bismide with* x < 0.034, Appl. Phys. Lett. **105** (2014) 222104.

J. Kopaczek, M.K. Rajpalke, W.M. Linhart, T.S. Jones, M.J. Ashwin, R. Kudrawiec, T.D. Veal, *Photoreflectance spectroscopy of GalnSbBi and AlGaSbBi quaternary alloys*, Appl. Phys. Lett. **105** (2014) 112102.

M. Lahti, A. Chaudhuri, K. Pussi, D. Hesp, I.M. McLeod, V.R. Dhanak, M.O. King, M. Kadodwala, D.A. MacLaren, *The structural analysis of Cu*(*111*)-*Te (root 3 x root 3) R30 degrees and (2 root 3 x 2 root 3)R30 degrees surface phases by quantitative LEED and DFT*, Surf. Sci. **622** (2014) 35.

W. Li, T. Dittrich, F. Jäckel, J. Feldmann, *Optical and Electronic Properties of Pyrite Nanocrystal Thin Films: the Role of Ligands*, Small **10** (2014) 1194.

E.F. Mai, M.A. Machado, T.E. Davies, J.A. Lopez-Sanchez, V.T. da Silva, *Molybdenum carbide nanoparticles within carbon nanotubes as superior catalysts for gamma-valerolactone production via levulinic acid hydrogenation*, Green Chemistry **16** (2014) 4092.

J.D. Major, L. Bowen, R. Treharne, K. Durose, Assessment of photovoltaic junction position using combined focused ion beam and electron beam-induced current analysis of close space sublimation deposited CdTe solar cells, Progr. Photovolt. 22 (2014) 1096.

J.D. Major, R.E. Treharne, L.J. Phillips, K. Durose, *A low-cost non-toxic post-growth activation step for CdTe solar cells*, Nature **511** (2014) 334.

G. Mandi, G. Teobaldi, K. Palotas, *Contrast stability and 'stripe' formation in scanning tunnelling microscopy imaging of highly oriented pyrolytic graphite: the role of STM-tip orientations*, J. Phys. –Cond. Matt. **26** (2014) 48.

B.G. Mendis, M.D. Shannon, M.C.J. Goodman, J.D. Major, R. Claridge, D.P. Halliday, K. Durose, *Direct observation of Cu, Zn cation disorder in Cu<sub>2</sub>ZnSnS*<sub>4</sub> *solar cell absorber material using aberration corrected scanning transmission electron microscopy*, Progr. Photovolt. **22** (2014) 24.

I.Z. Mitrovic, M. Althobaiti, A.D. Weerakkody, V.R. Dhanak, W.M. Linhart, T.D. Veal, N. Sedghi, S. Hall, P.R. Chalker, D. Tsoutsou, A. Dimoulas, *Ge interface engineering using ultra-thin La*<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub> *tilms: A study into the effect of deposition temperature*, J. Appl. Phys. **115** (2014) 11.

I.Z. Mitrovic, M. Althobaiti, A.D. Weerakkody, N. Sedghi, S. Hall, V.R. Dhanak, S. Mather, P.R. Chalker, D. Tsoutsou, A. Dimoulas, C. Henkel, E.D. Litta, P.E. Hellstrom, M. Ostling, *Interface Engineering Routes for a Future CMOS Ge-based Technology, Dielectrics for Nanosystems 6: Materials Science*, Processing, Reliability, and Manufacturing **61** (2014) 73.

T. Moorsom, M. Wheeler, T.M. Khan, F. Al Ma'Mari, C. Kinane, S. Langridge, D. Ciudad, A. Bedoya-Pinto, L. Hueso, G. Teobaldi, V.K. Lazarov, D. Gilks, G. Burnell, B.J. Hickey, O. Cespedes, *Spin-polarized electron transfer in ferromagnet/C*<sub>60</sub> *interfaces*, Phys. Rev.B **90** (2014) 12.

A.R. Neale, Y. Jin, J. Ouyang, S. Hughes, D. Hesp, V. Dhanak, G. Dearden, S. Edwardson, L.J. Hardwick, *Electrochemical performance of laser micro-structured nickel oxyhydroxide cathodes*, J. Power Sources. **271** (2014) 42.

S. Nedev, S. Carretero-Palacios, S.R. Kirchner, F. Jäckel, J. Feldmann, *Microscale mapping of oscillatory flows*, Appl. Phys. Lett. **105** (2014) 161113.

E. Pastor, F.M. Pesci, A. Reynal, A.D. Handoko, M.J. Guo, X.Q. An, A.J. Cowan, D.R. Klug, J.R. Durrant, J.W. Tang, *Interfacial charge separation in Cu\_2O/RuO\_x as a visible light driven CO<sub>2</sub> reduction catalyst, Phys. Chem. Chem. Phys. 16 (2014) 5922.* 

E.M. Perassi, C. Hrelescu, A. Wisnet, M. Doblinger, C. Scheu, F. Jäckel, E.A. Coronado, J. Feldmann, *Quantitative Understanding of the Optical Properties of a Single, Complex-Shaped Gold Nanoparticle from Experiment and Theory*, ACS Nano **8** (2014) 4395.

A.M. Peterson, C. Pilz-Allen, T. Kolesnikova, H. Mohwald, D. Shchukin, *Growth Factor Release from Polyelectrolyte-Coated Titanium for Implant Applications*, ACS Appl. Mater. & Interf. **6** (2014) 1866.

A.M. Peterson, C. Pilz-Allen, H. Mohwald, D.G. Shchukin, *Evaluation of the role of polyelectrolyte deposition conditions in growth factor release*, J. Mater. Chem. B **2** (2014) 2680.

M.P. Polak, P. Scharoch, R. Kudrawiec, J. Kopaczek, M.J. Winiarski, W.M. Linhart, M.K. Rajpalke, K.M. Yu, T.S. Jones, M.J. Ashwin, T.D. Veal, *Theoretical and experimental studies of electronic band structure for GaSb<sub>1-x</sub>B<sub>ix</sub> in the dilute Bi regime*, J. Phys. D-Appl. Phys. **47** (2014) 355107.

M.K. Rajpalke, W. M. Linhart, M. Birkett, K.M. Yu, J. Alaria, J. Kopaczek, R. Kudrawiec, T.S. Jones, M. J. Ashwin, T.D. Veal, *High Bi content GaSbBi alloys*, J. Appl. Phys. **116** (2014) 043511.

M.K. Rajpalke, W.M. Linhart, K.M.Yu, M. Birkett, J. Alaria, J.J. Bomphrey, S. Sallis, L.F.J. Piper, T.S. Jones, M.J. Ashwin, T.D. Veal, *Bi-induced band gap reduction in epitaxial InSbBi alloys*, Appl. Phys. Lett. **105** (2014) 212101.

H.R. Sharma, J.A. Smerdon, P.J. Nugent, A. Ribeiro, I. McLeod, V.R. Dhanak, M. Shimoda, A.P. Tsai, R. McGrath, *Crystalline and quasicrystalline allotropes of Pb formed on the fivefold surface of icosahedral Ag-In-Yb*, J. Chem. Phys. **140** (2014) 17.

D.G. Shchukin, E. Shchukina, *Capsules with external navigation and triggered release*, Curr. Opin. in Pharmacol. **18** (2014) 42.

T. Simon, N. Bouchonville, M.J. Berr, A. Vaneski, A. Adrović, D. Volbers, R. Wyrwich, M. Döblinger, A.S. Susha, A.L. Rogach, F. Jäckel, J.K. Stolarczyk, J. Feldmann, *Redox shuttle mechanism enhances photocatalytic H*<sub>2</sub> generation on Ni-decorated CdS nanorods, Nat. Mat. **13** (2014) 1013.

J.A. Smerdon, K.M. Young, M. Lowe, S.S. Hars, T.P. Yadav, D. Hesp, V.R. Dhanak, A.P. Tsai, H. R. Sharma, R. McGrath, *Templated Quasicrystalline Molecular Ordering*, Nano Lett. **14** (2014) 1184.

C. Sole, N.E. Drewett, L.J. Hardwick, *In situ Raman study of lithium-ion intercalation into microcrystalline graphit*e, Faraday Discussions. **172** (2014) 223.

X.Y. Song, Z.W. Qiu, X.P. Yang, H.B. Gong, S.H. Zheng, B.Q. Cao, H.Q. Wang, H. Mohwald, D. Shchukin, *Submicron-Lubricant Based on Crystallized Fe*<sub>3</sub>O<sub>4</sub> *Spheres for Enhanced Tribology Performance*, Chem. Mater. **26** (2014) 5113.

K.L. Syres, A.G. Thomas, D.M. Graham, B.F. Spencer, W.R. Flavell, M.J. Jackman, V.R. Dhanak, Adsorption and stability of malonic acid on rutile TiO<sub>2</sub> (110), studied by near edge X-ray absorption fine structure and photoelectron spectroscopy, Surf. Sci. **626** (2014) 14.

R.E. Treharne, L.J. Phillips, K. Durose, A. Weerakkody, I.Z. Mitrovic, S. Hall, *Non-parabolicity and band gap re-normalisation in Si doped ZnO*, J. Appl. Phys. **115** (2014) 0635051.

A.S. Urban, S. Carretero-Palacios, A.A. Lutich, T. Lohmüller, J. Feldmann, F. Jäckel, Optical trapping and manipulation of plasmonic nanoparticles: fundamentals, applications, and perspectives, Nanoscale **6** (2014) 4458.

S.K. Vasheghani Farahani, T.D. Veal, J.J. Mudd, D.O. Scanlon, G.W. Watson, O. Bierwagen, M.E. White, J.S. Speck, C.F. McConville, *Valence-band density of states and surface electron accumulation in epitaxial SnO*<sub>2</sub> films, Phys. Rev. B **90** (2014) 155413.

## **Publications** (Continued)

## New funding in 2014

P.V. Wadekar, J. Alaria, M. O'Sullivan, N.L.O. Flack, T.D. Manning, L.J. Phillips,
 K. Durose, O. Lozano, S. Lucas, J.B. Claridge, M.J. Rosseinsky, *Improved electrical mobility in highly epitaxial La:BaSnO<sub>3</sub> tilms on SmScO<sub>3</sub>(110) substrates,
 Appl. Phys. Lett. 105 (2014) 052104.* 

J.J. Walsh, G. Neri, C.L. Smith, A.J. Cowan, *Electrocatalytic CO*<sub>2</sub> *reduction* with a membrane supported manganese catalyst in aqueous solution, Chem. Comm. **50** (2014) 12698.

H. Wang, A. Pyatenko, N. Koshizaki, H. Mohwald, D.G. Shchukin, *Single-crystalline ZnO spherical particles by pulsed laser irradiation of colloidal nanoparticles for ultraviolet photodetection*, ACS Appl. Mater. & Interf. **6** (2014) 2240.

H.Q. Wang, X.H. Yan, G. L. Li, C. Pilz-Allen, H. Mohwald, D. Shchukin, Sono-Assembly of Highly Biocompatible Polysaccharide Capsules for Hydrophobic Drug Delivery, Adv. Healthc. Mater. **3** (2014) 825.

B.L. Williams, J.D. Major, L. Bowen, L. Phillips, G. Zoppi, I.Forbes, K. Durose, *Challenges and prospects for developing CdS/CdTe substrate solar cells on Mo foils*, Sol. Ener. Mater. Sol. Cells **124** (2014) 31.

B.L. Williams, A.A. Taylor, B.G. Mendis, L.Phillips, L.Bowen, J.D. Major, K. Durose, Core-shell ITO/ZnO/CdS/CdTe nanowire solar cells, Appl. Phys. Lett. 104 (2014) 5.

R.T. Woodward, L.A. Stevens, R. Dawson, M. Vijayaraghavan, T. Hasell, I.P. Silverwood, A.V. Ewing, T. Ratvijitvech, J.D. Exley, S.Y. Chong, F. Blanc, D.J. Adams, S.G. Kazarian, C.E. Snape, T.C. Drage, A.I. Cooper, Swellable, *Water- and Acid-Tolerant Polymer Sponges for Chemoselective Carbon Dioxide Capture*, J. Am. Chem. Soc. **136** (2014) 9028.

L. Zhao, Z. Qi, F. Blanc, G. Yu, N. Xue, X. Ke, X. Guo, W. Ding, C.P. Grey, L. *Peng, Investigating Local Structure in Layered Double Hydroxides with* <sup>17</sup>O NMR Spectroscopy, Adv. Func. Mat. **24** (2014) 1696.

Z.L. Zheng, X. Huang, D. Shchukin, *A cost-effective pH-sensitive release system for water source pH detection*, Chem. Comm. **50** (2014) 13936.

O.D. Zhuang, E.A. Anyebe, A.M. Sanchez, M.K. Rajpalke, T.D. Veal, A. Zhukov, B.J. Robinson, F. Anderson, O. Kolosov and V. Fal'ko, *Graphitic platform for self-catalysed InAs nanowires growth by molecular beam epitaxy*, Nanosc. Res. Lett. **9** (2014) 321.

## Patents

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

## Theses

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

Master's: G. Smith 'Photoctalytic hydrogen generation with size-controlled semiconductor nanocrystals'

SIRE hold approximately  $\pm 23,000,000$  in active grant income. In 2014 the following new grants were added to our portfolio.

### Engineering and Physical Sciences Research Council

F. Blanc, Dynamic Nuclear Polarization Solid-state Nuclear Magnetic Resonance Spectroscopy of Insensitive Nuclear Spins, £60,624

K. Durose and A. Walker, Centre for Doctoral Training in New and Sustainable PV, £5,260,808

K. Durose, Equipment for CDT in New and Sustainable PV, £280,000

K. Durose, SUPERSOLAR HUB extension #1, £150,000

J.A. Lopez-Sanchez, Novel Biorenewable polyester resins, Impact Acceleration Account, £74,862

J.A. Lopez-Sanchez, Bio-renewable Formulation Information and Knowledge Management System, **£20,167** 

G Teobaldi, Impact Acceleration Account, £40,000

#### **European Commission**

D. Shchukin, SONO Engineering – Electronic structures Sono-Engineering of Semiconductor Nanoparticles for efficient Solar Energy Exploitation: Low toxic cost efficient environment friendly antifouling materials, £185,340



#### FAPESP

A. Cowan, Charge carrier dynamics in ZnO rods sensitized with CdTe quantum dots: photoelectrodes for water splitting, £3,640

#### Harbin Institute of Technology (China)

F. Blanc, Dynamic Nuclear Polarization Enhanced Solid-state Nuclear Magnetic Resonance Spectroscopy, **£2,000** 

#### Royal Society of Chemistry

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

G. Teobaldi, Advanced new linear-scaling constrained

density-functional theory approaches, £11,995

#### The Royal Society

Y. Grunder, Alternative solvents for electrochemical processes, £1,000

Y. Grunder, Electro Chemistry in non-aqueous solvents, £134,337

#### University of Liverpool and Pilkington NSG Ltd

T. Veal and V. Dhanak, Optimizing transparent conducting oxide glass coatings for solar cells and displays, Knowledge Exchange Voucher, £14,600





## 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 and materials chemistry
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	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 and hybrid nanomaterials
Lopez-Sanchez, Dr Jose Antonio	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	PV materials and devices
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
Veal, Dr Tim	timveal@liverpool.ac.uk	+44 (0)151 794 3872	Semiconductor physics



Stephenson Institute for Renewable Energy

### 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 3363 E: carlaj@liverpool.ac.uk

www.liverpool.ac.uk/stephenson-institute

