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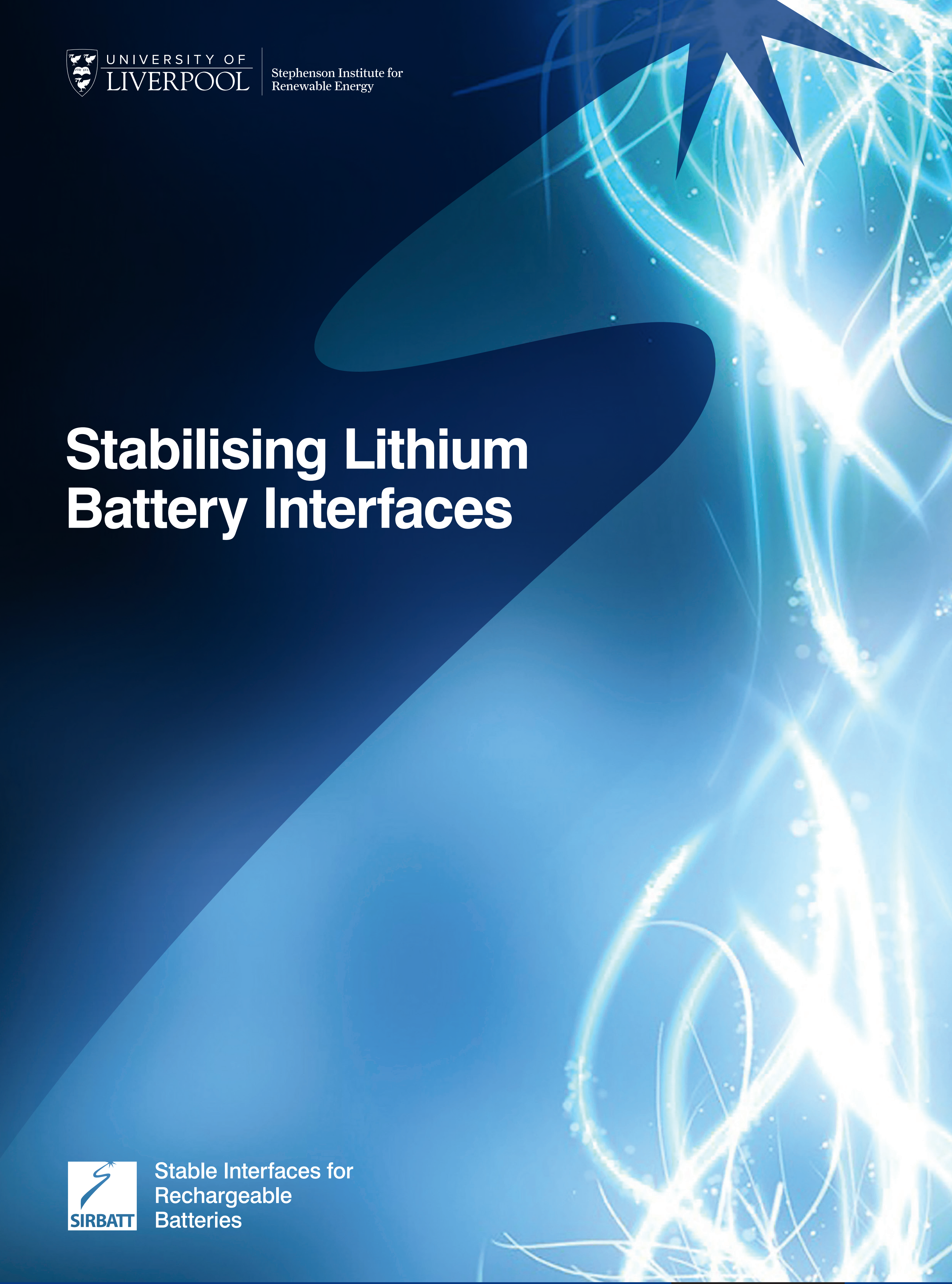

Stabilising Lithium Battery Interfaces

SIRBATT

Stable Interfaces for
Rechargeable
Batteries

LIFE CHANGING
World Shaping

Stable Interfaces for Rechargeable Batteries

Content

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SIRBATT

Exploring the issues that limit the lifespan of batteries used in stationary battery storage

SIRBATT (Stable Interfaces for Rechargeable Batteries) has been funded by the European Commission's Framework Seven Programme (FP7), to enhance the lifetime of batteries used in electric vehicles (EVs) and stationary storage by improving the structure and reactions at lithium battery electrode and electrolyte interfaces. With a work programme running from 1 September 2013 to its completion on 31 August 2016, SIRBATT is an innovative consortium with 11 full partners from across Europe representing six universities and one research institute, in addition to engaging four industrial partners.

The scientific aim of SIRBATT was a radical improvement in the fundamental understanding of the structure and reactions occurring at lithium battery electrode/electrolyte interfaces achieved through a programme of collaborative research and development. The diversity of the research organisations in the partnership was chosen to provide a wide range of complementary expertise in areas relating to the study of battery electrode interfaces, covering both experimental and theoretical aspects of this important area of study.

A major outcome of this project has been the development of micro-sensors to monitor the internal temperature of lithium cells in order to maintain optimum operating conditions, allowing for longer battery life times that can be scaled for use in industrial grid scale batteries. The cells created consist of candidate electrode materials in which the complex interfacial region and surface layers have been well characterised and understood via utilisation of a suite of advanced *in situ* measurement techniques and complemented by the application of transformative modelling methods. The knowledge from these initial studies has been used to develop candidate electrode materials with an optimised cycle life and stability, for example by the use of novel stable lithium salts and the inclusion of stable film-forming additives into the electrolyte.

www.sirbatt.eu

> *"Lithium battery lifetimes need to be 5-10 times longer, if companies are to invest in stationary battery storage to counter Li-ion batteries existing price premium."*
>
> ***Dr Laurence Hardwick, SIRBATT Coordinator***

The importance of batteries

The need to reduce carbon dioxide (CO_2) emissions from the burning of fossils fuels has led to Europe looking towards increasing the development and use of alternative 'green' energies. However, electricity supplies gained from, for example, wind, wave and solar power are intermittent as they are dependent upon external factors. As a result the storage of energy produced by these means is now crucial in the levelling out of supply and demand. If such energies are to be used on a larger scale there needs to be a mass market solution, therefore major improvements in stationary energy storage technology are now paramount.

Batteries are one of the main contenders for stationary energy storage with lithium-ion batteries having applications for providing uninterruptible power supply, power quality, transmission, distribution and load shifting. Whilst at the moment energy storage in bulk power management is served by pumped hydro power and compressed air storage, their geographical specific locations may not be the most practical energy storage solution. Batteries now have to demonstrate the ability to store energy efficiently, within certain power, lifetime and safety specifications, at a price-point that is ultimately affordable by the energy industry, before they can be considered for bulk power management.

SIRBATT has specifically aimed to address:

Power – Electrode material has been designed and synthesised with a nano-scale architecture to allow rapid ion diffusion into the host structure, therefore permitting high discharge/charge cycles.

Lifetime – Improved understanding of the electrode/electrolyte interface and its ageing processes leading to batteries with greater cycle and shelf-life. Key to this development being the identification of the actual nature and composition of the solid electrolyte interphase (SEI). The SEI is a protecting layer formed on the negative electrode of lithium batteries as a result of electrolyte decomposition, mainly during the first cycle. Battery performance, irreversible charge 'loss', rate capability, cycle life, calendar life and safety are highly dependent on the quality of the SEI in particular.

Safety – In some respects engineering of the battery pack for stationary applications is less restrictive than for electric vehicles due to the non-requirement to protect the battery from high velocity impact. However, due to the scale up – the potential of huge energy release during catastrophic runaway, leads to the requirement of an exceptionally high safety standard. Like lifetime, safety is greatly enhanced by better understanding and control of passivation layers on battery electrodes and the use of micro-sensors to monitor internal temperature and pressure within cells.

The level of monitoring and control within a battery pack can be improved considerably. Current, voltage and resistance are the only three parameters that can be currently externally monitored, and most battery management systems (BMS) are set to respond to ensure that these parameters remain within safety limits. However there are numerous other parameters that could be monitored to ensure the conditions to allow for a stable electrolyte interphase is maintained.

Quantitative measurements of the heat generation rate inside a single battery during normal and abuse conditions are required to design and develop a suitable thermal management system for scaled-up batteries.

SIRBATT intends to integrate fibre Bragg grating (FBG) sensors into lithium pouch cells for real-time temperature monitoring at different positions within the cell, whilst the cells are operating under various charge and discharge conditions, such as high current, short circuit, and over-charge.

Cost – This was addressed through the selection of candidate electrode materials that minimised raw material cost by avoiding expensive/rare elements and the investigation of low-cost routes to nanoparticle electrode material synthesis.

Research highlights

Modelling and Simulation of the Electrode Interface

Via application of state-of-the-art Density Functional Theory (DFT) methods executed on modern Tier-0 and Tier-1 High Performance Computing (HPC) facilities, we have been exploring innovative concepts in the formation, evolution and stability of solid electrolyte interphase (SEI) on both high energy-density and high power-density electrodes for Li-ion batteries. DFT work in this study has focused on lithium metal anodes and lithium manganese oxide cathodes.

Density functional theory screening of gas-treatment strategies for stabilisation of high energy-density lithium metal anodes

To explore the potential of molecular gas treatment of freshly cut lithium foils for non-electrolyte-based passivation of high energy-density Li anodes, DFT has been used to study the decomposition of molecular gases on metallic lithium surfaces. By combining DFT geometry optimisation and molecular dynamics, the effects of atmospheric (N_2, O_2, CO_2) and hazardous (F_2, SO_2) gas decomposition on several crystallographic cuts of metal Li have been investigated and the emerging electronic, elastic and chemical properties analysed (Figure 1). The simulations suggest that exposure to different molecular gases can be used to induce and control reconstructions of the metal Li surface and substantial changes (up to over 1 eV) in the work function of the passivated system. Contrary to the other considered gases, which form metallic adlayers, SO_2 treatment emerges as the most effective in creating an insulating passivation layer for dosages ≤ 1 mono-layer. The substantial Li→adsorbate charge transfer and adlayer relaxation produce marked elastic stiffening of the interface, with the smallest change shown by nitrogen-treated adlayers. Experimental strategies towards stabilisation of high energy-density Li metal anodes via gas pre-treatment of the Li electrodes are being optimised based on the gained atomistic knowledge [1].

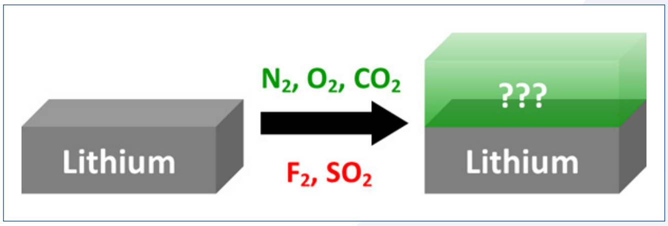

Figure 1: Density Functional Theory screening of gas-treatment strategies for stabilisation of high energy-density lithium metal anodes.

(Sub)surface promoted disproportionation and absolute band alignment in high-power $LiMn_2O_4$ cathodes

Spinel lithium manganese oxide $LiMn_2O_4$ (LMO) is a promising alternative cathode material, not only for its low cost, non-toxicity and safety, but also for its high operating potential and rate capability, which make it appealing for high-power electromotive applications. However, integration of LMO in commercial LIB cathodes is hampered by the tendency of the material to degrade upon cycling, which leads to battery power fading and irreversible capacity loss. LMO degradation has been associated with the material tendency to disproportionation ($2Mn^{3+} \rightarrow Mn^{4+} + Mn^{2+}$) and dissolution of Mn^{2+} ions in the electrolyte.

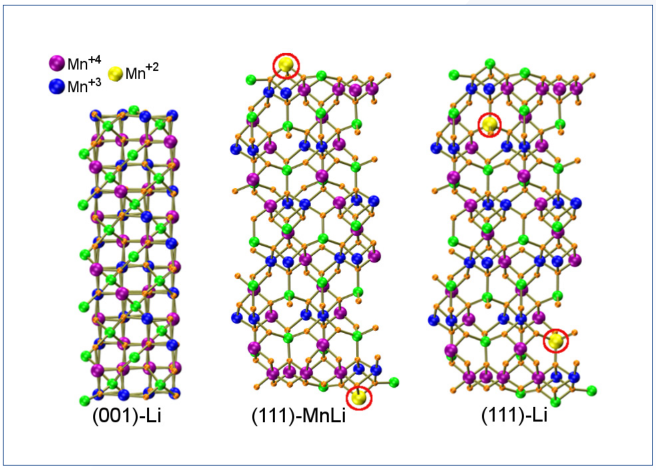

Figure 2: Surface and subsurface-promoted disproportionation in high-power $LiMn_2O_4$ cathodes.

To overcome these limitations and stabilise LMO to deliver its potential for high-power Li-ion batteries, growing research efforts have been directed to characterisation and understanding the evolution of the material and its interfaces upon cycling. Prompted by the established link between LMO surface morphology and composition on the one hand and electrochemical performances on the other, extensive DFT modelling has been executed to provide atomically resolved insight into the mechanisms responsible of surface Mn^{3+} disproportionation (Figure 2). We have uncovered previously overlooked relationships between the experimentally measured tendency of certain LMO surfaces to form highly effective SEIs upon wetting by the electrolyte and the surfaces' – unexpectedly reducing – electron structure and band-alignment. The theoretical predictions are being extended by considering the role of coating for the electrochemical performances of LMO cathodes [2].

Partners involved in this research:

- University of Liverpool, United Kingdom (Group Leaders)
- Centre National de la Recherche Scientifique, France
- Universita degli Studi di Camerino, Italy
- Centro de Investigacion Cooperativade Energias Alternativas Fundacion, Spain
- Johnson Matthey PLC, United Kingdom.

References:
[1] S. L. Koch, B. J. Morgan, S. Passerini, G. Teobaldi, J. Power Sources (2015) 296 150.
[2] I. Scivetti, G. Teobaldi, J. Chem. Phys. C (2015) 119 21358.

Lithium-ion Electrode Interfaces in Conventional Liquid Electrolytes

$ZnFe_2O_4$ (ZFO)

$ZnFe_2O_4$ (ZFO) is a promising negative electrode (anode) material for lithium-ion batteries (LIBs) with a specific theoretical capacity ca. 1000 mAh g^{-1} resulting from a conversion-alloying reaction. There is a capacity fading and loss of electronic conductivity due to volume changes and particle aggregation during cycling. However, this drawback can be overcome by coating with a carbon shell ZFO nanoparticles (ZFO-C). The solid electrolyte interphase (SEI) is a protecting layer formed upon electrode surfaces due to electrolyte decomposition. This film has a great influence on the battery performance. Therefore, it is important to understand the reactions that occur at the electrode/electrolyte interfaces and the composition of the SEI to improve the efficiency and cycle life of LIBs.

In our study we examined the SEI formation via a number of *in situ* techniques in order to get deep insight into the film's composition. SEI evolution was studied by multiple-edge soft X-ray absorption spectroscopy (XAS), [1] for ZFO-C anodes at selected charges during the first Li uptake. Experiments were performed at the BEAR beamline (ELETTRA synchrotron, Trieste) probing locally the SEI growth in the 2-100 nm thickness range, using for the first time both total electron (TEY) and total fluorescence (TFY) yield techniques. Accurate depth profiling of the SEI thickness evolution was made possible demonstrating the SEI is formed essentially during the first Li uptake process. The results are shown in Figure 1 and represent the first direct determination of the SEI thickness during the charging process. Moreover, XAS analysis shows that the SEI grows preferentially around the ZFO-C nanoparticles (Figure 1, bottom). SEI phase evolution was analysed with X-ray fluorescence (XRF) by distinct As valence states in the subsequent stage of SEI formation at the European Synchrotron Radiation Facility (ESRF, LISA beamline). The formation of As-F complexes (see Figure 2, right-hand side) with different local coordination N was observed and measured at various SEI evolution stages [2].

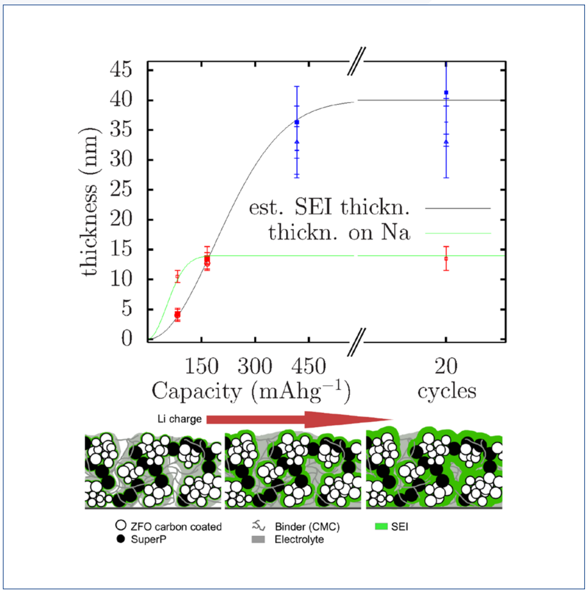

Figure 1: Top: SEI thickness as a function of capacity during first Li uptake and after 20 full charge/discharge cycles. Bottom: Pictorial view of the SEI formation. In an initial stage (left) a thin SEI is formed by electrolyte decomposition. In an intermediate phase during the Li uptake (centre), the SEI grows around the active nanoparticles. At a later stage (right-hand) a thicker SEI is formed preferentially upon the ZFO nanoparticles.

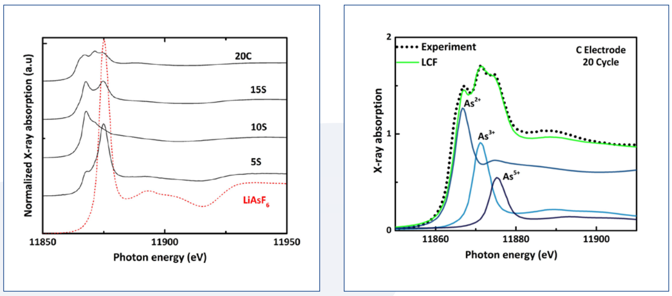

Figure 2: Left: As K-edge (XAS) spectra of graphite electrodes compared with the electrolyte salt solution $LiAsF_6$ reference spectrum. Right: evidence of presence of different As complexes (As^{5+}, As^{3+} and As^{2+} spectral components) in the SEI.

To complement the X-ray studies *in situ* Raman studies of a ZFO-C free-standing electrode were carried out. *In situ* Raman spectroscopy is a sensitive, non-invasive and non-destructive technique that allows *in operando* investigating chemical bonding of surface electrode species during the galvanostatic cycling. Raman spectra have been collected at different stages during the discharge and charge curves. The spectrum at the open-circuit potential (OCP) presents only the D and G Raman bands associated to the carbon shell of the ZFO nanoparticles, suggesting a uniform coating. Raman bands assigned to poly(ethylene)oxide species and organic lithium alkyl carbonates are visible at potentials that coincides with SEI layer formation [3] (Figure 3). The detection of these bands may be due to a temporary surface enhancement Raman effect from the zinc nanoparticles formed during the conversion reaction of ZFO. The observation of these polymeric species on the carbon coating as a result of the Raman enhancement of zinc nanoparticles encapsulated in a carbon shell is analogue to shell isolated nanoparticles Raman spectroscopy (SHINERS).

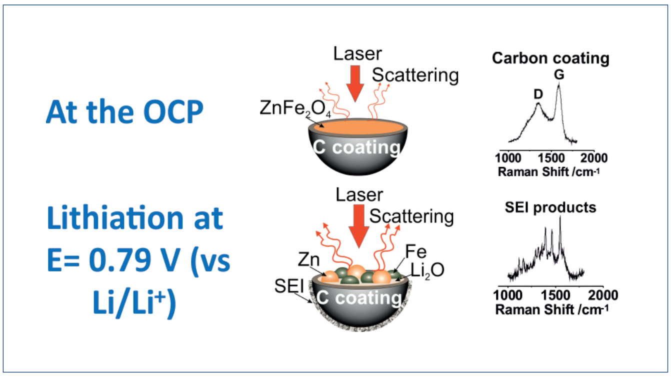

Figure 3: Solid electrolyte interphase products are detected on carbon-coated $ZnFe_2O_4$ by Raman due to temporary surface enhancement effect of zinc nanoparticles.

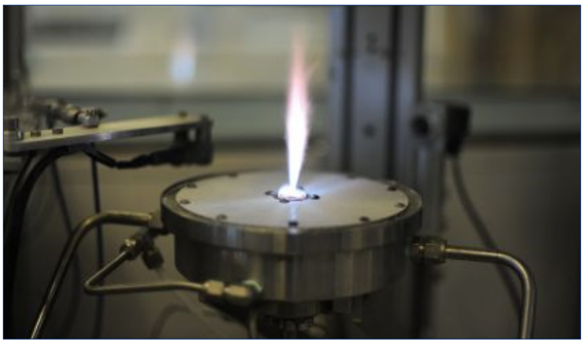

Figure 4: Flame spray pyrolysis.

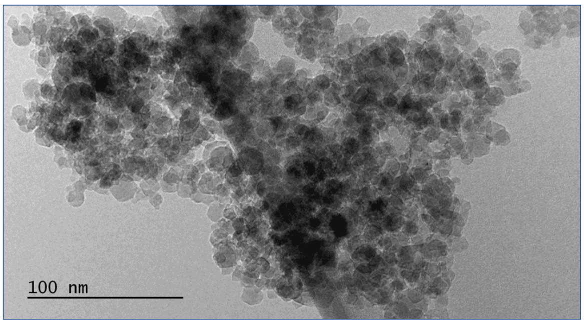

Figure 5: TEM images of flame spray made LTO

$Li_4Ti_5O_{12}$ (LTO)

$Li_4Ti_5O_{12}$ (LTO) is presently considered as one of the most promising alternative negative electrode (anode) materials for realising safer, long-lasting, high power lithium-ion batteries and is, for such reasons, already utilised in commercial cells. While the enhanced safety and advanced long-term cycling stability, resulting from the relatively higher lithium (de-)insertion potential and the negligible volume variation upon (de-)lithiation, respectively, are, to a great extent intrinsic to LTO, the high power performance, i.e., the rate capability of the material is highly dependent on the utilised synthesis method and the resulting particle size and morphology. However, one of the major challenges toward the commercialisation of nano-sized LTO is the development of easily scalable synthesis methods, providing large batches of active material at competitive prices.

A highly attractive method for the large-scale preparation of metal oxide nanoparticles appears to be flame spray pyrolysis (FSP). LTO nanopowder was synthesised on an up-scaled FSP rig (Figures 4 and 5). The product had high phase purity and nearly spherical particles with homogeneous particle size distribution. Small particles offer high rate capability benefit providing specific capacities of 133, 131, 129, 127, 124, and 115 mAh g^{-1} when applying C rates of 1C, 2C, 5C, 10C, 20C, and 50C, respectively. Furthermore LTO was extensively characterised, e.g., by electrochemical methods, X-ray diffraction and Raman microscopy and showed that lithium insertion and removal proceeds within both the minor anatase and the majority LTO phase in the sample [4].

Studying the SEI with Redox shuttles

The SEI formed at carbonaceous anodes makes the Li-ion battery a viable technology, because it inhibits solvent-decomposition reactions. However, passivation is never 100% complete and SEI ‘leakage’ appears as the main contributor to Li-ion battery ageing. There has been a great deal of experiments focusing on the chemical analysis of SEIs over the past decades. Still, a direct evaluation of their passive character has not been much regarded. Within SIRBATT, an electrochemical method based on a soluble Redox shuttle was applied (Figure 6). In particular we focused on the effect of additives to scavenge soluble electrolyte degradation products such as alkoxide anions [5].

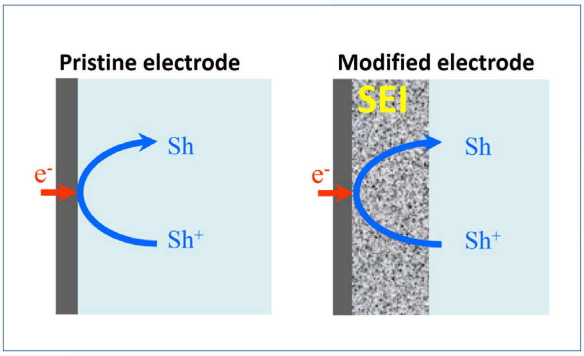

Figure 6: Principle of the Redox shuttle method.

Partners involved in this research:

- Universita degli Studi di Camerino, Italy (Group Leaders)
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- Centre National de la Recherche Scientifique, France
- Centro de Investigacion Cooperativade Energias Alternativas Fundacion, Spain
- Johnson Matthey PLC, United Kingdom
- SGL Carbon GmbH, Germany
- Karlsruher Institut fuer Technologie, Germany.

References:
[1] A. Di Cicco *et al.*, Adv. Ener. Mater. (2015) 5 1500642.
[2] S. J. Rezvani *et al.*, J. Phys. Chem. C (2016) 120 4287.
[3] L. Cabo-Fernandez, F. Mueller, S. Passerini, L. J. Hardwick, Chem. Comm. (2016) 52 3970.
[4] A. Birrozzi *et al.*, J. Electrochem. Soc. (2015) 162 A2331.
[5] M. T. Dinh Nguyen, C. Delacourt, J. Electrochem. Soc. (2016) 163 A706.

Lithium-ion Electrode Interfaces in Non-conventional Electrolytes

Synthesis of new electrolyte salts and additives for the formation of stable SEIs

New lithium salts are highly desirable as they form more stable solid electrolyte interphase (SEI) films on electrode surfaces, thus prolonging the lifetime of Li-ion cells. To this end the lithium salt of 5,6-dicyano-2-(trifluoromethyl)benzimidazolide (LiTDBI) and of lithium 5,6-dicyano-2-(trifluoromethyl)imidazopyrazine (LiTDPI) were synthesised (Figure 1 and 2) [1, 2]. These new salts are thermally stable up to 270 and 350°C respectively and have a wide electrochemical stability window in liquid solvents with conductivity over 1 mS cm^{-1}.

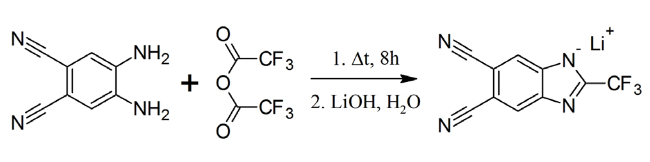

Figure 1: Synthesis of lithium 5,6-dicyano-2-(trifluoromethyl) benzimidazolide (LiTDBI) salt.

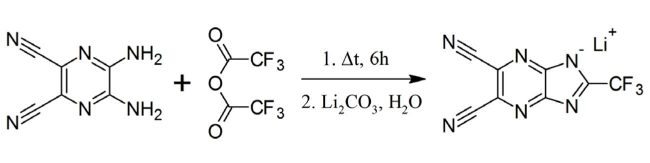

Figure 2: Synthesis of lithium 5,6-dicyano-2-(trifluoromethyl) imidazopyrazine (LiTDPI) salt.

Solid polymer electrolytes

We have assembled polymer-based test cells. Cells have been mounted using conventional graphite electrodes casted on copper current collectors, Li foil and the lithium 4,5-dicyano-2-(pentafluoroethyl)imidazolide (LiPDI) polymer membrane that acts as both, electrolyte and separator. Cycling at 55 and 70 °C, the assembled cells have delivered specific capacities very close to the theoretical capacity of graphite: 320 mAh/g @ 55 °C and 370 mAh/g @ 70 °C; with coulombic efficiencies of 98% and stable after more than 50 cycles. Regarding the electrode-electrolyte interfaces, X-ray photoelectron spectroscopy (XPS) experiments have been performed in both electrodes to determine the SEI composition so as to understand the role of the SEI composition on the electrochemical performance. Among many other components, the formation of lithium nitrate (Li_3N) has been confirmed upon the Li electrode, which is highly beneficial for the electrode stability. At the same time, the solid polymer membrane is less stable in the graphite electrode side according to the CF-based compounds detected.

Partners involved in this research:

- Politechnika Warszawska, Poland (Group Leaders)
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- Johnson Matthey PLC, United Kingdom
- SGL Carbon GmbH, Germany
- Karlsruher Institut fuer Technologie, Germany.

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[1] L. Niedzicki, *et al.*, J. Power Sources (2016) 306 573.
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Investigation of Lithium Metal – Electrolyte Interfaces

Li metal anode morphology was studied in great detail during plating and stripping (Figure 1) [1]. After cycling homogeneous regions can still be found (Figure 1.a), however there are areas where a cracking of the SEI has evidently taken place, which reveals a great deal of information over the Li deposition process. For instance, Figure 1.b highlights the formation of a number of bulky protrusions. These blocks of lithium appear to have a layered structure that is parallel to the surface and, most importantly, they are still covered with the web-like pattern observed earlier. This shows that the inhomogeneous lithium growth does not take place outside of the SEI, but rather underneath it, pushing the SEI with it as exemplified in Figure 1.c. Upon SEI rupture, Li nucleation takes place, but is soon interrupted by the passivation of the new formed Li globules. Nevertheless, a uniform deposition continued underneath the SEI, which shielded Li metal from extensive reactivity with the electrolyte.

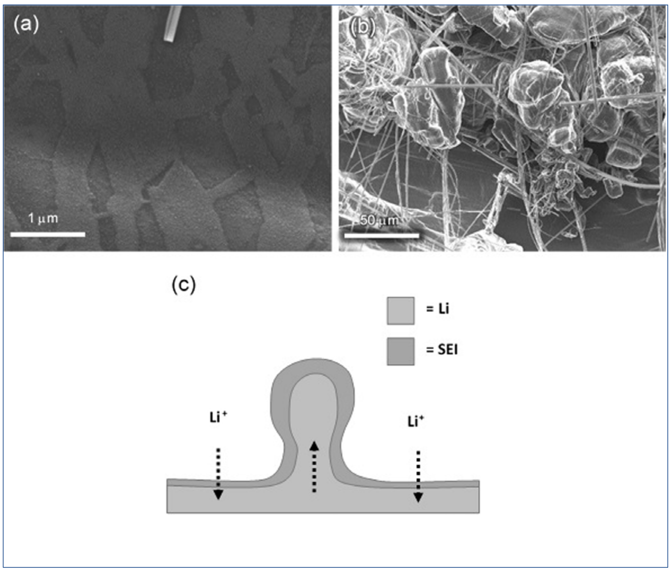
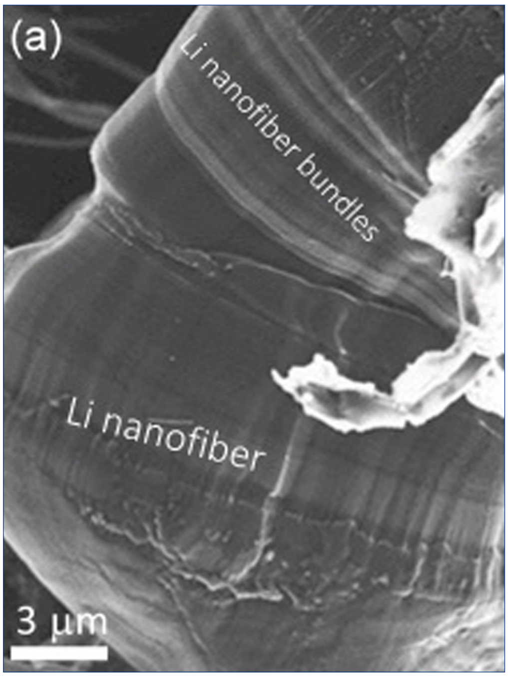


Figure 1: SEM micrographs illustrating fully plated Li electrodes; (a) overview of a fully plated Li electrode; (b) area where inhomogeneous plating has taken place; (c) scheme depicting the lithium block extrusion process.

The SEI ‘unzipping’ along well-defined lines is in support of the idea that the primary, mineral SEI breaks up alongside either grain boundaries or crystallographic planes, that is, where the cohesive intermolecular/interatomic forces are weaker. A sample Scanning Electron Microscopy (SEM) micrograph and a model to describe this process are illustrated in Figure 2. The exposure of Li fibres and the subsequent extrusion of fresh Li from what resembles a ridge, as portrayed in Figure 2.b, leads to the exposure of a new Li surface, which pushes both the native SEI and the previously deposited fibrous lithium out of the plane. As the concave shape inside the ridge suggests, no favoured Li deposition takes place; on the contrary, due to the rapid formation of a favourable SEI, there is no uncontrolled nucleation and no dendrite whiskers form.



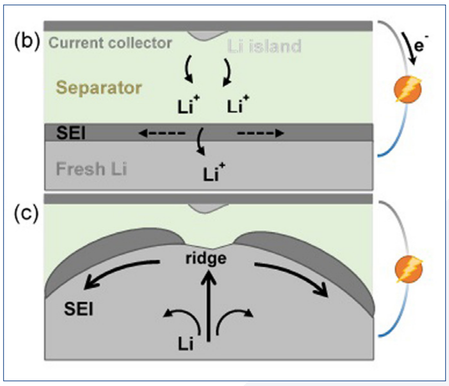


Figure 2: (a) SEM micrograph showing Li nanofibre bundles extruded from the native SEI; (b and c) model of the SEI rupture mechanism proposed.

Instrumental development for *in situ* lithium metal studies

The surface of clean lithium foils has been characterised using X-ray photoelectron spectroscopy (XPS) to determine the degree of cleanliness, but most important ultraviolet photoelectron spectroscopy (UPS) has been used to measure the work function of these surfaces. The work function change has been monitored upon gas dosing and experimental results are in agreement with DFT calculations. An ultra-high vacuum (UHV) Li evaporator has been designed and built at CIC Energigune that guarantees the production of clean Li films that can be deposited in any UHV-compatible surface.

Their behaviour upon electrochemical cycling will be tested by means of electrochemical impedance spectroscopy (EIS), XPS, UPS and UHV Raman spectroscopy (Figure 3). The latest is a Raman system that has been built at CIC Energigune and it is capable of performing *in situ* Raman experiments and UHV Raman experiments.

Partners involved in this research:

- Karlsruher Institut fuer Technologie, Germany (Group Leaders)
- University of Liverpool, United Kingdom
- Politechnika Warszawska, Poland
- Universita degli Studi di Camerino, Italy
- Centro de Investigacion Cooperativade Energias Alternativas Fundacion, Spain.

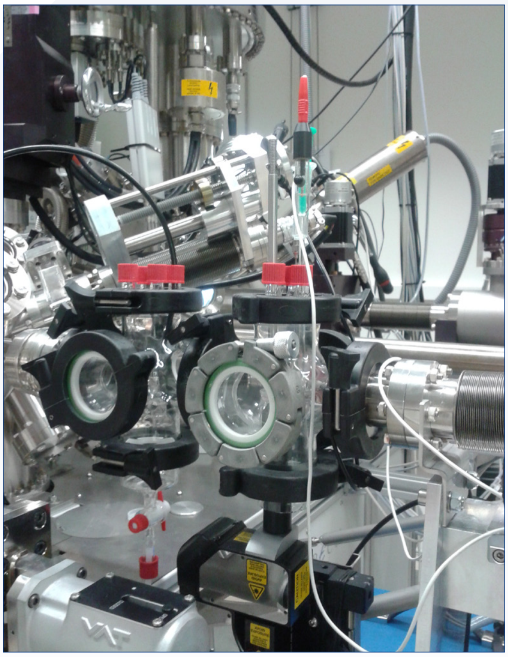


Figure 3: In situ and UHV Raman system, coupled to XPS system. Designed and built in-house at CIC Energigune.

Reference:
[1] L. Grande *et al.*, ACS Appl. Mater. Inter. (2015) 7 5950.

Micro-sensors for Real Time Cell Control and Performance

Although lithium batteries have been extensively studied and widely used in many different applications, the level of monitoring and control within a battery pack is still very low. Current, voltage and resistance are the only three parameters that can be currently externally monitored, and most battery management systems are set to respond to ensure that these parameters remain within safety limits. However, there are numerous other parameters that could be monitored to ensure the conditions to allow for a stable electrolyte interface is maintained. The main concern with the thermal behaviour of lithium batteries is the possible significant temperature increase during high power input and/or output. Quantitative measurements of the heat generation rate inside a single battery during normal and abuse conditions are required to design and develop a suitable thermal management system.

In general, optical fibre Bragg grating (FBG) sensors have been widely used to measure local static and fluctuating temperature, pressure, refractive index, strain, and bending. In particular, they have been used for real-time measuring of the internal temperature of fuel cells. Unlike other thermoelectric sensors, they are immune to electromagnetic interference, non-conductive and chemically inert. In addition, they have the advantages of small dimensions, flexibility and the possibility of monitoring multiple points in the same optical fibre.

In present work, fibre Bragg sensors have been tested and integrated into lithium batteries in order to *in situ* measure the internal temperature during charging/dis-charging under various conditions. Assembly of lithium-ion pouch cells and the positioning of the sensors are shown in Figures 1 and 2, with an example of temperature variation data shown in Figure 3. The use of these sensors can be considered a promising option for the design of large-scale battery packs and can be deemed to be a feasible technique for *in situ* monitoring temperature variations during galvanostatic cycling at different C-rates. However, the signal processing needs to be further developed in order to improve sensitivity and optimise data acquisition.

A new design is under development for the integration of FBG sensors in order to monitor adequately any point of interest in the lithium-ion cells, in particular the hot spots [1]. In the future we will be aiming to monitor more accurately in real-time and *in operando* the existing temperature and pressure variations within the lithium-ion cells. The discrimination of internal temperature and pressure variations in the cells will be achieved by placing in the same area two fibre Bragg sensors, in which one of them is coated with polytetrafluoroethylene for measuring only temperature variations.

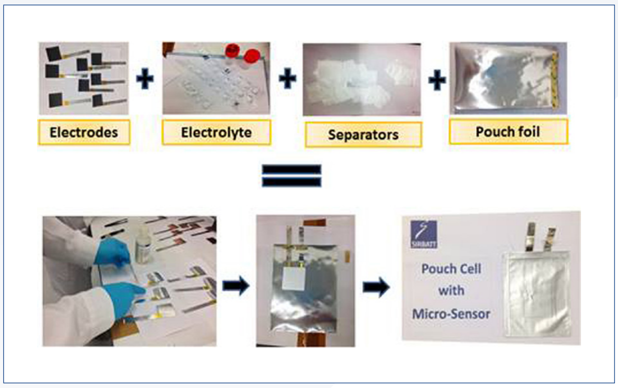


Figure 1: Assembly of the battery components and the integration of fibre Bragg grating sensors into the pouch-bag cell.

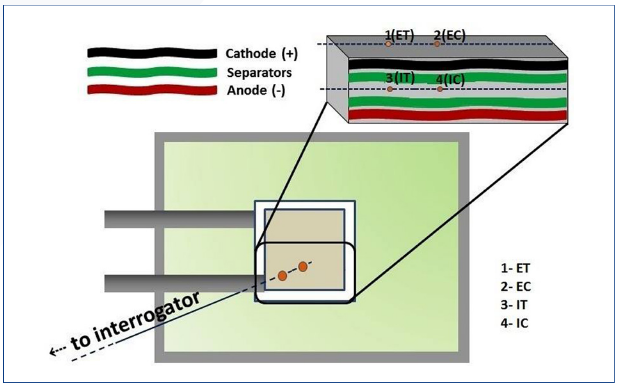


Figure 2: Schematic diagram of the position of the internal and external optical fibre sensors.

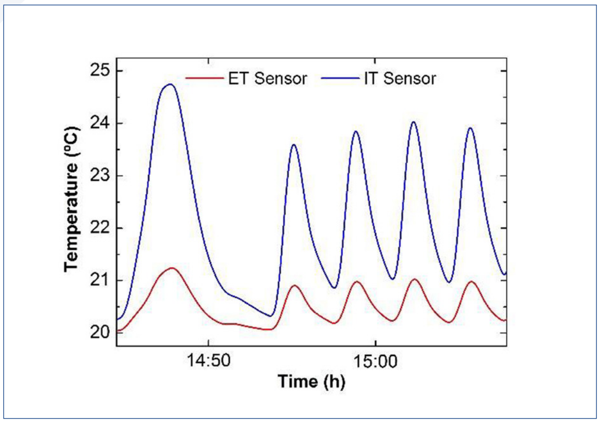


Figure 3: Example temperature variation data registered by the internal (IT sensor) and external (ET sensor) fibre Bragg grating sensors during the galvanostatic cycling of a Li-ion pouch cell at a rate of 8C.

Partners involved in this research:

- Universidade de Aveiro, Portugal (Group Leaders)
- Universita degli Studi di Camerino, Italy
- Johnson Matthey Battery Systems, United Kingdom
- Iberdrola Ingenieria y Construccion SAU, Spain
- Karlsruher Institut fuer Technologie, Germany.

Reference:

[1] S. Novais *et al.*, J. Lightwave Technology (2016) submitted.

Consortium members

University of Liverpool, United Kingdom

The University of Liverpool was founded in 1881. The Chemistry department at Liverpool was ranked 1st in the UK for 4* and 3* research (world leading and internationally excellent) in the REF2014 Research Excellence Framework (http://results.ref.ac.uk/Results/ByUoa/8).

In the Times Higher Education subject rankings, Chemistry at the University of Liverpool ranked 1st for outputs, 2nd overall and 3rd for impact – as such, Liverpool is currently one of the best places to do Chemistry research in the UK.

In 2011 the Stephenson Institute for Renewable Energy (SIRE) was established as a £10m interdisciplinary Chemistry and Physics research institute that will play a leading role in renewable energy research (www.liverpool.ac.uk/stephenson-institute). The research strengths within SIRE bring a combination of expertise in electrochemistry, spectroscopy, solid state chemistry and computational modelling.

Liverpool is well equipped for research into electrode interfaces and battery chemistry with high integrity argon filled glove boxes for handling air-sensitive materials, a range of electrochemical equipment and a variety of spectroscopic and analytical tools including state-of-the-art Raman, infrared and scanning probe microscopy instrumentation.

Scientists involved

Dr Laurence Hardwick holds a Readership within the Department of Chemistry and a member of SIRE. He has over 14 years' experience in the field of lithium ion batteries, with particular focus on probing the electrode interface with a variety of spectroscopic *in situ* techniques such as Raman and infrared.

Dr Gilberto Teobaldi is a Senior Lecturer within the Department of Chemistry and a member of SIRE, specialising in the development and application of both first principles and molecular mechanics methods to model the properties of photo-electro-chemical interfaces and functionalised surfaces.

The research activities in the field of lithium batteries and modelling by the team at Liverpool are recognised by funding from National and EU Bodies totalling more than €4.0m over the past four years.

Working on the project are **Dr Laura Cabo Fernandez**, who has a PhD from the University of Liverpool and has worked on *in situ* Raman studies of different anode and cathode materials for lithium ion batteries, and **Dr Ivan Scivetti** with a PhD from the Queen's University of Belfast and has worked on first principles simulations of condensed matter for over a decade.

Dr. Glenda Wall is the SIRBATT Project Manager, and has 14 years' experience working within EC funded projects.

Karlsruher Institut fuer Technologie, Germany

Karlsruher Institut fuer Technologie (KIT) is among the leading engineering research institutions worldwide. KIT combines the status of the University of Baden-Württemberg and the large-scale research institute of the Helmholtz Association, the largest science organisation in Germany. KIT makes major contributions to top national and international research and was founded in cooperation with the University of Ulm and supervises the Helmholtz Institute Ulm for Electrochemical Energy Storage (HIU). Associated partners are the German Aerospace Center (DLR) and the Center for Solar Energy and Hydrogen Research Baden-Württemberg (ZSW).

Within HIU the KIT group focuses on five main fields of electrochemical energy storage, namely: Basic research in electrochemistry; materials research; theory and modelling of electro chemical processes; system considerations and analytical methods. Within this group, expertise is present in electrochemistry and materials science and engineering, and, as support, analytical chemistry, synthetic chemistry and polymer chemistry.

Scientists involved

Prof Stefano Passerini, chemist, has been working since 1986 on basic and applied research devoted to study and characterise materials and systems for electrochemical energy storage. His main topics of research are: Polymer electrolytes; inorganic sol-gel materials and ionic liquids; and lithium batteries.

Markus Ding studied chemical engineering at Technische Universitat Munchen. His bachelor's thesis was on lithium-air batteries and he had an internship on lithium-sulfur/silicon batteries. In 2013, he undertook a research internship at Lawrence Berkeley National Laboratory, USA, on hydrogen-bromine Redox flow batteries. His master's thesis was focused on carbon composites joining Prof Passerini's group in 2014 as a PhD student working on the investigation of the solid electrolyte interphase on lithium metal.

Stephan Koch studied chemistry at Heidelberg University and did his master's project on dye-sensitised solar cells at Ecole Polytechnique Federal de Lausanne, Switzerland. In 2012, he became a member of the Passerini group as a PhD student with the focus on *in situ* methods for investigation of the lithium metal electrolyte interface.

Centre National de la Recherche Scientifique, Laboratoire de Reactivite et de Chimie des Solides, France

The Laboratoire de Reactivite et de Chimie des Solides (LRCS) is a research laboratory located in Amiens, France, and is operated jointly by the University of Picardie Jules Verne and the CNRS. The laboratory employs about 70 scientists and there are different research themes; most of them related to electrochemical energy storage and conversion, such as materials synthesis and crystal chemistry, Li-ion batteries, all-solid-state batteries, Li sulfur and Li oxygen batteries, hydrogen storage materials.

The LRCS has a strong background in research on Li-ion batteries. The laboratory is renowned for its expertise in the development of in-depth characterisation tools/fixtures to study new materials.

Scientists involved

Dr Charles Delacourt is a CNRS researcher who works on characterising and modelling ageing processes in lithium-ion batteries.

Two research engineers are members of the SIRBATT team at CNRS: **Dr Gregory Gachot** specialises in mass spectrometry. He develops analytical tools for studying electrolyte degradation mechanisms in Li-ion batteries and the impact of additives on the battery life; **Dr Sylvie Grugeon** aims to understand electrolyte degradation processes in batteries to improve their properties – solvents, salts, additives. She also works on Li-ion battery safety, by studying processes related to the electrolyte evolution during thermal runaway and combustion.

A professor in chemistry at the University of Picardie, **Prof Stephane Laruelle**'s research focuses on the negative electrode conversion-reaction mechanism, electrolyte electrochemical/thermal degradation and properties, Li-ion battery ageing, formation, and safety. He is responsible for the Battery Safety thematic of the national network within the French energy hub RS2E.

Postdoctoral researcher, **Dr Minh Thu Dinh Nguyen** has a PhD from the University of Paris-Sud, graduating in 2012. Her research interest focuses on catalysts for hydrogen production in proton exchange membrane electrolysers and Li-ion batteries.

Politechnika Warszawska, Poland

Politechnika Warszawska (WUT) is the leading institute of technology in Poland. There are 20 Faculties covering almost all fields of science and technology. The Faculty of Chemistry at the Warsaw University of Technology is one of the top three chemical Faculties of Polish universities of technologies and consists of 42 full professors including 27 tenured professors, 12 associate professors (PhD, DSc), 79 assistant professors, eight senior lecturers and 13 lecturers.

The SIRBATT group has significant experience in the field of Li-ion batteries and has a well-equipped laboratory in the area of synthesis and characterisation of polymer electrolytes.

Scientists involved

Prof Władysław Wieczorek leads the Polymer Ionics Research Group and is a graduate of WUT, having completed his PhD thesis there. In 1993 he won the NATO scholarship moving to Guelph in Canada as a post-doctoral fellow. Additionally, he has worked at Chalmers University in Goeteborg and the Institute for Materials Science in Messina. He is very active in the field of solid ionic conductors for various applications.

Prof Marek Marcinek graduated from WUT and was honoured by Fiat for the best master's thesis in 1999, defending his PhD with honours in 2003 and DSc (Habilitation) in 2012. He has worked at the Lawrence Berkeley National Laboratory, USA and on many energy storage research programmes. In 2007 he was awarded a 2 year grant by the Foundation of Polish Science.

Postdoctoral research associate **Dr Leszek Niedzicki** and PhD student **Tomasz Trzeciak** are also involved in the SIRBATT project.

Universita degli Studi di Camerino, Italy

The School of Science and Technology at the Universita degli Studi di Camerino employs researchers with multi-disciplinary skills in the field of material science. Its chemists, physicists and mineralogists have been involved for many years in projects and collaborations dealing with the synthesis and characterisation of functional materials related to energy storage and conversion devices, for example in fuel cells and Li-ion batteries. A strong background is present in synthesis, electrochemical, morphological and the structural characterisation of functional materials.

The motivated SIRBATT group of scientists at Camerino has an internationally recognised expertise in: sol-gel and solid-state synthesis and electrochemical characterisation of advanced materials for Li-ion batteries; *in situ* structural and electronic characterisation using state-of-the-art techniques such as X-ray Diffraction and X-ray Absorption Spectroscopy with synchrotron radiation. The activity has resulted in many publications in international journals and patents.

Scientists involved

Prof Andrea Di Cicco is a professor of physics. His main research activity is the development and execution of X-ray absorption, scattering and photoemission experiments performed at international synchrotron radiation facilities, and currently researching matter under extreme conditions and materials for energy applications. He has been responsible for, or participated in, several scientific projects covering the development and exploitation of synchrotron radiation applications on disordered, ill-ordered and nanostructured materials.

Camerino's SIRBATT research group includes recognised professors and researchers in chemistry, **Dr Francesco Nobili** and **Dr Roberto Tossici** and in physics **Prof Roberto Gunnella** in addition to several technologists, post-doc and PhD students – all with the necessary expertise in material science, electrochemistry, and X-ray fine-analysis of nanomaterials. In the last decade, the group as a whole has published many papers on the development of new methods and materials for fuel and Li-ion cell applications and technology.

Centro de Investigacion Cooperativade Energias Alternativas Fundacion, Spain

Centro de Investigacion Cooperativade Energias Alternativas Fundacion (CIC Energigune) is an energy research centre with headquarters in the Basque Country which aims to become an international benchmark in its field. The Centre has the backing of public institutions and administrations, and of companies directly related to the energy sector. They have two different research areas: electrochemical energy storage and thermal energy storage which are equipped with state-of-the-art characterisation techniques.

The research group at CIC Energigune has a sound background in the synthesis, modelling and characterisation of energy storage materials as well as in the structural and surface analysis of energy related materials. Besides national and regional funding, the structure and surface analysis group is currently involved, as a partner, in three EU projects including SIRBATT. In 2016, a new Horizon 2020 project will be coordinated by this research group.

Scientists involved

Prof Teofilo Rojo is a professor of inorganic chemistry at the University of the Basque Country and Scientific Director of CIC Energigune. His research focuses on solid state chemistry and materials science, emphasising the study of materials for lithium and non-lithium based batteries to improve power and energy density. Associate researcher at the Structure and Surface Analysis group at CIC Energigune, **Dr Miguel Angel Munoz**, is an expert in ion scattering, electron-related spectroscopies and diffraction, and scanning probe techniques; his research has been dedicated to fundamental and applied studies of surfaces and interfaces in energy and environmental related materials for electric energy storage, hydrogen storage and heterogeneous catalysis.

Dr Oleksandr Bondarchuk manages the Surface Analysis Platform at CIC Energigune and is an experienced scientist, active in the area of thin film and cluster growth and characterisation under ultra-high vacuum conditions by using surface characterisation techniques.

Finally, **Dr Javier Carrasco** is an associate researcher in the Computational Studies group at CIC Energigune. The group is devoted to understanding important phenomena in surface materials and nano-science in the power storage field. Using concepts from quantum mechanics, solid state physics, and statistical mechanics.

Universidade de Aveiro, Portugal

Universidade de Aveiro was founded in 1973 and has grown into a successful, dynamic and competitive institution. Through strategic options the quality of research produced has been confirmed by the excellent results of successive evaluations carried out by the Portuguese national funding agency for science and technology (FCT). The Optical Sensor Laboratory is established within in the Department of Physics and the Institute of Nanostructures, Nanomodelling and Nanofabrication (I3N) and is well equipped for research into *in situ* measurement using fibre Bragg grating sensors.

The University has been working on real-time measurements, with fibre Bragg sensors in lithium batteries for safety usage, for several years and has published a number of papers on the subject of lithium batteries having a strong track record in this area. The research group brings their expertise on *in situ* measurement parameters of lithium battery for large-scale application to the SIRBATT project.

Scientists involved

Dr Joao L. Pinto is a full professor in the Department of Physics and leads the Optical Group. His current research interests include optical communications, Bragg gratings systems, optical image processing, holography and promotion of physics in society. He is presently a member of I3N-Aveiro, Institute of Nanostructures, Nanomodelling and Nanofabrication and collaborates with IT-Aveiro, Institute of Telecommunications.

Dr Fatima Domingues, a postdoctoral researcher granted by FCT of Portugal, has been working at the Optics and Optoelectronics Laboratory on the development real-time measurement, temperature and pressure, inside the lithium battery for large-scale application.

Johnson Matthey Battery Systems, United Kingdom

Johnson Matthey Battery Systems (JMBS) is a leading producer of Li-ion battery packs and as part of Johnson Matthey plc, is a producer of Lithium-ion battery systems for electric, hybrid and plug-in hybrid electric vehicles. Its battery and charger systems are designed and manufactured to full automotive standards, incorporating all the exacting requirements of packaging design, thermal management, electronics, and vehicle integration. JMBS' system design and assembly expertise understanding of the applications engineering of cells are supported by a chemistry-agnostic system development strategy, supported by strategic partnerships with leading global cell manufacturers. Their know-how and capabilities support the electrochemical evaluation of next generation Li-ion cells at the device integration stage. JMBS own IP related to a new battery management system (BMS) with increased functionality, reliability and battery pack safety but with reduced size, weight and cost.

Scientists involved

Dr Allan Paterson is JMBS' chief electrochemist. He investigates new battery technologies and their application in next generation low carbon EV and HEV applications and has over 16 years' experience in the field of lithium batteries, including developing novel high energy densities materials and next generation battery technologies. With a PhD in Chemistry from University of St Andrews on the development of advanced manganese based cathode materials for rechargeable lithium ion batteries, he leads the Electrochemistry Team and has managed a range of research and development collaborative programmes at JMBS.

Principal scientist **Dr Valentina Gentili** has more than 11 years' expertise across a wide range of disciplines within the lithium ion battery field. This includes research into advanced polymer electrolytes, synthesis of nano-materials for Li-ion cells; as well as the electrochemical and thermal characterisation and testing of commercial cells and the next generation Li-ion technology for use in cutting edge energy systems for HEV, PHEV and BEV platforms. She has a PhD in Chemistry from the University of St Andrews having researched novel 'Nanomaterials for use as anodes in Lithium-ion Batteries', and leads research and development projects including, internal JMBS, UK government and EU commission supported collaborative projects.

Johnson Matthey, United Kingdom

Johnson Matthey (JM) is a speciality chemicals company focused on catalysis and materials science. Their products and technologies are used to control emissions from vehicles and factories, remove unwanted impurities in oil refining processes and produce chemicals from sustainable feedstocks. They also work on battery and fuel cell technologies for the production of clean, green electricity.

The Technology Centre, based at Sonning Common, UK, undertakes research activities for the Johnson Matthey group worldwide. The Catalysis and Materials Department develops core technology for JM in the area of nanoparticle synthesis, including flame spray pyrolysis, enamels, conductive pastes, battery materials, new pigments, protective coatings and inkjet printing.

Following recent acquisitions and internal development, JM is now a considerable player within battery technologies. JM is a leading global supplier of lithium iron phosphate with major manufacturing facilities in North America and Asia and research and development capabilities in Europe.

Scientists involved

Dr James Cookson has held various positions within JM since 2005, exploring nanotechnology, catalysis and battery materials. He was involved in the creation of JM's battery materials business and its subsequent technical integration. James is the author of several publications and patents. Senior scientist **Dr Hanna Rajantie** joined JM in 2001. She has expertise in process development, materials science and electrochemistry and has worked in the area of emission control technologies and fuel cells before joining the Battery Group in the Catalysts and Materials Department in 2013.

SGL Carbon GmbH, Germany

SGL Carbon is one of the world's leading manufacturers of carbon-based products, ranging from graphite and carbon products to carbon fibres and composites. Their core competencies include high temperature technologies and extensive experience in application and engineering know-how. SGL products are used, for example, in steel, aluminium, automobile, chemical, semiconductor, solar, battery, and fuel cell industries. Their central research and development unit, Technology and Innovation (T&I), is located in Meitingen, Germany. Within T&I, special focus is given to carbon-based materials for electrochemical energy storage and conversion systems such as batteries and fuel cells. SGL's portfolio includes amorphous carbons as well as artificial graphite as anode materials for lithium ion batteries, gas diffusion layers for fuel cells, bipolar plates and carbon felts for redox flow batteries, and graphite foils for thermal management.

Scientists involved

Dr Christian Schreiner, chemist, obtained his PhD on the synthesis and characterisation of ionic liquids for electrochemical applications. After working on polymers and ionic liquids during a post-doc position at Virginia Tech, USA, he joined the University of Muenster where he worked on electrolyte components – salts, solvents, additives – for lithium ion batteries and the SEI formation on graphite by various analytical methods. Since joining SGL Carbon, he has been involved in various topics related to the development of graphite- and carbon-based anode materials for current and next generations of lithium ion batteries.

Iberdrola Ingeniería y Construccion S.A.U.

Iberdrola is one of the major energy engineering companies in the world in electric generation, networks, renewable and nuclear energy. The Company, belonging to Iberdrola Group, offers a wide range of services in both domestic and international markets with a leading position in the development of large projects in the energy field and use of innovative technologies for the design and optimisation of all production and logistics processes.

In the area of nuclear generation, they offer a wide range of products: engineering and construction of new nuclear power plants; modernisation of operating plants; accelerators and fusion and dismantling of nuclear facilities. Their services cover both conceptual and basic engineering, including the definition of systems and processes, such as integral projects and operational support.

Scientists involved

Andres Gomez Navarro is a project engineering manager and head of innovation in the Nuclear Department at Iberdrola, having been with the company for 28 years. He is a qualified industrial engineer specialising in energy technologies and holds a higher degree in multiphase flow and heat transfer from ETH Zurich. Additionally, he is a member of the Official College of Industrial Engineers and the Spanish Nuclear Society, where he is Iberdrola's representative on their Technical Committee.

Senior project engineer within the Nuclear Generation Department, **Carlos Contreras Lora**, holds a degree in marine engineering with speciality in steam turbines and electrical machines, and an MSc in electricity generation technologies and rotating machinery. He is a member of the Spanish Nuclear Society.

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