Publishable summary

SIRBATT project, “Stable Interfaces for Rechargeable Batteries” consisting of 11 full partners from the European Area (six Universities, one Research Institute and four industrial partners) has been a large scale multisite collaborative RTD project funded by the European Commission under the ENERGY.2013.7.3.3 – “Understanding interfaces in rechargeable batteries and super-capacitors through in situ methods” call for research.

SIRBATT has put together a multidisciplinary team of leading European Universities (University of Liverpool (ULIV), Karlsruher Institut fuer Technologie (KIT), Politechnika Warszawska (WUT), Università degli Studi di Camerino (UNICAM) Universidade de Aveiro (AVE), Centre national de la recherche scientifique (CRNS)), Research Institutes (CIC Energigune (CIC)) and Industries (Johnson Matthey (JM), Johnson Matthey Battery Engineering Systems (JMBS), SGL Carbon (SGL), Iberdrola (IBR)) with the overall goal of fundamental understanding of the structure and reactions occurring at lithium battery electrode/electrolyte interface which would lead to longer lifetime lithium batteries.

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. 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.

Within the project **Stable Interfaces for Rechargeable Batteries** (SIRBATT) we have investigated lithium-ion battery electrode chemistries to deliver the long-term cycle life batteries required by future societies. Within the programme SIRBATT has undertaken a wide program of experimental and theoretical research of Li-ion battery electrode interfaces and also includes the innovative step of the integration of Li-ion cells with microsensors to monitor internal and external temperature.

The list of the scientific publications, published within the project three year timeframe– 12 in leading peer-review journals such as Advanced Energy Materials, The Journal of Physical Chemistry C and Chemical Communications, Journal of the Electrochemical Society - as well as numerous videos explaining the activities and scientific achievements of the project are available in the project website https://www.liverpool.ac.uk/sirbatt/. It is noted that 2 patent applications have been submitted to National Patent Offices.

In addition to technical aspects, SIRBATT has organised two international workshops in Spain and USA in 2015 and 2016 to disseminate the work from the project and to engage with the Sister programmes (Hi-C, Influence and Baccara) funded within the same call, as well as complementary European and USA research activity.

Summary description of project context and main objectives

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 (Stable Interfaces for Rechargeable Batteries) is a multisite collaborative project consisting of 11 full partners from the European Area (six Universities, one Research Institute and four industrial partners). The diversity of the research organisations in the partnership was been 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 contemporary area. SIRBATT has developed microsensors to monitor the internal temperature of lithium cells in order to maintain optimum operating conditions to allow long-life times that can be scaled for use in grid scale batteries. These cells will comprise of candidate electrode materials in which the complex interfacial region and surface layers were well characterised and understood via utilisation of a suit of advanced in situ and ex situ measurement techniques, complemented by the application of transformative modelling methods. The knowledge from these studies is presently being exploited 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.

Scientific Aims and Objectives

The scientific aim of SIRBATT is, therefore, a radical improvement in the fundamental understanding of the structure and reactions occurring at lithium battery electrode/electrolyte interface which will be achieved through an innovative programme of collaborative research and development. The scientific objectives are to:

(1) Fully characterise the chemistry of interface layers (solid electrolyte interphase and passivation films) with a suit of advanced in situ analytical techniques and state-of-the-art computational methods on a selection of lithium battery electrodes in conventional and non-conventional electrolytes;

(2) Use the generated understanding of the interface layers to develop electrode/electrolyte interfaces that allow high cycle life (for example to move towards achieving 5000+ cycles, to 80% initial capacity) of lithium cells, thereby demonstrating that lithium batteries are sufficiently robust for grid scale batteries, due to their long-term stability;

(3) Develop microsensors to monitor lithium cells in order to maintain optimum operating conditions to allow the operation of long-life time devices that can be scaled for use in grid scale batteries.

Significant scientific outcomes from SIRBATT project:

The key findings from this three-year collaborative research programme include computational studies that show that strain-engineering of lithium manganese oxide spinel ($LiMn_2O_4$) surfaces (a lithium-ion battery cathode material) via metal-oxide core-shell nanoparticle synthesis, could allow the generation of zero-bias solid electrolyte interphase (SEI) forming layers. This result provides a new rational route for material design whereby the surface is fabricated to form a stable interface just by putting the material in contact with the battery electrolyte (removing the requirement for an electrochemical formed layer), thus conceivably removing the requirement for formation cycles during battery manufacturing.

Green electrode formulations have been demonstrated to provide similar electrochemical performance to more conventional and widely industrially used electrode formulation. In particular, it has been demonstrated that for a wide range of Li-ion anode and cathode electrode formulations, a carboxymethyl cellulose**/**water formulation allows the preparation of stable electrodes, being at the same time cheaper and greener than the more conventional use of the fluorine-containing binder polyvinylidene fluoride and the harmful solvent N-methyl-2-pyrrolidone binder/solvent system.

To evaluate long cycle life a Lithium-ion coin cell, consisting of a graphitic anode and lithium iron phosphate ($LiFePO_4$; provided by ALEEES) as the cathode, has been cycled for over 2500 times, showing 40% capacity fade. 1750 cycles were achieved with 20 % capacity fade. This exceeds the project target for 500 cycles and moves us a step closer to the long-term goal for Li-ion batteries to the achievement of 5000+ cycles. When the capacity values obtained by single side coin cell electrode are projected considering the assembling of the final cells, energy density values of 95 Wh/kg and 150 Wh/dm^3, can be estimated.

An unexpected detection of SEI growth products during the lithiation process of carbon-coated $ZnFe_2O_4$ was made. SEI components on the carbon coating were assigned from the Raman data as the polyethylene oxide type and organic alkyl carbonates (RCO_2Li). This result is important as it demonstrates the suitability of in situ Raman spectroscopy to detect SEI products on an electrode interface under potential control. It enables a convenient method to follow the progress of SEI formation in real time. It also demonstrates that in situ generated metal nanoparticles could act as a temporary generator of the SERS effect.

We could prove that the stable cycling of Li metal electrodes in ionic liquid based electrolytes is possible for several thousands of hours. During a long-term cycling experiment in the ionic liquid electrolyte 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ($Pyr_{14}TFSI$) with lithium bis(trifluoromethylsulphonyl)imide (LiTFSI) (9:1 mol ratio), no dendrite growth that would represent a safety problem was detected.

Fibre-Bragg Grating sensors have been successfully integrated in Li-ion pouch cells and were shown to be more responsive and more accurate compared to traditional thermocouples placed on the outside of the cells under a variety of testing conditions. We hope to take forward the knowledge of the microsensor integration gained from this work to develop sensing technology for safety monitoring next generation lithium-ion cells and other alternative battery chemistries.

Main Results

SIRBATT has undertaken a wide program of experimental and theoretical research of Li-ion battery electrode interfaces and integration of Li-ion cells with microsensors, of which the main results are highlighted below and reported according to work package.

Work Package 3: Modelling and Simulation of the Electrode Interface

Characterisation of buried interfaces between epitaxial $Li_4Ti_5O_{12}$ ($Li_7Ti_5O_{12}$) and α-Li_2TiO_3 focused on Density Functional Theory **(DFT)** investigation the lowest formation energy structure for the buried interface [α-Li_2TiO_3//$Li_{4(7)}Ti_5O_{12}$] formed after the first Li-intercalation in spinel $Li_4Ti_5O_{12}$ (111)-oriented single crystal. The energy favourable models were characterised in terms of electronic structure and elastic properties. Based on the computed phase-diagram for the considered phases, growth of an extended α-Li_2TiO_3 layer on $Li_4Ti_5O_{12}$ substrates, acting as solid electrolyte, could be achieved by suitably tuning bias and O_2 contamination in the electrolyte.

Structural and electronic characterisation of $Li_4Ti_5O_{12}$ and $LiMn_2O_4$ interfaces focused on interfaces of $Li_4Ti_5O_{12}$ and $LiMn_2O_4$. Specifically, DFT screening of several α-Li_2TiO_3 surfaces was carried out with the aim of identifying the energy favoured termination of the phase experimentally detected after the first Li insertion (extraction) in (from) single crystal $Li_4Ti_5O_{12}$ (111). The simulations indicate the α-Li_2TiO_3 (100) surface to be energetically favoured, which explains the experimentally observed tendency to faceting of α-Li_2TiO_3 phases grown epitaxially to $Li_{4(7)}Ti_5O_{12}$(111). The role of Li vacancies in promoting organic solvent (ethylene carbonate, **EC**) decomposition was also investigated and its non-negligible role in activating formation of solid electrolyte interphase **(SEI)** on α-Li_2TiO_3 demonstrated.

Given the current debate on the optimal simulation approach for $LiMn_2O_4$ bulk and surfaces, we started by considering the problem of bulk and evaluated the role of different simulation protocols for the agreement with available experimental results on the structure, cation and magnetic ordering of the material. The bulk-focused work was extended by the investigation of the relative energy of several $LiMn_2O_4$ surfaces and the dependence of the results on the adopted simulation protocol for different magnetic orderings. For the lowest-energy surface models, we then studied the adsorption of both EC and dimethyl carbonate **(DMC)** on $LiMn_2O_4$ surfaces, paying special attention to the effects that different approaches to the description of both 3d sites (Mn) and van der Waals corrections may have on the simulated results. An extended characterisation of the electronic structure for the considered vacuum-exposed surface and $LiMn_2O_4$/solvent (EC and DMC) interfaces was presented and discussed with respect to both experimental and, where available, theoretical data. The current unavailability of simultaneously atom- and time-resolved experimental characterisation of the considered interfaces makes the results presented novel and of potential high interest to the experimental community. Most notably, the simulations revealed that Mn^{2+} sites in $LiMn_2O_4$, for specific crystallographic cuts [i.e. (111) Mn&Li terminated and (111) Li-terminated] are a ground state property of the surfaces, whose formation does *not* require electrochemical cycling of the substrate.

Identification of structural and electronic factors governing Li-ion diffusion and ageing of $Li_4Ti_5O_{12}$ and $LiMn_2O_4$ interfaces focused mainly on $LiMn_2O_4$ given the larger amount of experimental characterisation results from the literature. Given the lack of published result on the matter, we focused on the surface-dependence interplay between cathode state of charge, Li-ion intercalation, and Li-ion co-adsorption in electrolyte/$LiMn_2O_4$ cathode interfaces.

Based on experimental compelling evidence of a marked surface-dependant difference in the reactivity, SEI formation and evolution of $LiMn_2O_4$ cathodes exposing (111) and (110) surfaces, we carefully considered the structure, electronic properties and dynamics of model (111) and (110) interfaces with a standard organic solvent for the electrolyte (EC) as a function of the state of charge of the system, which was found to induce semiconductor↔metal transitions in the substrate. This line of work was extended by considering the role of strain in tuning the reduction drive of $LiMn_2O_4$ surfaces. The modelled effect was substantial with changes up to over one 1 eV in the substrate work-function for strain values as small as 5%. The results indicate that strain-engineering of $LiMn_2O_4$ surfaces via metal-oxide core-shell nanoparticle synthesis, could be very meaningfully explored towards definition of zero-bias SEI-forming layers.

Furthermore, we carried out also a detailed study of the effect of Li-ion intercalation in EC/$LiMn_2O_4$(111) and EC/ $LiMn_2O_4$ (110) interfaces on the overall electronic properties of the system as a function of the intercalation depth of the Li-ion. This work was complemented by explicit simulation of the role of hole-excess, as expected during the initial stages of cathode discharge (battery re-charge), for the electronic properties and dynamical evolution of lithiated EC/$LiMn_2O_4$(111) and EC/$LiMn_2O_4$(110) interfaces. This work revealed an important role of intercalating Li-ions at the surface in altering the redox properties of surrounding electrolyte molecules, making the latter substantially more reducible. Based on these results, atomistic simulation of solvent decomposition on $LiMn_2O_4$ surfaces should not overlook the presence of ion adsorption on the surface.

Structural and electronic characterisation of metal-oxide coated $LiMn_2O_4$ interfaces and composition of Graphitic carbon anodes SEI's considered Al_2O_3 coating of $LiMn_2O_4$ surfaces and modelling of redox shuttle electrochemistry towards understanding of the SEI passivating role for solvent reduction.

Following validation of novel procedures for computationally efficient pre-optimisation of amorphous Al_2O_3 models based on carefully controlled approximations, we investigated the possibility of coating-driven change in the relative energy, thence stability, of different $LiMn_2O_4$ crystallographic faces. The role of the amorphous Al_2O_3 coating and its interface with $LiMn_2O_4$ for the electronic properties of the composite was also studied. Notably, for all the considered Al_2O_3–coated $LiMn_2O_4$ substrates, we found the coating to strongly interact with $LiMn_2O_4$ and invariably donate electronic charge to $LiMn_2O_4$. We also validated directly the experimentally suggested proposition that hetero metal-oxide coating of $LiMn_2O_4$ should be effective in preventing Mn disproportionation ($2Mn^{+3} \rightarrow Mn^{+2} + Mn^{+4}$) at the $LiMn_2O_4$ surface resulting in dissolution of Mn^{+2} into the electrolyte. We found this not to be the case, given the electron transfer from the Al_2O_3–coating to the $LiMn_2O_4$ and the ensuing reduction of Mn^{3+} sites at the interface. Accordingly, electron-accepting coatings, i.e. coatings with a larger electron affinity than $LiMn_2O_4$ or providing different interface charge redistribution, should be designed to suppress Mn disproportionation in $LiMn_2O_4$. These elements, currently unavailable in the specialised literature, should be useful for future, better informed, strategies toward stabilisation of LMO cathodes via hetero metal-oxide coatings.

With the aim of improving our understanding of battery ageing, we investigated the passivation degree of the SEI towards solvent reduction. The passivating character is characterised by two properties: the electron transfer at the passivated electrode and the solvent transport through the SEI film. To describe these properties, a characterisation method based on introduction of a redox shuttle in the electrolyte was implemented. The way the electrochemistry of the shuttle is modified by the presence of the film provides information about the passivating character. Mathematical models were developed to simulate voltammograms at either (rotating or stationary) flat or porous electrodes, before or after the SEI formation. The models account for the presence of a soluble redox couple that is used as an electrochemical sensor of the SEI properties. Ferrocene/ferrocenium was selected as the shuttle. From a model-based analysis of data collected after SEI formation with different formation charges at flat electrodes, SEI-related parameters such as its porosity and the effective kinetic parameters of the shuttle reaction (modified because of the presence of the SEI) could be determined. The larger the formation charge, the lower the SEI porosity. The kinetic rate constant of the shuttle reaction was also found to decrease with an increase in formation charge. These parameters directly reflect the SEI quality in terms of passivation. The approach was then extended to graphite porous electrodes. We found that SEIs formed in similar conditions as those at a glassy carbon electrode are way less passivating toward the shuttle reaction. Finally, voltammograms of the shuttle at pristine porous graphite electrodes were analyzed with the model in order to determine geometric parameters of the porous electrode, such as its electroactive surface area and its tortuosity.

Work Package 4: Lithium-ion Electrode Interfaces in Conventional Liquid Electrolytes

WP4 focused on three main tasks: the optimisation of materials – electrode active materials, binders and electrode formulations, electrolyte additive; the full electrochemical and ex-situ characterisation of interfacial behaviour; and *in situ* studies of electrode interfaces (and bulk). The main results follow:

Materials, electrodes and charge/discharge behaviour. Two generations of active anode and cathode materials have been synthesised and characterised (structure, morphology, and electrochemical properties). As first generation anodes, graphite SBG-1, $ZnFe_2O_4$-C and $Li_4Ti_5O_{12}$ (**LTO**, prepared by flame-spray pyrolysis (**FSP**)) have been synthesised. As first generation cathodes, $LiMn_2O_4$ ((**LMO**, synthesised by flame-spray pyrolysis and comparative solid state literature routes) and $LiFePO_4$ (LFP commercial sample supplied by ALEEES) have been used. As second generation anodes, improved graphite SBG-2, $Zn_{0.9}Fe_{0.1}O$-C, C-coated **LTO** have been synthesised. As cathodes, several surface coated LMO and $LiNi_{0.5}Mn_{1.5}O_4$ (**LNMO**) samples have also been synthesised.

It has been demonstrated that for all materials a carboxymethyl cellulose (**CMC)/H_2O formulation** allows the preparation of stable electrodes, being at the same time cheaper and greener than the use of polyvinylidene fluoride (**PVdF**)/ N-methyl-2-pyrrolidone (**NMP**) binder/solvent system.

Regarding the **first-generation materials**, LTO prepared by **FSP** shows good performances, suggesting that the FSP synthesis is a viable method for obtaining high-performance LTO. In particular electrodes based on this optimised LTO nanopowder, using CMC as binder, and copper as current collector revealed excellent rate performance, 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. Targeting the commercial application of thus synthesised nanoparticles, we optimised also the electrode composition, comparing three different binding agents (CMC, PVdF, and poly(acrylic acid), PAA) and substituting the copper current collector by aluminium. The results of this comparative analysis show, that the combination of nanoparticulate LTO, CMC, and an aluminium current collector appears most suitable toward the realisation of environmentally friendly and cost-efficient lithium-ion anodes, presenting very stable cycling performance for more than 1000 cycles at 10C without substantial capacity decay.

In comparison, the LMO sample prepared by FSP shows poorer performances (capacities lower than 100 mAh g^{-1}) than those prepared by comparative route. This has been ascribed to the nano-dimensional nature of the material, promoting additional degradation mechanisms.

Cycling data of the graphite (SBG-1), ZFO-C and LFP show capacity values in line with the theoretical ones (ca. 350, 1000 and 170 mAh g^{-1} respectively).

Progressing onto the **Second-generation materials**, SBG-2 graphite (with a modified surface) shows improved rate capability than SBG-1 at room temperature (25^{o}C), but reduced stability in **LP30** (ethylene carbonate, EC: dimethyl carbonate DMC 1:1 w/w 1M $LiPF_6$) at high temperature (50°C) (probably because of high surface reactivity). C-coating LTO using cellulose results in an improved rate capability and interfacial stability. At 50°C the stabilities among uncoated and C-coated LTO are comparable. Li_2TiO_3 phases were also grown over TiO_2 substrates and their bulk and surface compositions characterised. Coating of LMO by oxides, results in improved rate capability and interfacial stability, especially at high temperature (50°C), although C-coating is ineffective. LNMO prepared by a solid state route exhibits good performances, in contrast to one prepared by FSP. Oxide coating of LNMO resulted in-decreased performances. $Zn_{0.9}Fe_{0.1}$-C is more stable at high temperature than 1st-gen $ZnFe_2O_4$-C.

Inductively coupled plasma mass spectrometry (**ICP-MS**) analysis of electrolyte solutions, in which materials were immersed for prolonged times, confirmed that **Mn dissolution** from LMO is accelerated at the higher temperature of 50^0C.

Electrolyte additives such as boron esters were synthesised and characterised. The addition of a fluorinated boron ester additive to LP30 electrolyte resulted in improved capacity retention for graphite/LFP cell, but reduced performance for graphite/LMO cell. It was further demonstrated that addition of LiFSI salt can improve thermal stability of SEI.

Redox shuttles experiments were conducted using ferrocene/ferrocenium redox couple on (a) glassy carbon electrode; (b) several kinds of graphite electrodes. The evolution of SEI growth has been followed by monitoring the activity of the redox couples, and the impact of SEI formation toward relevant kinetic parameters, such as current density, has been determined.

***Ex situ* measurements**

An innovative solution for monitoring the growth of the SEI was developed for X-ray methods. Arsenic (**As**) atoms present in the electrolyte solution were used as a local probe for monitoring the SEI growth on different electrodes.

The electrolyte salt commonly used in Li-ion cells is $LiPF_6$, even with potential issues coming from possible HF formation because of PF_6^- decomposition in the presence of moisture. X-ray experiments have been performed using a mixture of $LiPF_6$ and $LiAsF_6$ electrolyte salts to exploit X-ray beam cross-section at the As K-edge within the composite electrodes. In fact, while $LiAsF_6$ has been discarded for commercial applications because of its toxicity, however its lithiation reactions are similar to those of $LiPF_6$ in which for both electrolytes the LiF and $Li(As/P)F_x$ phases are expected to be the components of the inorganic, inner layer of the SEI.

High-quality As K-edge spectra were collected in fluorescence mode for a set of carbon-coated $ZnFe_2O_4$ and graphite (SBG-1 and SBG-2) electrodes allowing the characterisation of the inorganic components of SEI formed over graphite and ZFO-C electrodes. Detailed structural results were derived for different Li contents in different electrodes including the estimated thickness of the SEI layer, contribution of different **As** oxidation states, and As local structure.

In different experiments, involving "soft X-rays" interaction with a SEI formed by decomposition of LP30 electrolyte ($LiPF_6$ 1M in EC:DMC 1:1), the combination of X-ray absorption spectroscopy **(XAS)** in total electron yield **(TEY)** and total fluorescence yield **(TFY)** modes allowed to follow the dynamics of growth of SEI over ZFO-C (initial nucleation around carbon, then percolation through electrode and growth of a bulk SEI).

Correspondingly, **XAS/X- ray photoelectron spectroscopy (XPS) combined spectroscopies** followed SEI formation over ZFO-C and demonstrated the reversibility of an external “gel-type layer” of SEI. Its composition consisted in part of di-(Li alkyl carbonates) and it was found to contribute to the reversible capacity. Evidence of a partially reversed redox process, taking place within the SEI by charge–discharge cycling, was also obtained.

This was confirmed by **XPS analysis of SEI surface over graphite (SBG-1 and SBG-2) binder-free electrodes**, finding different distributions of organic (Li_2CO_3, $ROCO_2Li$, polyethylene oxide (PEO), ROLi) and inorganic species (LiF and $Li_xPF_yO_z$).

Besides conventional XPS experiments, **hard X-ray photoemission (HAXPES)** was performed on carbon-coated ZFO. These HAXPES experiments allow to obtain compositional information in the same way XPS do but with increased probing depth which is very useful for SEI studies. The combination of XPS and HAXPES provided a picture of the outermost surface layer (SEI region) combined with subsurface information (electrode/SEI interface). In the case of ZFO, the formation of lithium oxide at the very end of the conversion reaction of C-coated ZFO has been identified. This could be associated to a gradual reaction from the core to the particle surface, even segregation of metallic species. The formation of metallic Fe and Zn is detected by means of XPS and HAXPES as well as the thickness of the SEI layer.

***Ex situ* Raman** spectroscopy of the film formed on the surface of a gold electrode cycled in LP30 commercial electrolyte was carried out. To check the influence of the electrode surface morphology, electrochemical studies and spectra were recorded on a roughened surface and also on electrodes after deposition of shell isolated nanoparticles (**SHIN**) (for use for the shell isolated nanoparticles for enhanced Raman spectroscopy (**SHINERS**) technique). Surface layers on gold formed during electrolyte reduction were measured with SHINERS. SEI products were detected. Peaks related to vibrational modes of ν(C=O), ν(C=C), ν(C-O-C) and ν (C-H) have been detected. There is also an additional peak at approximately 1434 cm^{-1} associated with lithium alkyl carbonates.

In situ measurements

EIS characterisation of LTO anodes prepared with PVDF, CMC, or PAA binders allowed to assess the stability of CMC-based electrodes. The EIS response of all 1st and 2nd generation materials was investigated at T = 25 °C and T = 50 °C, in order to monitor the ageing of the cells and, particularly, of the passivation layers formed at electrode/electrolyte interface. All the Nyquist plots revealed features related to passivation layer, charge-transfer and diffusion to blocking electrodes. Among the other results, it has been demonstrated that, in LP30 electrolyte, for the graphite, SBG-2 undergoes a more pronounced ageing than SBG-1 at high temperature. Coated LTO and LMO appear instead more stable, even at high temperature, than the respective uncoated first-gen LTO and LMO. Also $Zn_{0.9}Fe_{0.1}$-C showed higher resistance to ageing at high temperature than $ZnFe_2O_4$-C.

For ***in situ* Raman**, a three-electrode configuration cell has been used to collect spectra during the first discharge-charge cycle of different anode (SBG-1, SBG-2, ZFO, ZFO-C, $Zn_{0.9}Fe_{0.1}O$-C and LTO) and cathode (LFP, LMO, LNMO) materials. The spectra show the evolution of characteristic peaks of each material as the lithium is inserted or extracted. Among the most interesting results: (a) SBG-2 graphite presents a sharper G peak and the relative intensity of this peak with respect to the D band is also higher when compared with the SBG-1 spectrum, suggesting a more ordered structure in SBG-2 or the presence of fewer defects at the edges; (b) LTO shows the presence of an anatase form, which has a great contribution in both the electrochemical and spectroscopy results; (c) the carbon coated $ZnFe_2O_4$ shows the appearance and disappearance of peaks that can be related to SEI compounds at potentials between 0.80 and 0.69 V during the discharge process, with a temporary enhancement of the Raman signal (surface enhanced Raman spectroscopy, SERS) produced by Zn nanoparticles formed during the conversion reactions in the same potential window, while at lower potential these bands disappear due to an increase in the SEI thickness inhibiting the SERS or the formation of LiZn during the alloying reaction; (c) for $Zn_{0.9}Fe_{0.1}O$-C, the SEI-related signals observed for first-gen ZFO-C are lacking due to the fact that the signal-enhancing Zn is formed at much lower potentials (below 0.3V) than those corresponding to SEI formation.

***In situ* XAS** measurements were carried out using a modified closed electrochemical cell from EL-CELL. The cell geometry was modified for the X-ray absorption measurement optimisation. The In-situ measurement was carried out on Fe K-edge during the first half cycle of the lithiation. Theoretical spectra of model compounds with several possible cations and O lattice arrangements have been predicted in order to fit experimental data. Preliminary results confirm the metallisation and amorphisation of the Fe metal in below 0.7 V and the inversion of the spinel structure within the lithiation process. Further analysis is in progress.

SIRBATT has therefore set up and developed a wide range of ex situ and in situ measurement techniques to critically examine the chemistry of the bulk and the surface of electroactive materials, as well as to follow the development of passivation and SEI films on electrode surfaces. SIRBATT has synthesised a wide range of anode and cathode Li-ion battery electrode materials via a number of synthetic routes and tested them in conventional and additive containing electrolytes at different temperature and cycling regimes. Green electrode formulations through processing from water using a fluorine-free binder has been a further highlight form this section of the project.

Work Package 5: Lithium-ion Electrode Interfaces in Non-Conventional Electrolytes

The aim of this workpackage was to synthesise new salts and electrolyte additives and then to test them within novel electrolyte formulations with selected generation one and two electrode materials.

All the materials are completely new and are used as a continuous relevant story of new types of anions and present continued relevance with a novel potential to the existing state of art. Most of the synthesis are one step synthesis and cut the material used in final electrolyte of almost by half. New salts LiTDI and LiPDI (lithium 4,5-dicyano-2-trifluoromethylimidazolate and lithium 4,5-dicyano-2-pentafluoroethylimidazolate) 1st generation, as a new non-conventional salt were synthesised and sent to partners with a procedure of making liquid electrolyte. As an additive the LiHDI (lithium, 5-dicyano-2-heptofluoropropylimidazolate) was proposed in 1st generation of additive material. Based on our experiments the 2nd generation of non-fluorine salt LiPCP (lithium pentacyano propenide) was proposed and LODI as an additive. New salts exhibit very high thermal stability up to 350^{o}C and were stable within a wide electrochemical stability window.

In order to assess the stability of the new lithium salts, soluble redox organic molecules were used as reducing agent. The reduced form of these molecules were first prepared by lithiation in tetrahydrofuran (THF) and the new salts were then added to the as-obtained solution. Reduced forms of the molecules are radical anions and provide a strong colour to the solution. A change in colour upon addition of the salt is ascribed to the oxidation of the radical anion along with the chemical reduction of the lithium salt. Hence, it is a handy and visual method to assess the salt stability.

Results indicate that both FSI^- and $FTFSI^-$ easily reduce (presumably because of the F-S bond cleavage). On the other hand, there is no colour change for PF_6^-, $TFSI^-$, TDI^- and HDI^-, even in the reduced form of dibenzene, which indicates that they are stable at potentials of 0.5 V vs Li or higher.

Electrochemical stability of new salts

In parallel with the chemical stability experiments, the SEI formation on graphite electrodes in carbonate electrolytes containing the different salts was studied. SEI formation tests were conducted on two different graphite materials, namely the SBG1 graphitic carbon, as well as a synthetic graphite (KS-6, supplied by Imerys). The comparison of the differential capacity plots on both graphite materials shows consistently a large magnitude of the SEI formation peaks with KS-6, which is ascribed to its large BET surface area. Results also show that the onset of the SEI formation peak is also shifted to slightly higher potential for KS-6 (10 to 15 mV). This effect is minor with respect to the salt effect, but seems to be consistent amongst all samples (every experiment was repeated twice).

The type and concentration of the Li salt in the electrolyte is shown to have a greater effect on the potential shift of the SEI formation peak; the trend of the onset potential is LiHDI > LiTDI > $LiPF_6$ (maximum of the peak at 0.93V > 0.85V > 0.78V, respectively). This is clearly an effect of the anion.

Solid Polymer Electrolytes (SPEs)

Ionic conductivity and transference numbers were characterised by Electrochemical Impedance Spectroscopy.

For non-modified two-component SPEs, conductivities are very high, especially for low temperatures, 0.1 mS cm^{-1} order of magnitude values are obtained already at 40°C.

T_{Li+} experiments used Li|electrolyte|Li cells and were performed at 40ºC. Very good lithium cation transference numbers were obtained for all membranes especially those with higher salt content. A value of 0.3 is obtained for few compositions which is quite high in comparison to 0.2 which is a typical value for SPEs based on conventional salts (such as $LiPF_6$).

Initial experiments of the passive layer formation were done for PEO systems. Samples were closed in the symmetrical Swagelok cells and impedance evolution was measured by EIS. For all the cases stable passive layers was grown.

Electrochemistry of cells with $PEO_{10}LiPDI$ as electrolyte

Electrochemical cells were assembled with the $PEO_{10}LiPDI$ membrane. Both Li/graphite cells and Li/LFP cells were made. In both cases, the performance were found to be very low and much below the theoretical capacities. A possible explanation is that regular porous electrodes were used for assembling cells. Electrodes containing the polymer electrolyte should be used instead.

The SEI characterisation of graphite/Li cells at 55 and 70 °C LiPDI10-PEO was carried out. Thanks to a special cell design did succeed in disassembling the cell components for the study of the electrodes and electrolyte surface. XPS measurements were carried out in the graphite electrode surface, Li anode surface and membrane surface.

The formation of Li_3N that would help towards the stabilisation of the Li anode has been confirmed. The slight degradation of the electrolyte in the graphite electrode has also been observed.

The electrochemical performance of the cells has been found to be outstanding: 350 mAh/g and 370 mAh/g at 55 and 70 °C respectively with a coulombic efficiency of 98% during the first 15 cycles. Long-time tests (>100 cycles) are being performed currently, however, these were started with membranes that were stored in the glove box for a couple of months. The results show that capacity is much lower at the beginning and it improves after cycling almost reaching the abovementioned values. This is an indication of water intake by the membranes.

Electrochemical performance in liquid electrolytes (and additives)

Electrochemical SEI formation studies have been carried out on graphite based electrodes using LiTDI electrolyte with and without LiHDI additive (2 %). XPS studies show some differences in carbon, fluorine and oxygen spectra between untested graphite electrodes and the ones tested with LiTDI electrolyte and LiHDI additive.

A series of graphite-based electrodes have been tested in LiTDI-based electrolytes with or without 2% HDI additive. Results shows the life cycle testing at 1C rate in LiTDI in EC:DMC (1:2)+2% HDI additive following initial solid-electrolyte interphase (SEI) formation at either 0.1C, 0.5C, 1C or 3C rate in the first five cycles. For comparison, over 100 cycles at 1C rate can be obtained in standard LP30 electrolyte regardless of the initial cycles C-rate.

The better capacity retention for the intermediate C-rates (0.5C and 1C) imply that a more stable SEI is formed in the initial cycles that allow for longer cycling. XPS results indicate that the SEI with LiTDI+LiHDI contain C-O, C-N and carbonate functions. There is also some evidence of metal fluorides.

Electrochemical cycling with LMO electrodes has also been carried out with LiTDI electrolyte + 2 % LiHDI. The LiTDI+ LiHDI electrolyte resulted in an increase (2 %) in capacity retention.

The electrochemical behaviour of graphite SBG-2 has been characterised with two electrolyte systems: (i) LiTDI 1M in EC:DMC 1:2; (ii) LiTDI 1M + LiHDI 0.1M + EC:DMC 1:2, at 4 different temperatures: T = 40 °C, 30 °C, 25 °C (r.t.), 10 °C. Charge/discharge performances have been evaluated by CC/CV protocol at 1C charge/discharge rate.

Electrochemical impedance spectroscopy measurements on graphite electrode have been performed at the same temperatures every 5th cycle and at E = 0.09 V (LiC_6/LiC_{12} plateau)

At relatively high temperature (T = 40 °C and T = 30 °C) the cells with both electrolyte system undergo accelerated ageing and severe capacity fade, however the LiTDI 1M + LiHDI 0.1M + EC:DMC 1:2 system seems more effective in retarding performance degradation.

Analysis of EIS data shown the LiTDI 1M + LiHDI 0.1M + EC:DMC 1:2 system seems to exhibit better interfacial behaviour (lower and more stable Rct at high temperature).

$LiFePO_4$ behaviour has been evaluated at T = 25 °C by CC/CV charge/discharge cycles and EIS at E = 3.45 V ($LiFePO_4/FePO_4$ plateau). For both electrolyte systems, poor performances have been obtained, with similar interfacial properties (R_{ct} steadily increasing in the range 50 to 200 Ω during 100 cycles for both electrolytes).

Ionic liquids

Ionic liquids are salts in which the ions (cation and anion) are poorly coordinated, which results in these solvents being liquid at room temperature. Seven types of Ionic liquids have been synthesised as a possible candidate for SIRBATT baseline materials. Of the obtained ionic liquids, two ionic liquids were selected out of the preliminary screening by conductivity measurements and electrochemical stability tests: these were 1-Butyl-3-methylimidazolium 4,5-dicyano-2-(trifluoromethyl)imidazolide (BMImTDI) and 1-Butyl-3-methylimidazolium 4,5-dicyano-2-pentafluoroethylimidazolate (BMImPDI). All ILs were characterised thermally and electrochemically showing the potential in application as an alternative for conventional electrolytes.

Work Package 6: Investigation of lithium metal – electrolyte interfaces

WP6 was focused on the investigation of the lithium metal electrolyte interface. We characterised the lithium metal interface with a variety of ex situ and in situ techniques to better understand how the SEI changes with cycling and under certain storage conditions. In order to best study the lithium deposition process a new in situ setup for light (or optical) microscopy was developed specifically for the research of Li metal electrodes. This method is ideal to investigate the dendrite growth in situ, one of the greatest safety concerns of Li metal anodes.

The initial literature survey led to a **focus** of our research **on non-conventional electrolytes** as carbonate solvent-based systems typically lead to low cycling efficiency and strong dendrite growth.

Work was dedicated to the synthesis of electrolytes suitable for the use with Li metal electrodes. As identified within the literature survey, novel electrolyte systems, mainly based on ionic liquids, were prepared. This work went in close collaboration with WP5, to make use of the novel anions developed within that part of the SIRBATT project.

Various experiments were performed to develop a deeper understanding of the SEI on Li metal and how this affects the electrochemical performance as well as safety issues (e.g. dendrite growth).

We could prove that the **stable cycling** of Li metal electrodes in ionic liquid based electrolytes is possible for several thousands of hours. During a long-term cycling experiment in $Pyr_{14}TFSI$ with LiTFSI (9:1 mol ratio), **no dendrite growth** that would represent a safety problem was detected. However, it was found that during long operation, the SEI grows thicker and thicker, which finally to a large overvoltage during cycling limiting the energy efficiency.

Key for the safe operation of lithium anodes is the choice of an appropriate electrolyte and the permanent **control of the cell voltage** (**i.e. electrode potential**).

A great variety of experiments was performed to clarify what testing conditions actually lead to a stable and safe operation.

If the electrode is overloaded, i.e. a too strong current or voltage pulse is applied, strong electrolyte decomposition as well as SEI crack formation is found, which directly goes along with dendrite growth and pitting dissolution.

Post-mortem SEM investigations of cycled electrodes revealed that dendrites form in nanofibres in bundles inside cracks of the SEI. It is likely this dendrite growth process actually causes the SEI cracking. To further clarify the process of morphological changes of Li metal electrodes, a **novel setup for *in situ* light microscopy** was developed. Experiments with this setup allowed the investigation of **dendrite growth** and unveiled that **pitting dissolution**, despite not being of direct safety concerns, is another deleterious process that happens at strong electrochemical biases. The so far mostly neglected presence of pitting dissolution on Li metal electrodes, proven with in situ light microscopy, might potentially be the first damage to the Li surface and the trigger for dendrite growth. To this end, three electrode measurement of symmetrical Li metal cells, enriched with impedance spectroscopy, clarified that the electrode potentials of the plated and stripped electrode strongly diverge within a half-cycle. In fact, it was observed that **the stripped electrode is polarised more strongly**, pointing to the option that Li stripping is more difficult than plating, which is rather unexpected following the omnipresent discussion of solely dendrite growth.

To get more insight into the chemical composition of the SEI on Li metal electrodes, in situ Raman and IR experiments were conducted. However it was found that the **high energy of Raman laser irradiation inevitably leads to electrolyte decomposition** on the electrode. Therefore, conventional Raman experiments (in situ or ex situ) were found to be unusable and the **SHINERS technique was applied**. As the process of Au nanoparticle integration to the metal surface typically involves aqueous solvents, an alternate route was followed. The **SHINERS nanoparticles** were deposited **on the Raman window instead of on the electrode** itself. First measurements proved that, in case of close proximity of the Raman window to the electrode (thin electrolyte film), this approach is a valid option, as the Au nanoparticles led to strong signal enhancement of species on the Li metal surface despite not being integrated in the surface film directly. This method, as soon as fully developed, has the **potential to generally increase the usefulness of SHINERS** as it allows a much broader range of samples to be investigated.

A great step towards the further understanding of Li metal electrodes is clearly the investigation of the primary SEI (the native SEI and artificial alternatives) conducted within this project. A large set of UHV experiments, in collaboration with DFT modelling of WP3, focused on the products of exposure of ultraclean Li surfaces with N_2, CO_2 and O_2, gases that are typically present during the synthesis of Li foils for battery research. It was found that Li does not easily react with dinitrogen to form Li_3N, but that this process usually involves surface contaminants like LiOH. The **products formed by O_2 and CO_2 exposure** lead to a **lower work function than for pure Li**, a very uncommon feature of a “passivation” layer.

Following this fundamental research, a new setup for the creation of pure Li surfaces and in situ treatment with liquids was developed that can be applied with standard lab equipment (no UHV necessary). This work was intended to **replace** the omnipresent **native SEI** film **with an artificial primary SEI**. First experiments with amines led to a stable Li surface and are a promising start in this new research area.

The properties of LiTDI and LiHDI in EC/DMC solvent mixtures were investigated as possible future electrolyte systems. It was shown with impedance spectroscopy that the SEI formed on lithium metal anodes in those novel electrolyte mixtures is more stable than standard LP30. Especially the addition of **low amounts of LiHDI leads to a stable interfacial resistance**. These imidazolium anions based new anions, developed mainly in WP5, were also implemented into polymer electrolyte mixtures on a PEO basis (PEO + Li salt + corresponding ionic liquid). However, those ternary systems were found to be hardly conductive and hence, their performance for lithium plating/stripping experiments was consequently inferior to other existing technologies.

Work Package 7: Micro-Sensors for Real Time Cell Control and Performance and Management of Large-Scale Batteries

The main objectives of WP7 were (i) the definition of large scale application scenarios, (ii) the investigation of micro-sensors for lithium ion batteries, and (iii) cell performance analysis. A detail review of the last advances reported in the literature was carried out in order to identify the most interesting solutions to be applied to the cells. Fibre Bragg grating sensor networks were designed for real time monitoring of internal temperature and pressure, during charging and discharging under various conditions. The performance of such micro-sensors was evaluated in the lab for generic operating conditions of the cells.

Definition of large scale application scenarios

The requirements in backup electrical batteries systems for nuclear power plants were modelled, as substitute of actual fuel systems. So, realistic requirements for such batteries were developed, for usual operations and for emergency conditions, enough to guarantee a proper performance in all circumstances. We derived the design requirements (such as ambient conditions, operating conditions, discharge curves, and others) for batteries that could operate in nuclear power plants are defined. A specific scenario for lithium-ion batteries was proposed.

Also, specific requirements such as qualification procedures that shall be undertaken in order to qualify the batteries for nuclear plants, were described in this deliverable. So, type testing (test plan, test sequences, acceptance criteria) needed in order to fulfil this qualification process was described in this document. Based on information from the application analysis, large-scale analysis (including: operating temperature conditions duty cycles, energy throughput, etc.), cell level testing analysis was carried out through cell models.

These models were utilised to perform a full electrochemical and thermal characterisation, key parameters for the calibration and optimisation for the Battery Management System. The data obtained were used to build an electrothermal virtual model which will allow support the application analysis through simulation.

Investigation of micro-sensors for lithium ion batteries

For theses analysis, we have supplied characteristics data for one of the plant battery banks, in order to simulate a similar bank capacity with the batteries developed. Data supplied was related to system voltage, nominal capacity, internal resistance, short-circuit current, equalisation voltage, discharge current chart (A/V), and the demand curve for battery (A/t).

Fibre Bragg sensors were chosen for performing real time measurements of the battery performance. They have the advantages of being relatively small and flexible and they offer immunity to electromagnetic radiation and multiplexing capabilities. The sensors were recorded on commercially available photosensitive optical fibres (Fibercore PS1250/1500) and calibrated on a thermal chamber (Model 340, Challenge Angelantoni Industry). The FBG data for calibration and in-situ measurements were collected with the sm125 interrogation unit (Micron Optics Inc., USA) with a specified wavelength resolution of 1 pm at 2 Hz sampling rate). The thermal calibration of sensors was made inside the thermal chamber in a range of temperatures between 10ºC and 35ºC, in steps of 5ºC.

Bragg sensors assembly in pouch cells was successfully achieved. Internal sensors were located between the separators, one placed in the central part of the active area and other placed near of the tab-electrode connection. In addition, external sensors were placed in direct contact with the surface of the pouch cells and thermal paste was used to increase contact surface and conductivity. Five charge-discharge cycles at various **C**-rates (1C, 2C, 5C and 8C) (please note a C-rate is a measure of the rate at which a battery is discharged relative to its maximum capacity. A 1C rate means that the discharge current will discharge the entire battery in 1 hour) were carried out in order to analyze the response of the sensors. As expected, the response followed the galvanostatic cycling and the highest wavelength variation occurred at 5C and 8C, with $\Delta\lambda$ values between 0.05 and 0.07 nm. In general, it was found that the battery performance did not change significantly upon the sensor network integration and it could be monitored successfully.

To summarise the sensor work within SIRBATT research, we were able to integrate optical fibre sensors into Li-ion pouch cells. Such sensors can be used to investigate different physical and chemical parameters. For the discrimination of pressure and temperature within the pouch bag, a hybrid sensor composed by two sensors connected in series (a fibre Bragg grating and a Fabry-Perot interferometer) has been developed. Both sensors exhibited different sensitivities to temperature and pressure. Using the appropriate signal processing, it was possible to infer the variations of these two parameters. This sensor revealed to be much more precise and reliable than any other existing technology (integration into battery gives much faster and more relevant results than external measurement). And our approach solves the separation of pressure and temperature influence to the actually measured signal shift, which has not been fully addressed by competing research groups. It should be highlighted that temperature and pressure control is very important for the Li-ion cell safety as well as lifetime.

Cell performance analysis

The initial part of the work to be carried out in work package 7 was the investigation of the performance at cell level to support the application analysis for large-scale devices. Originally, it was planned to perform testing on three of the six enhanced cells with integrated sensing units. One cell was to be utilised to perform a full electrochemical and thermal characterisation, thus providing technical understanding of the performance of the cell as a function of temperature and state of charge and key parameters for optimisation for the Battery Management System. The second and third cells were to be used for ageing tests.

The six cells with the embedded sensors arrived one month before testing; however, upon inspection, five cells were discovered to be at low voltage (< 2 V) and the sixth cell, although had a good initial OCV upon inspection, showed very low cell capacity upon cycling and high internal resistance. The recovery process on three cells of the 5 cells was performed. However, none of the cells were suitable to perform testing in accordance with the original testing plan. Consequently, the testing procedure was adapted to try to maximise the information that could be obtained from the cells and the sensors, three new tests were performed instead. These included an ambient temperature change test, peak power test and steady state analysis.

Ambient temperature change test involved the changing of the temperature of the surrounding chamber through a series of steps to measure the external and internal temperature readings against that of the chamber and measure the temperature lag. The pulse power test used a series of ten second discharge pulse currents to probe the thermal response of the cell at increasing current levels. Between each pulse, the cell was subjected to a low base current of sixty seconds before each pulse. This test was performed at 40°C to lower the internal resistance of the cell. The steady state analysis test measured the temperature evolution of the cell from application of a root mean square current. By applying a repetition of alternating discharge and charge currents for 10 seconds at 50 % state of charge, the steady state of the cell can be reached when the temperature increase reached a plateau. This test was performed at both 23 and 40°C.

The ambient temperature test showed that on average, the external thermocouples take five minutes to match that of the chamber with the internal sensor, a further minute behind. Interestingly, all internal sensors did not all show the same lag time, the sensor furthest from the tabs had the fastest thermal response, followed by sensor nearest the tabs and then the middle sensor. Furthermore, at lower temperatures, the embedded sensors recorded a lower temperature than the outside thermocouple, however, at higher temperatures, the inverse is true.

The pulse power test probed both the electrochemical and thermal response of the cell using a series of current pulses from 0.1 to 5A in 0.1A increments. The current was increased incrementally until the voltage drop from the pulse reached close to the lower voltage limit of the cell. At each pulse, the external and internal temperatures were recorded on each sensor position. As expected, the thermal response of the internal sensors were faster than the external sensors at each pulse. Although the temperature recorded by the internal sensor was higher than the external, the ΔT rise for both sensors were in good agreement at all pulse currents. From the analysis of the data, the direct current internal resistance (DCIR) and power was additionally calculated. The DCIR of the cell was determined to be 240 mΩ and the power calculated at 10W.

The steady state analysis test was performed at both 23 and 40°C. At 23°C, an RMS current of 1.5A was applied and at 40°C, 2.5A was used. At 40°C, the internal resistance is lower allowing higher currents in discharge and charge to be used without reaching the upper and lower voltage limits. In both tests, the results showed that the measurement at the internal sensors began to increase before the external sensors along with a steeper rise from the applied discharge and charge pulses.

Overall, the results from the tests conducted do show that the embedded Fibre Bragg Grating micro-sensors inside the cell only show a small thermal lag to exterior environment, have faster response to pulse testing and display a higher recorded temperature compared to exterior thermocouples. This testing study has shown that internal sensors have the benefit of being more responsive and have more accurate temperature readings of the cell under a variety of conditions compared to that of the traditional measurement of thermocouples placed on the outside of the cells.

The second part of the work to be carried out in work package 7 was for three of the prototype cells with embedded micro-sensors to be built into integrated module system. However, this was no longer feasible due to unforeseen cell situation. As an alternative, JMBS proposed to model and simulate a 12 V module based on data from testing data generated within SIRBATT. The proposal was agreed with partners and as a consequence of the change, the activities for WP7 was re-edited to account for the new plan.

For development of the conceptual 12 V module, performance data; rate capability and thermal behaviour recorded during testing by both external and internal sensors was used. This data however was not extensive and robust enough to fully develop the virtual module, the model was therefore developed partially upon data obtained from previous work package characterisation and supplemented with commercial LFP based pouch cell data.

To account for various features in the module, two models were developed in two different environments: a detailed Electrochemical-Thermal model available for integration at system level in Matlab-Simulink; and a detailed cell thermal model for integration into a module/battery thermal model in ANSYS.

In order to simulate typical application, information was collected and collated on typical power requirements, duty cycles, and usage patterns specific for stationary energy storage applications. The applications included emergency back-up system for nuclear power plants, off-grid storage for solar and wind power, data-centre Uninterruptible Power Supplies (**UPS**) and emergency back-up for nuclear power stations. The duty cycles simulated included the power requirements for emergency situation in nuclear power plant, peak shaving management for off-grid storage and frequency regulation for data-centre UPS. The simulations of each predicted the evolution of state of charge, voltage and internal and external temperature. Using ANSYS, a 3D virtual prototype was developed to allow simulation and evaluation of thermal gradients to optimise the design of the thermal management system.

In summary, Li-ion for stationary storage has been considered via a paper study as an alternative to lead (Pb)-acid for back-up power for nuclear power plants. The requirements for such a system have been investigated and the key parameters that a Li-ion system must meet have been documented.

Microsensors that can sense both the change in temperature and internal pressure of the cell have been incorporated into pouch (or coffee-bag) cells containing Li-ion negative and positive electrodes and tested under real cell conditions. It was revealed that the microsensors were much more time responsive than conventional thermocouples.

By combining the data of the requirements for a backup power batter system and electrochemical land thermal data (from the microsensors) a cell –level model was developed

Work Package 1: Administration, Financial and Project Management

The main objectives of this work package were: a) to make sure that the activities in each of the different work packages (tasks, deliverables and milestones) are carried out in line with the agreed budget and timing; b) to coordinate the communication among the project's partners; c) to manage the communication with the European Commission and the respect to the reporting and financial management as detailed in the contract between the EU and SIRBATT consortium; d) to organise the regular biannual scientific meetings; e) To coordinate the overall legal, contractual, financial and administrative management of the consortium.

The project management was efficient and well appreciated by the partners at the end of the project. Special attention to promote and facilitate the interaction and collaboration between the different partners was made through the award of travel grants that supported mobility of young researchers between partners.

Work Package 2: Dissemination & Exploitation

The main objectives of this work package were: a) set up and maintain the project website https://www.liverpool.ac.uk/sirbatt/, which has links to the publically available outputs from the project. All peer reviewed publications are open access, b) To disseminate the knowledge gained in the SIRBATT project to the wider scientific community as well as the general public, which will include a non-specialist audience

Knowledge of the project goals was disseminated through an initial project leaflet, followed up with an updated leaflet with early results and achievements highlighted. Both leaflets where distributed to all the partners and they dispersed them to co-workers in their institution, visitors and to external collaborators, as well as circulating them at nation and international meetings and conferences.

An end-of-project brochure was produced that highlighted the main scientific outcomes from the project. This was very useful to disseminate the SIRBATT project in different events such as scientific/technology and industrial seminars, workshops, conferences and exhibitions.

The whole consortium was highly engaged in dissemination activities. Within the project three year timeframe more than12 in leading peer-review journals such as Advanced Energy Materials, The Journal of Physical Chemistry C and Chemical Communications, Journal of the Electrochemical Society - as well as numerous videos explaining the activities and scientific achievements of the project are available in the project website. More peer reviewed publications are under review or in development, so the final number of outputs is likely to be much greater. It is noted that 2 patent applications have been submitted to National Patent Offices, with one being published.

A plan for using and disseminating the foreground was defined to allow the consortium to develop future exploitation plans.

Potential impact

As described in the previous sections and shown by the scientific publications published in leading peer-review journals (see the Annex I: “scientific publication list”) SIRBATT has undertaken leading research in the fields of organic and inorganic materials chemistry, electrochemistry, advanced electrode and electrode interface characterisation and modelling and micro sensor technology. The significant impact outcome from the research was the successful incorporation and testing of microsensors within a Li-ion pouch cell. The microsensors were shown to be much more time responsive than conventional thermocouples.

Specifically microsensors for batteries could have substantial impact in the design, maintenance and controlling safety of small and large stationary battery installations. Further development of these sensors would involve optimisation of delivery of both temperature and pressure within a single sensor.

A potential short term impact wold be the use of these sensors by cell manufacturers to test cell safety profiles during production and or battery module and pack designers to understand how to manage heat load and distribution within their large format batteries.

The SIRBATT project has had impacts through the development of microsensors in-line with the Cooperation Work Programme (2013 EC (2012) 4536 as of 09 July 2012) which is based on the EU strategy document: ‘Europe 2020: A strategy for smart, sustainable and inclusive growth' in that it will led to growth that is smarter, more sustainable and more inclusive. Specifically SIRBATT will boost research and innovative in a range of key EU priority areas relating to climate change and energy:

Smart Grids (and Energy Storage) through the European Technology Platform for Electricity Networks of the Future (SmartGrids ETP) that is encouraging the integration of decentralised renewable energy sources, more flexible and smarter electricity grids with appropriate storage options, better facilitate the connections and operation of generators of all sizes and technologies and significantly reduce the environmental impact of the whole electricity supply system.

Employment of stationary energy storage technology to support a more distributed and diverse power generation network through the development of microsensors that allow this interconnection and flow of information on the status of health of large battery installations.

Under the Energy work Programme (Work Programme 2013 – Cooperation theme 5 – ENERGY – EC C(2012) 4536 as of 09 July 2012.) it is stated that there is an urgent need to bring new, high performance technologies to the market and to ensure EU leadership on low carbon energy technologies and that this scale requires a European approach.

The achievements of the SIRBATT project was fully in-line with supporting the goals of The Energy Road Map 2050 – that targets a 20% reduction in energy usage by 2020 and an 80-95% reduction by 2050 through a shift in the EUs current energy system to largely decarbonise the energy – This can only be achieved if localise energy storage technologies can be developed. Lithium batteries remain one of the most promising technologies to enable us to achieve this. By demonstrating extremely long cycle life a lithium-ion coin cell, SIRBATT has highlighted the prospective use of Li-ion technology as a for long life time applications. The SIRBATT coin cell consisted of a graphitic anode and lithium iron phosphate ($LiFePO_4$; supplied by ALEES) as the cathode, has been cycled for over 2500 times, showing 40% capacity fade. 1750 cycles were achieved with 20 % capacity fade. This result exceeded the project target for 500 cycles and moves us a step closer to the long-term goal for Li-ion batteries to the achievement of 5000+ cycles with less than 20% capacity fade. The challenge is to take this excellent result at the coin cell level and replicate it at scale.

Main dissemination activities

Partners were profoundly engaged in dissemination activities and attended and presented talks and posters on SIRBATTs research at numerous national and international conferences.

SIRBATT organised two international workshops in Spain and USA in 2015 and 2016 to disseminate the work from the project and to engage with the Sister programmes (Hi-C, Influence and Baccara) funded within the same call, as well as complementary European and USA research activity.

The first workshop in Spain, in September 2015 entitled “Understanding Lithium Battery Interfaces” had over 60 attendees. Representatives from Hi-C, Influence and Baccara gave the keynote and invited talks. Further external leading academics in battery interfaces from Europe gave invited presentations. SIRBATT work was well disseminated with talks from partners Universidade de Aveiro (Portugal), Universita Degli Studi di Camerino (Italy), Karlsruher Institut fuer Technologie (Germany) and Centre National de la Recherche Scientifique (France). Industry partners from the SIRBATT network presented their experience of energy storage with talks Johnson Matthey Battery Systems, UK) and Iberdrola, Spain.

Overall the Workshop provided a wide overview of the work currently being undertaken within battery science across Europe. It also provided an opportunity for networking and collaboration within the community.

The Project held its second Workshop ‘Controlling Lithium Battery Interfaces’ in the USA on in May 2016 which was attended by some 50 battery scientists. External leading academics in battery interfaces from the United State of America gave keynote and invited talks. Furthermore, two representatives from BACCARA, one of the other three successful projects with SIRBATT’s EC call, attended with talks, outlining results from their project’s work. From the University of Liverpool talks and posters were presented on battery interface research.

Talks and posters provided a wide overview of research currently being undertaken within the subject; and the Workshop ended with a summary and discussion of the current state of battery science across Europe and the USA. Future areas of research and possible exploitation were outlined and overall the event offered a unique opportunity for networking and collaboration within the wider battery community.

A Networking Workshop in May 2014 between China MOST and EU was attended by representatives from SIRBATT (ULIV and CIC) which gave an opportunity to disseminate European battery research activity within SIRBATT to the Chinese. The meeting gave an excellent opportunity to network with Chinese battery researchers.

Knowledge of the project goals was disseminated through an initial project leaflet, followed up with an updated leaflet with early results and achievements highlighted. Both leaflets where distributed to all the partners and they dispersed them to co-workers in their institution, visitors and to external collaborators, as well as circulating them at nation and international meetings and conferences.

An end-of-project brochure was produced that highlighted the main scientific outcomes from the project. This was very useful to disseminate the SIRBATT project in different events such as scientific/technology and industrial seminars, workshops, conferences and exhibitions.

Exploitation of Results

The application of microsensors within Li-ion cells that can provide both temperature and pressure readings has been identified by the SIRBATT consortium to be of great interest, as it fits into the long-term technological goal of advanced sensors to monitor and control the battery chemistry in order to prolong life. Additionally, the sensors can thereby be used to provide data, so that an accurate second life and economic value can be ascertained at the end of a particular application when it could be reused within another. As such a patent will be filed, potentially bringing in license money to fund further activities in the field of integrated microsensors. For the purpose of the patent application, SIRBATT partners are presently continuing our joint research work despite having no project funding. We will also contact other potentially interested companies for R&D projects. In addition, joint research proposals will be written if there appears a suitable call in H2020 or national funding agencies.