Hi-C: Novel *in situ* and *in operando* techniques for characterization of interfaces in electrochemical storage systems

September 2013-February 2017
Final report

Hi-C Concept and Objectives

Batteries and super-capacitors are highly important elements in the development of a society based increasingly on sustainable energy. Both are complex electrochemical systems transporting various species through materials and across interfaces. Interface properties and dynamics are governing e.g. ionic and electronic transport, reactivity/degradation, stability, kinetic barriers and phase mobility. In the Hi-C project, new and improved techniques for *in situ* characterization on the nanoscale have been developed. These are combined with advanced modeling and computational methods to obtain a detailed understanding of electrochemical processes at an atomic and molecular level.

The fundamental knowledge obtained was used to optimize new and existing electrode materials and SEI (Solid Electrolyte Interface) formation for lithium ion batteries and supercapacitors.

The Hi-C consortium possesses together a wide variety of competences within materials synthesis/fabrication, advanced characterization and computational techniques. Bio-Logic Science Instruments Ltd (former Uniscan Instruments Ltd) has in the Hi-C project developed a scanning electrochemical microscopy cell for *in situ* characterization of interface reactions in battery cells. VARTA Microbattery GmbH is one of the significant battery and supercapacitor manufacturers in Europe. Haldor Topsøe A/S is a major producer of catalysts, but is expanding also into battery materials.

Project coordinator

Professor Poul Norby

Poul Norby is an expert in synthesis and structure/property relations in inorganic materials. He has specific focus on rechargeable batteries including new materials and nanostructures, structural analysis and *in situ* studies especially using synchrotron X-ray diffraction.

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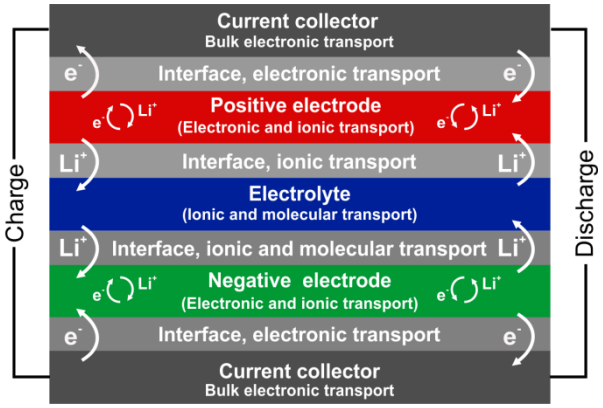
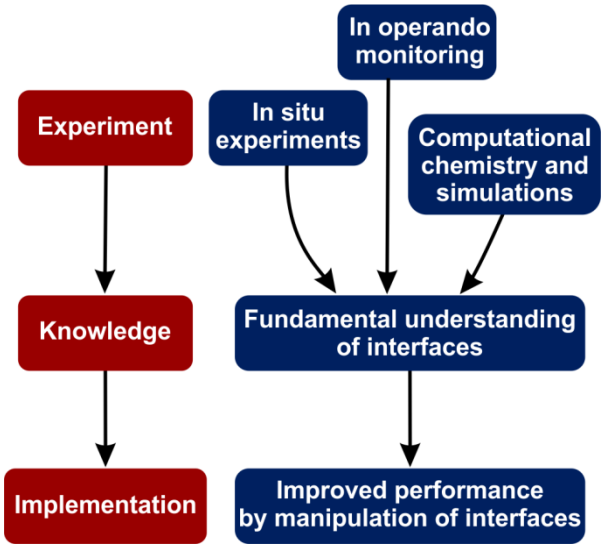
Main objectives of the Hi-C project

- Understand the important interfaces in an operating battery on an atomic and molecular scale.
- Develop *in situ* characterization methods for studies of formation and nature of interfaces in electrochemical storage cells.
- Devise methods to control and design interface formation, stability and properties.
- Develop *operando* methods for on-board monitoring commercial batteries.

The ability to understand, control and manipulate interfaces in batteries and supercapacitors is the fundamental challenge in the Hi-C project. An electrochemical cell may be seen as a series of interfaces. Ionic and electronic transport across the interfaces are crucial for the performance of the devices.

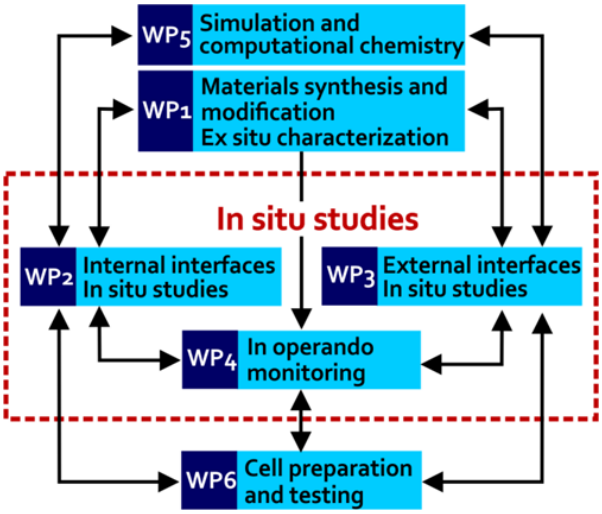


The idea of the project was to build up a knowledge foundation through *in situ* and *operando* studies combined with computational methods. The knowledge gained would then be applied on selected systems in order to demonstrate an improvement in performance by interface manipulation:



Development of various *in situ* characterization methods was essential to the project, and a crucial part was the close interaction with computational studies, synthesis and modification of materials and experimental studies of interfaces.

This was reflected in the organization of the workpackages in the Hi-C project and their interactions:



Materials synthesis and optimization

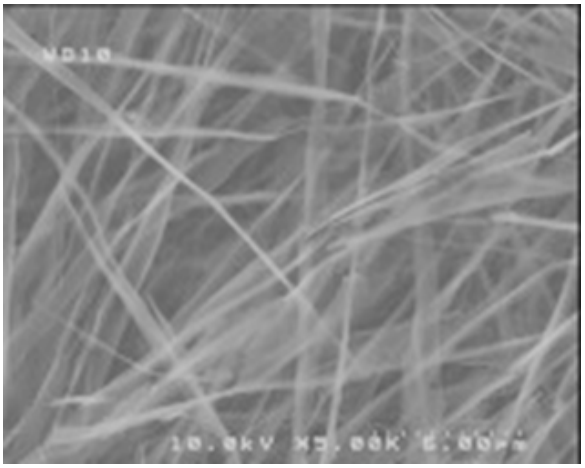
The materials included in the Hi-C project were state-of-the-art and commercially available $LiFePO_4$, Li-NMC, LTO, silicon nanowires, graphite and materials for supercapacitors, e.g. graphite and activated carbon. In addition new materials for optimization were included, e.g. $LiFeBO_3$ and conversion battery materials related to FeF_3/Li.
The novel high-capacity positive electrode material Li_2VO_2F was discovered and patented by one of the partners in the consortium and was included in the Hi-C project.

Intercalation materials, supercapacitors, alloys and conversion systems have been studied. In the last phase of the project a decision for optimization of materials was made, and $LiFeBO_3$, Li_2VO_2F and a hybrid supercapacitor system were chosen for optimization.

Silicon nanowires

Silicon nanowires have attracted much attention as negative electrodes for lithium ion batteries due to a very high capacity and suitable capacity retention. A novel method based on galvanostatic

etching of p-doped Si wafers and subsequent alkaline treatment for obtaining self-supported Si submicron wire carpets linked to conductive bare silicon substrate was developed.



The nanowires can easily be prepared by a low-cost technique where the length and the aspect ratio can be controlled by changing the electrochemical etching time. Indirect bipolar electroanodization (IBEA) produces nanowires with 100 µm maximum length and diameters ranging in the order of 300-1000 nm.

The Si nanowire electrode performance can be increased by activation by voltage sweeping which increases the capacity six fold from 0.05 to 0.3 mAh/cm^2 at the cycling rate of 320 mA/cm^2. For silicon, one of the more successful strategies for dealing with the capacity loss associated with electrochemical cycling and continuous electrolyte decomposition has been the use of battery electrolyte additives. Of these, fluoroethylene carbonate (FEC) and vinylene carbonate (VC) has been very successful at extending battery cycle life. Superior electrochemical activity during the activation of the electrode is achieved with VC and FEC additives. Galvanostatic cycling performed after cyclic voltammetry exhibits also better performances. Nanowires provide a stable and excellent capacity of 0.6 mAh/cm^2 at a regime, which corresponds to C/2.5.

Interfaces, transport properties and performance optimization in $LiFeBO_3$

- Increased capacity to 160-180 mAh/g
- Obtained more than 130 cycles

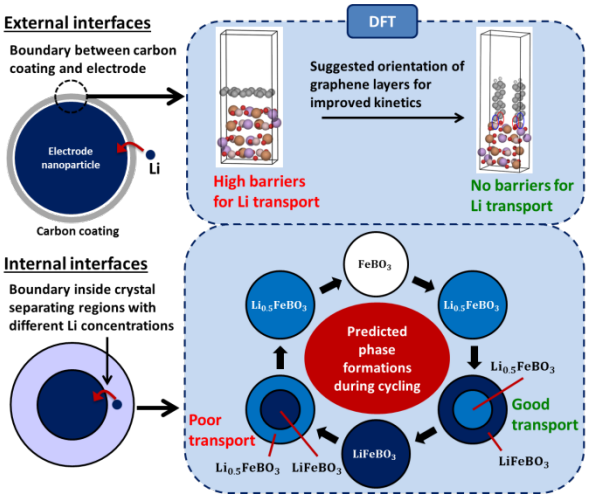
Optimization of lithium iron borate

$LiFeBO_3$ is a very promising potential battery material but its challenging chemistry has been a major reason for the slow progress and very scarce knowledge. In the Hi-C project, new ways of synthesizing $LiFeBO_3$ were developed leading to significantly better performances. Synthesis of comparably pure compounds resulted in a material with high purity, but with rather low electrochemical activity showing a capacity of only 35 mAhg^{-1} compared to a theoretical capacity of 220 mAhg^{-1}. Different ways to increase the electrochemical activity were explored of which the most successful proved to be nanosizing and embedding in a conductive graphitic carbon matrix. The optimized $LiFeBO_3$ delivered a specific capacity of 160-180 mAhg^{-1}, which is among the highest values reported so far. In Hi-C more than 130 cycles for this system were shown for the first time, which demonstrates applicability beyond proof of concept for using $LiFeBO_3$ as a cathode material.

Li transport mechanisms in $LiFeBO_3$

Density Functional Theory (DFT) investigations have been performed to study the effect on the transport kinetics and overpotentials associated with Li ion transport across protective graphene/graphite coatings on $LiFeBO_3$. By computational investigations the angular orientation of the graphene coating and the role of defects in the carbon coating on the transport mechanisms have been investigated and optimized. The work showed that Li transport through pristine and parallel graphene coatings is severely impeded, and that large structural defects or significant misalignments between the carbon coating and

the $LiFeBO_3$ particles are required to achieve fast charge/discharge kinetics.



Potential bottlenecks for transport of Li ions and electrons are both internal and external interfaces. Top panel: A suggested new orientation of the graphene layers can improve the Li-ion diffusion across the coating–electrode interface. Bottom panel: DFT Investigations and convex-hull analysis find that a stable interface between $Li_{0.5}FeBO_3$ and $LiFeBO_3$ exists, and that both the ionic and electronic transport in $Li_{0.5}FeBO_3$ is significantly lower than in $FeBO_3$ and $LiFeBO_3$.

Intra-particle interfaces in $LiFeBO_3$

Intra-particle interfaces in Li_xFeBO_3 may influence the ionic and electronic transport during battery charge and discharge. DFT and Non-equilibrium Green's functions (NEGF) calculations were carried out and showed that the Li transport occurs by a pseudo-1D zig-zag movement of Li interstitials/vacancies along the *c*-axis and that the electronic transport shows relatively low activation barriers. A stable structure of a half-lithiated phase, $Li_{0.5}FeBO_3$, was found, supporting the experimental observations of a possible two-phase region between $Li_{\sim 1}FeBO_3$ and $Li_{0.5}FeBO_3$. These findings would support the large over-potentials observed experimentally.

The Hi-C Consortium

The Hi-C consortium consists of an interdisciplinary team from European research institutes and industry that has a long expertise with regards to battery and supercapacitor development. The consortium is composed of 8 organizations from 5 different countries.

Hi-C Partners

- Technical University of Denmark, Denmark
- Université François Rabelais de Tours, France
- Commissariat á l'Energie Atomique et aux Energies Alternatives, France
- Karlsruher Institut für Technologie, Germany
- Uppsala Universitet, Sweden
- Haldor Topsoe AS, Denmark
- Varta Microbattery GMBH, Germany
- Uniscan Instruments Ltd., United Kingdom (now Bio-Logic Science Instruments Ltd)

New vanadium oxyfluoride high capacity electrode materials

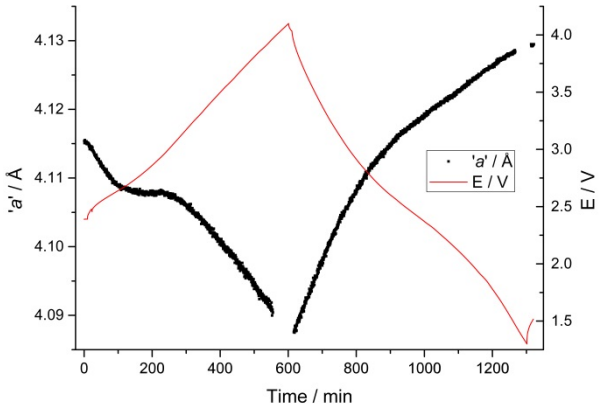
Computational and structural *in situ* investigations were performed and an optimized synthesis route was devised. An improvement in capacity and cycle performance was obtained by modifying the synthesis and using electrolyte additives.

In order to increase the energy density and specific energy of lithium ion batteries new high capacity electrode materials must be developed. During the Hi-C project a new group of high

capacity cathode materials were discovered and patented by one of the project partners (KIT). The materials may be structurally described as rock salt type and the properties and charge storage principle associated with this new materials class are still far from being understood. Initially the Li_2VO_2F was mechanochemically synthesized but the initial high capacity was followed by a steady capacity fading possibly due to vanadium depletion at the surface. Investigating alternative fabrication methods showed that sintering at 300°C resulted in a higher crystallinity which mitigated the dissolution problem. An improved cycling performance was demonstrated and within 50 cycles the sintered material outperforms the initial material. In a second approach, a novel electrochemical synthesis of Li_2VO_2F has been developed. Starting from a new compound, VO_2F, which has recently been reported by KIT, a disordered rock-salt Li_2VO_2F could be synthesized upon electrochemical and chemical lithiation of the VO_2F starting material. The electrochemically synthesized Li_2VO_2F showed higher specific capacity and higher cycling stability compared to the initial material. The newly developed synthesis for the electrochemical synthesized Li_2VO_2F allows an improved performance compared to the sintered and initial material for the first 100 cycles.

In situ studies of Li_2VO_2F

The development of the crystallographic unit cell upon galvanostatic charging and discharging shows an unexpected behavior. *In situ* synchrotron X-ray diffraction studies using a micro-battery cell reveals a plateau in the '*a*' unit-cell parameter upon charging. A similar plateau is not clearly observed for the discharging process. Li^+ ions are extracted from the structure during charging while the vanadium ions are oxidized from $V^{3+} \rightarrow V^{4+}$ and $V^{4+} \rightarrow V^{5+}$. Thus, since an octahedral Li^+ vacancy is smaller than a Li^+ ion in octahedral coordination and the ionic radius of $V^{3+} > V^{4+} > V^{5+}$ in octahedral coordination, it was assumed that the '*a*' unit-cell parameter would decrease during the entire charging process. The plateau in the development of the '*a*' unit-cell parameter is therefore unexpected. It could suggest that the extraction of Li^+ ions is linked to migration of some of the Li^+ ions from the octahedral sites into the interstitial tetrahedral sites. Migration behavior and coordination requirements and their behavior upon repeated charge/discharge cycles are important in order to understand e.g. overpotentials, capacity retainment and cycle stability.



Unit cell development and voltage profile during charge/discharge of Li_2VO_2F

Funding

Hi-C was funded by the 7th Framework Programme (Grant number 608575) ENERGY.2013.7.3.3:

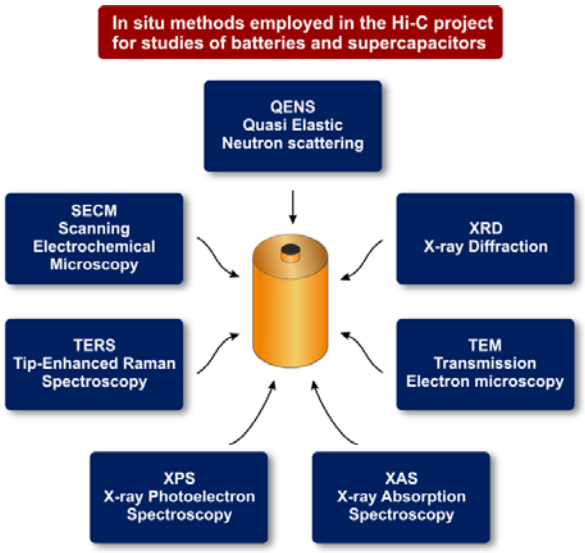
Understanding interfaces in rechargeable Batteries and super-capacitors through in situ methods

Total budget: 6.13 M€,
EU contribution: 4.65 M€.

In situ methods

In situ methods and equipment were developed for studies of materials and interfaces in batteries under operating conditions. Some of the unique techniques which have been developed in Hi-C are:

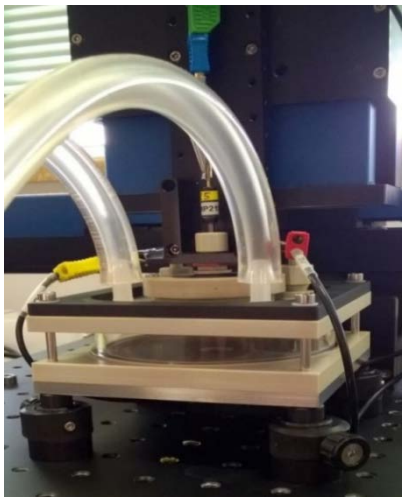
- Scanning electrochemical microscopy (SECM) cells and micro electrodes for electrochemical *in situ* characterization of electrode surfaces and SEI formation.
- *In situ* X-ray diffraction using a capillary based micro battery cell
- *In situ transmission electron microscopy (TEM) studies of battery cell.*
- Tip-enhanced Raman spectroscopy (TERS) under inert conditions.
- *In situ* X-ray photoelectron spectroscopy (XPS) for high pressure studies of electrode interfaces



A number of in situ methods were developed or employed in the Hi-C project. XPS, SECM and TERS are mainly surface characterization methods used for e.g. studies of SEI formation. XRD and XAS are bulk characterization methods, probing the atomic structure of solids. TEM methods are used for studying individual electrode particles and QENS is used for studying dynamic properties, e.g. ion transport.

Development of an *in situ* SECM cell

Scanning electrochemical microscopy (SECM) is a scanning probe technique using an ultra-micro-electrode (UME) which senses local electrochemical behavior of surfaces and interfaces in a liquid. The aim in Hi-C was to develop a new cell able to work *at in situ* conditions for lithium batteries. This requires a cell with a controlled atmosphere where water and air are absent. Additionally, to improve the resolution sufficiently to observe sub-micron features present in battery materials the UME probe size must be decreased. During the project a series of prototype SECM cells was developed, tested and subsequently improved. Going from ambient to a controlled environment requires a sealed cell for which different solutions were investigated.

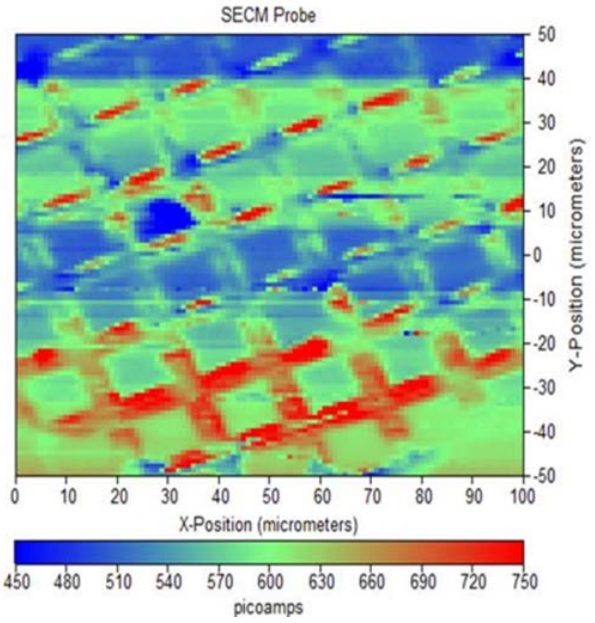


The 4th prototype sealed SECM cell.

The fourth prototype is a compact and hermetically sealed cell working with the commercial M470 base using optical post holders, which allows the cell to be fully prepared before it is put into place. Special attention was paid to the chemical compatibility between the sealed cell and battery materials. The latest tests show a very practical and usable cell.

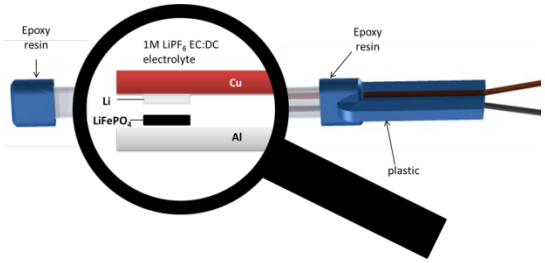
UME probe size improvement

At the beginning of the Hi-C project the smallest probe offered by Uniscan, 10 µm in diameter, was too large to effectively measure the majority of battery materials being investigated. Probes of this size is easily made simply by sealing a wire of known diameter in a glass capillary, heating it and pulling it and finally polishing it. For smaller probes this was more challenging but Uniscan accomplished to develop this technique to make made 5, 2 and 1 µm Pt UME probes. This represents an order of magnitude improvement in probe size, which allows much smaller features to be depicted. It is exemplified by the fine gold mesh shown in the figure below. Many areas of research will benefit from the resolution these UME's can provide both with the *in situ* cell but also with other SECM's.



Fine gold mesh measured with the 1 µm Pt probe

A capillary-based *in situ* battery cell for X-ray diffraction studies.

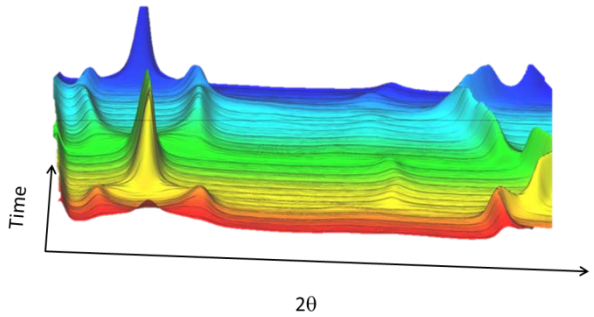


A sketch of the capillary based micro battery cell for in situ diffraction studies. The capillary is ca. 4 mm x 1 mm and the thickness of the electrode coatings range from 50 to 100 µm.

When investigating detailed structural features, defect distribution and interface formation using diffraction methods, it is important to obtain diffraction from only one of the component phases in the battery. In the Hi-C project we have therefore developed a capillary-based micro battery cell which allows the individual compounds in the battery to be investigated separately. The *in situ* cell has been used for a number of experiments at various synchrotron X-ray sources for time-resolved in situ studies of structural and microstructural evolution during charge/discharge conditions. Also, combined spatial- and time-resolved experiments were performed, investigating evolution of chemical gradients in positive electrodes during fast charge/discharge.

Investigating the lithiation mechanisms in $LiFePO_4$ (LFP) batteries has been one of the main challenges. A rate-dependent non-stoichiometry in the phases during the two-phase reaction ($Li_{1-x}FePO_4$ and Li_yFePO_4) was detected from detailed structural analysis using high resolution *in situ* synchrotron X-ray diffraction. The results were combined with *ex situ* TEM measurements (reported below) and computational modeling to understand the lithium transport during battery operation.

Similarly we have investigated the domain and defect formation during lithiation/delithiation of graphite using *in situ* synchrotron X-ray diffraction. The results from these experiments will be combined with computational studies on domain formation in graphite performed in the Hi-C project. The results will give a better understanding of the performance and optimization of graphite in lithium ion batteries by explaining the role of lithium transport and domain formation.



In situ diffraction data showing development of stacking faults and lithiated phases with time during lithium intercalation/de-intercalation in graphite.

TEM based methods for studying battery materials interfaces

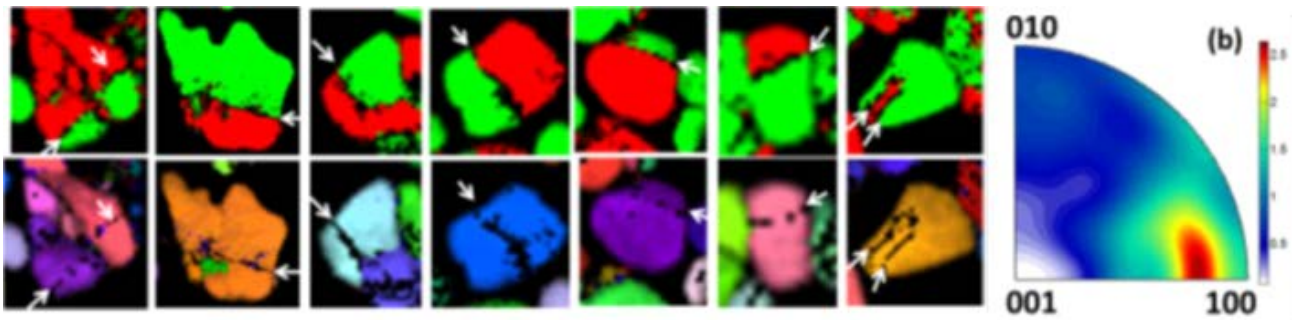
In situ TEM provides an opportunity to follow processes in model battery systems at high spatial resolution of a few Ångstroms to nanometers and good temporal resolution. Different imaging, diffraction and spectroscopic techniques can be combined for the analysis to gain a complete picture of the materials of interest. For the *in situ* TEM development within the Hi-C project the focus was on evaluating/ developing low-dose TEM techniques suitable for imaging the local structure and charging state without damaging the beam sensitive materials, and on developing reliable methods for preparation for *in situ* studies.

Imaging of the lithiation distribution in LFP/FP

Partially half-lithiated iron phosphate (LFP/FP) was used as a model system for characterizing the local charging state. The lithiation distribution in LFP/FP can be imaged by mapping the iron oxidation state using the Fe-$L_{3,2}$ edge, the Li-K/Fe-M edges, Kramers-Kronig analysis of the dielectric function and the plasmon center position in EFTEM (Energy Filtered Transmission Electron Microscopy) as well as by automated crystal orientation mapping (ACOM) as long as the sample thickness is uniform and there is no strong overlap of particles. However, the dose and time requirements for the different techniques differ by a factor of 50 with Kramers-Kronig and plasmon center analysis being most suitable for *in situ* TEM.

In situ TEM studies of solid state batteries.

While *in situ* TEM thus appears to be an ideal solution to understand the processes in battery



ACOM phase and orientation maps of single crystalline particles with an FP/LFP interface and the corresponding statistical analysis of the orientation distribution of the interface shown as orientation density in the inverse pole figure.

systems, reproducible and clearly interpretable experiments are extremely challenging due to local electron beam damage to the material of interest, contamination/defects due to sample preparation and artefacts due to limited sample volume and additional surfaces/interfaces. Only a few publications describe *in situ* TEM experiments, and all experimental contributions to understand and overcome the obstacles are valuable.

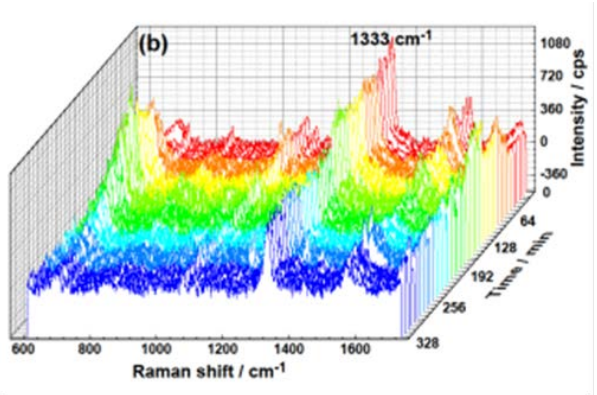
A beam-stable all solid-state fluoride ion battery was used to test and optimize *in situ* TEM approaches. A micron-sized battery was prepared and placed on a MEMS based setup suitable for *in situ* charging and discharging in the TEM. With this setup it was possible to follow the (de)fluorination of the Cu cathode *in situ* and identify impurity enrichment at the electrode/cathode interface. Failure occurred because of volumetric expansion during fluorination leading to fracture close to the electrolyte/cathode interface. However, this also illustrates a critical aspect of *in situ* TEM as the porosity in the sample is reduced compared to the bulk battery to maintain structural coherence in the thin sample, thus increasing the stress during volumetric expansion.

In situ tip-enhanced Raman spectro-scopy

Tip-enhanced Raman spectroscopy (TERS) is a combination of Raman spectroscopy and atomic force microscopy where the fine probe adds increased resolution and increases the intensity of the Raman signal making it possible to obtain very detailed information from very small areas, e.g. interfaces in lithium ion batteries.

A part of the Hi-C project was to acquire a TERS system, and to develop the technique to make it work with lithium ion battery materials on a nanometer scale. This requires a system with controlled atmosphere and ideal conditions regarding stability of temperature and vibrational environment.

The TERS system was built at KIT (HIU) and integrated with a glovebox in order to be able to study lithium ion battery interfaces under inert conditions. The most challenging aspect of developing a TERS setup for inert conditions is stability regarding drift and positioning. By adjustment of the external environment (glovebox and transmission) and replacement and upgrading of the optical coupling arm, the TERS instrument is now stable for operation under inert conditions. This was demonstrated by recording 800 TERS spectra at a same point on p-NTP adsorbed on a flat Au foil surface with an Au TERS tip. The system was stable throughout the 5.5 hours measurement as shown by the spectra in the graph below.

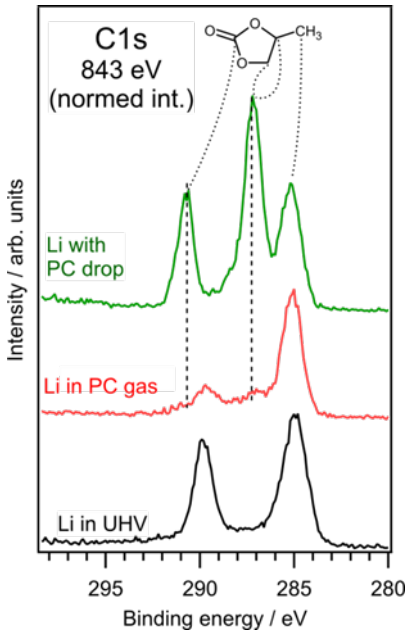


The graph shows every 20th spectrum from the 5.5 hour series. The TERS signal intensity retention is about 72 % in about 5.5 hours showing the high stability of the TERS setup.

In situ XPS

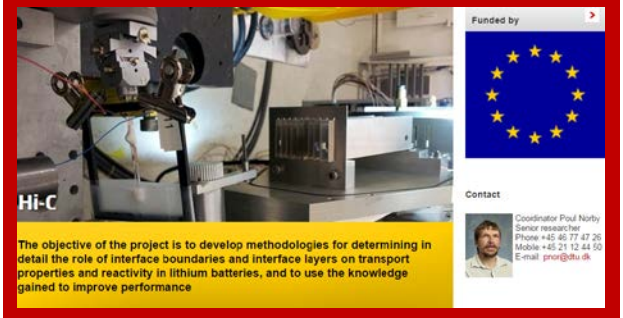
Using an advanced ambient pressure cell design at the SPECIES beamline at MAX-lab, Li metal was studied in presence of propylene carbonate (PC) vapor and for the first time in contact to a droplet of liquid PC (see Figure below). The results from these studies concerning PC adsorption, stability during measurement conditions and radiation exposure are the basis for further electrolyte

characterizations and the development of an *in situ* electrochemistry cell, which will enable battery electrode cycling directly in the ambient pressure photoelectron spectroscopy set-up currently developed at Uppsala University.



Carbon C1s spectra of lithium metal (black, bottom) showing hydrocarbon and carbonate residues and the same substrate exposed to PC vapor (red, middle), where two additional emissions at 287 eV and 291 eV indicate the presence of adsorbed PC molecules. The top spectrum (green) shows the C1s emission of a droplet of PC on a Li metal substrate where all three characteristic carbon components can be observed in stoichiometric intensity ratios.

Hi-C website: www.hi-c.eu



The prototype in situ XPS cell for electrochemical systems will be further tested at the MAX-IV synchrotron in Lund.

SEI formation and optimization - new electrolytes and additives

Spontaneous and induced formation of solid-electrolyte interface (SEI) layers is crucial for optimal performance of lithium batteries and supercapacitors. In Hi-C we have investigated new dinitrile electrolytes and efficient additives, such as vinylene carbonate (VC), fluoroethylene carbonate (FEC) and difluoroethylene carbonate (F2EC).

- Adiponitrile is an efficient electrolyte for lithium ion batteries when used with additives, e.g. FEC.
- For hybrid supercapacitors an improved performance was demonstrated using PC with 1M LiTFSI and $LiBH_4$ as an additive.

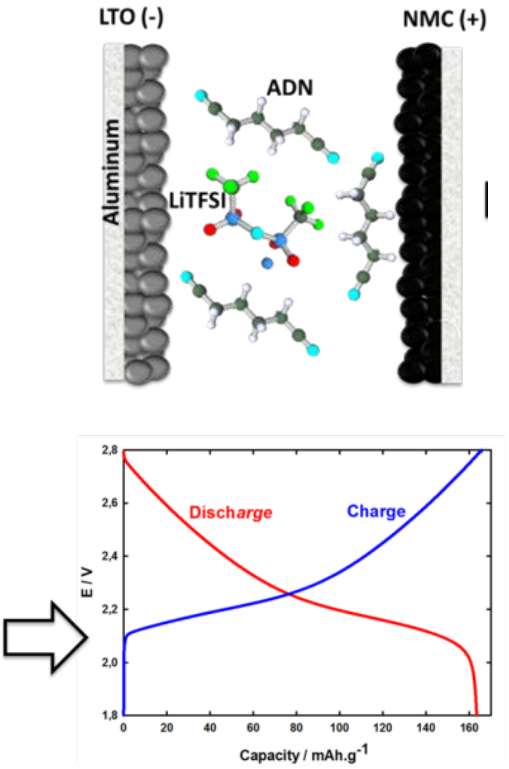
Efficient new additives

Efficiency and long term stability of batteries depends on formation of protective solid electrolyte interface (SEI) layers which reduce electrolyte reactions and decomposition. The SEI is regarded as being of crucial importance for Li ion batteries as soon as the working voltage of the electrodes is outside of the electrochemical window of the electrolyte. Understanding the formation of the SEI formed at the electrode/electrolyte interface is of prime importance in order to be able to control and optimize its functionalities and the resulting performances of active materials.

Dinitriles as new electrolyte solvents

Dinitrile-based electrolytes show poor performance when a graphite electrode is used due to formation of a resistive SEI layer. Graphite is an attractive electrode but to work well with dinitriles it requires the presence of an efficient SEI forming additive. VC, FEC, F2EC were tested as additives and reversible capacities were close to the theoretical capacity for graphite and with low irreversible capacities due to SEI forming. FEC is most efficient, and for each additive there is an optimum concentration. The formed SEI was characterized chemically and electrochemically and the mechanism of formation of the SEI elucidated using e.g. XPS. In LTO/NMC cells the dinitrile-LiTFSI combination is sufficiently stable without additives.

Adiponitrile (ADN) is an interesting solvent due to its chemical stability, high boiling point, high flash point, low vapor pressure and good solvating properties toward lithium salts. ADN with LiTFSI (1 M) allows the use of aluminium current collectors as almost no corrosion occurs at voltages up to 4.2 V. Full cell tests with LTO/NMC exhibit excellent rate capabilities, good reversibility and large capacities. As an example, cells were able to reach a capacity of 165 $mAh.g^{-1}$ at 0.1C and a capacity retention of more than 98 % after 200 cycles at 0.5C.



Charge/discharge curves of the LTO/NMC battery using the adiponitrile-based electrolyte.

Hybrid super-capacitor materials

Graphite and activated carbon materials provided by Varta Microbattery were tested in Hi-C. They were carried out in PC + LiTFSI (1 M) and in order to avoid aluminium corrosion and graphite anode exfoliation, $LiBF_4$ and SEI forming additives were added. The study shows that 5% $LiBF_4$ is enough for avoiding Al corrosion at up to 4.5 V.

Modelling and computational methods

In Hi-C it was sought to bridge complementary computational techniques from the different time and length domains to support and guide the experimental *in situ* observations.

Computational modelling of the structural and kinetic properties of interfaces in rechargeable batteries and super capacitors can serve as a

highly valuable tool in the prediction of superior materials compositions and interfacial coatings, as well as in the analysis and interpretation of data from *in situ* experiments. The insight obtainable from calculations ranges from a detailed atomic-scale understanding of chemical composition and structure of the interfaces, e.g., as obtained using density functional theory (DFT) level calculations, over molecular dynamics (MD) and finite element modeling (FEM) to describe diffusion processes at micro to mesoscopic length scales, to analytical/numeric solutions to describe the behavior of battery cells over long time scales and multiple cycles, such as the formation of a solid electrolyte interphase (SEI) on the electrodes and long charge/discharge times.

Hi-C Workshop

In October 2015 a joint workshop was held with the sister project Baccara in Tours, France.

Understanding Interfaces in Electrochemical Storage Systems

The workshop was held in Tours at the Lycée Descartes with 64 participants.

SEI-graphite interface model

Over the past decades, various experimental techniques have revealed that the molecular composition of the SEI depends on the type of electrolyte, anode material and lithium salts. It consists of different components such as Li_2CO_3, Li_2O, LiF, organic and polymeric species. However, none of the existing studies - experimental or numerical - provide clear insight on what the structural composition of an already formed SEI is and the steric orientation of its components near the graphite anode. Both the nature of the interface between SEI and graphite and the interactions which enable its adhesion are unknown.

In Hi-C we have built a stable SEI-graphite interface model at the atomic scale to describe he formation and structural properties of the SEI at the graphite anode. The SEI is represented by Li_2CO_3 as the latter is one of the main stable components when ethylene carbonate-based electrolytes are used. Within a DFT framework, we have studied different possibilities of Li_2CO_3 - graphite arrangement with the aim to clarify organization and adhesion of the SEI on the graphite anode and elucidate their mutual impact on Li transport. We have demonstrated that the stability of the model interface strongly depends on good connection between the two materials based on successful combination of their structural and electronic features. Having such a realistic model of the interface allows to numerically study the diffusion of lithium through the SEI to the anode and later on to possibly improve the process and mitigate the loss of lithium during charge / discharge cycles.

Improved model of Li ion battery behavior

When modelling entire battery electrochemical cell, atomic scale modelling techniques like DFT are no longer possible to apply, due to the size and time constraints of the system. Instead, the electrochemistry of the system can be described by a large number of equations describing different electrochemical processes in the system. A model particularly targeting Li-ion batteries was developed during the last decades, often referred to as the “Newman model”, and Hi-C has focused on improving the model to include descriptions of how the surface chemistry of the electrode materials evolves during battery

operation. The electrolyte decomposition reactions at the electrode surfaces described above leads to enlarged surface resistance, to pore clogging in the electrodes, and to depletion of salt in the electrolytes. These reactions can be described mathematically. The implementation of these chemical processes into the model then gives a description how the battery behaves during extended charge-discharge cycling, and can thus be directly compared to experimental data. This renders it possible to capture the bottle-necks and critical surface process for the battery behavior, and thereby gives directions to what problems are necessary to solve for constructing better battery chemistries.

Predicting state-of-health and state-of-charge

One of the most important electrochemical techniques to estimate surface processes within battery cells is impedance spectroscopy. This is often used to determine state-of-health and state-of-charge in different battery systems, which is crucial for many applications – not least electric vehicles. Using the developed Hi-C battery model, impedance data can be directly simulated based on the electrochemical cell description, and thereby directly compared to experimental data. This gives better insights into which processes in the battery which contribute to the impedance response, and thereby to that the impedance data can be analyzed in better detail in the battery management system.

Simultaneously, solving all the time-dependent equations governing the electrochemistry of a battery cell is very complex, and therefore advanced solvers are necessary. Within Hi-C, we have applied finite element techniques to construct realistic geometrical battery models and solve the equations describing different parts of the cell: anode, cathode and electrolyte.

Formation of boundary layers

A new pseudo-spectral method for solving the Nernst-Planck-Poisson equations to model the electric charge transport and current densities in batteries with a fixed potential difference across the full cell has been developed and implemented. The numerical treatment at the level of a full battery cell is generally very challenging, but the implemented method can provide exact solutions of the steady state, time-independent, equations. Using the new pseudo-spectral method, it is now possible to investigate the formation of boundary layers on the electrodes and long charge/discharge times to high numerical precision and efficient use of computational resources.

Dissemination activities

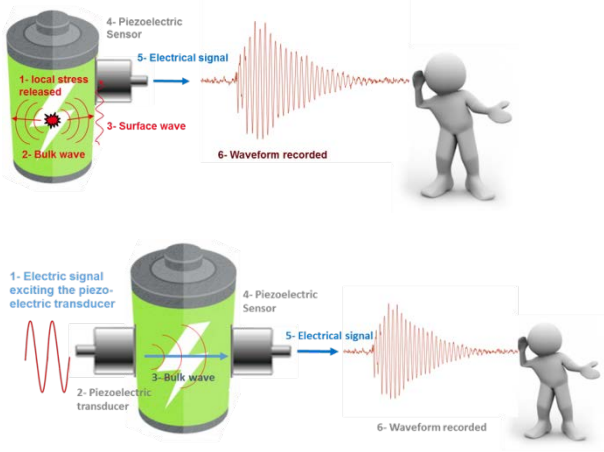
32	articles in international journals (26 are/are becoming Open Access)
1	book chapter
3	patent applications
1	PhD thesis (one more in progress)
4	reports
78	presentations at conferences workshops and international meetings
17	posters
3	internet announcements

Operando monitoring using acoustic methods and thermal sensing.

Operando methods have been developed to improve the safety of batteries and supercapacitors by on-board, non-electrochemical monitoring of battery health. Two patent applications have been submitted.

Several advanced *operando* methods are candidates for monitoring non-electrochemical signals arising from matter changes and constraints of Li ion and supercapacitor systems.

Ultrasonic acoustic emission sensors can detect acoustic waves generated by rearrangements due to mechanical stress such as lithium intercalation and release and heat flow sensors can detect the variation of heat released by the batteries during cycling. The aim was to develop acoustic methods and thermal sensing, coupled to electrochemical characterizations to follow the cell internal behavior.



The concept of acoustic emission, which is a passive technique, and ultrasound characterization, where the battery is actively probed with acoustic waves.

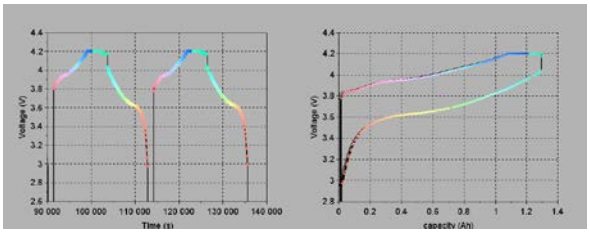
Acoustic emission as a non-invasive tool for the study of operating batteries

The acoustic emission technique was developed and evaluated in order to be used as a non-electrochemical method able to detect materials and interfaces changes in batteries during real operation e.g. early signs of degradation of battery materials during operation. It was possible to correlate the acoustic emission events to the operating conditions of formation (temperature, C-rate) and to the use of additives in the electrolyte and to correlate these results to the subsequent performance of the batteries (capacity, ageing). Acoustic emission is a very promising technique to study the formation phase of the batteries.

Ultrasound characterization of batteries under operation

Ultrasound characterization (UsC) is an active characterization technique in which acoustic waves of a defined wavelength are injected from a transducer to detect absorptive or reflective defects such as fatigue cracks.

Previously this technique has been only moderately successful but during the Hi-C project it was developed to a level allowing detailed analysis of commercial batteries allowing monitoring of state-of-charge and state-of-health independently of electrochemical parameters.



Left: evolution of the cell voltage versus time during two successive cycles charge- discharge. Colored dots superimposed on cell voltage correspond to each UsC measurement.

Thermal analysis of batteries and super capacitors under operation

Heat flow sensors were used to monitor the thermal behavior of batteries and supercapacitors. Thermal analysis of numerous batteries and different chemistries of Li-ion batteries were conducted comparing their thermal properties and thermal signature. By measuring the heat capacity of batteries as well as entropy and enthalpy variation during cycling it was possible to study the effect of the State-of-Charge. Ageing tests were used to evaluate the influence of the State-of-Health on these parameters. This technique could be used to propose an optimal management of the thermal behavior to avoid sharp temperature changes inside the battery and prevent the collapse of performance often observed on batteries.

Exploitation of results from the Hi-C project

Hi-C produced both commercial products and academic knowledge that are already being used in other projects.

Uniscan Instruments Ltd. has developed instrumentation for *in situ* electrochemical characterization of interfaces of operating batteries under inert conditions. The developed in situ cell with a controlled environment is designed to work with the existing M470 base and will expand the current product range.

Microelectrodes with diameters of 2 and 5 µm are now prepared in production batches and a small batch of 1 µm electrodes show excellent specifications. Extending the lower limit of the SECM resolution will be of benefit commercially and scientifically for existing users. With the new smaller probes full advantage of the instrument is possible and will thus be of interest to other areas such as biology, micro-/nano-patterned materials, porous membrane research, and materials research.

CEA is implementing on-board monitoring utilizing the developed *operando* methods and devices from Hi-C. (Two patent applications have been submitted).

Operando monitoring methods for acoustic characterization and thermal flux sensors of commercial batteries and supercapacitors will be applied as on-board systems for monitoring battery status during use. By detecting internal processes during formation and use, the safety will be increased, e.g. by improved prediction of thermal events in lithium ion batteries.

VARTA is developing a NMC/C battery cell using wound electrodes in a 1654 prototype coin cell.

KIT (HIU) has submitted a patent application regarding the lithium rich positive electrode materials related to Li_2VO_2F, developed during the Hi-C project.

In addition, LIRICHFCC, a FET EU project on the new class of powerful materials for electrochemical energy storage: Lithium-rich oxyfluorides with cubic dense packing) has been granted to further develop this series of materials. Four of the Hi-C partners (KIT, CEA, DTU and University of Uppsala) are included in the LIRICHFCC project.

At DTU, the academic exploitation of the Hi-C project results can be divided into experimental and computational work:

Development of the capillary based micro battery cell for in situ studies has been very successful, and the design has been used for a number of other studies and will contribute to a deeper knowledge on battery processes at the nanoscale. The in situ cell is being employed in the LIRICHFCC project as well as in internal DTU projects concerning sodium batteries and zinc-air batteries. The cell also forms the basis for submitted applications to national research council grants.

Development of the computational methods in the Hi-C project is presently being employed in several national and EU projects. In the LIRICHFCC project many of the methods regarding stability and transport properties are being used. An example of a national research project is MAT4BAT, where computational searches for new battery materials are being performed.

The updated list of publications and information about the project can be found at the Hi-C website:

www.hi-c.eu

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