Hi-C Newsletter
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Hi-C

Novel *in situ* and *in operando* techniques for characterization of interfaces in electrochemical storage systems

The objective of the Hi-C project is to develop methodologies for determining in detail the role of interface boundaries and interface layers on transport properties and reactivity in lithium batteries, and to use the knowledge gained to improve performance.
The methods used will be advanced multi-technique *in situ* characterization combined with computational methods. The findings will be used e.g. in design of artificial Solid Electrolyte Interface (SEI) layers, in optimization of morphology and particle-coating in cathode materials and in improving intra particle ionic mobility across buried interfaces.

In the project the primary goals are to:

1. Understand the important interfaces in an operating battery on an atomic and molecular scale.
2. Perform *in situ* characterization of formation and nature of interfaces in electrochemical storage cells.
3. Devise methods to control and design interface formation, stability and properties.
4. Prepare ion-conducting membranes, mimetic of the polymeric part of the SEI, in order to study their mechanical and electrochemical properties.

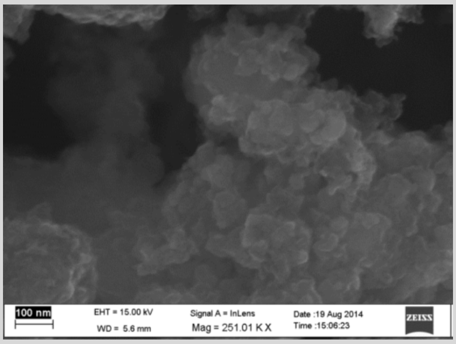
During the first 18 months of the Hi-C project the focus has been on:

- Synthesis, electrochemical characterization and distribution of materials within the consortium.
- Advanced characterization of materials using e.g. XPS (X-ray photoelectron spectroscopy) and transmission electron microscopy based methods..
- Development of *in situ* characterization techniques and instrumentation, especially using synchrotron X-ray diffraction, TERS (tip enhanced Raman spectroscopy) and SECM (scanning electrochemical microscopy).
- Forming the theoretical basis for computational studies of transport and interfaces in cathode materials.
- Developing *in operando* techniques for monitoring chemical and physical processes in commercial lithium batteries.
- Studying SEI formation and properties to investigate the role of electrolyte additives.

A few examples of achievements during the first 18 months:

Synthesis and materials distribution

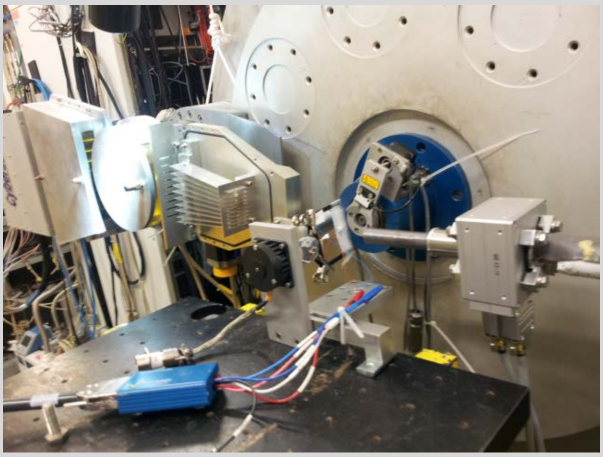
New and optimized synthesis methods for Hi-C materials have been developed. E.g. a new synthesis method for preparation of optimized $LiFeBO_3/C$ cathode materials with unprecedented electrochemical performance. Nanometer sized materials and efficient conducting coatings are essential for improving energy density, cycle stability and rate capability. In addition, intercalation- and conversion materials for lithium ion batteries have been prepared. The materials were investigated using e.g. TEM, high resolution synchrotron X-ray powder diffraction and XPS. Preliminary *in situ* synchrotron X-ray diffraction experiments during charge/discharge were performed.

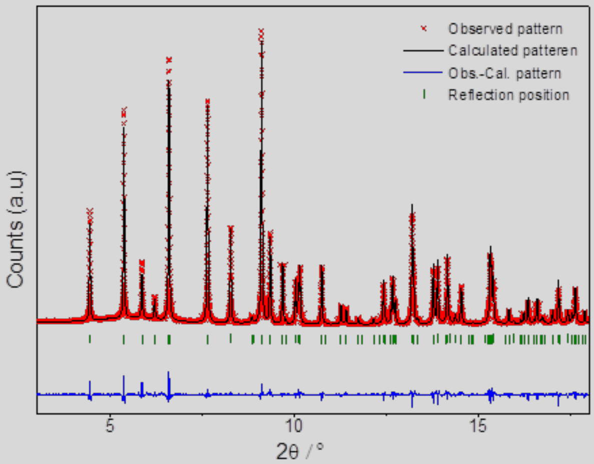


SEM image of one of the synthesized $LiFeBO_3$ materials.

Intraparticle interfaces:

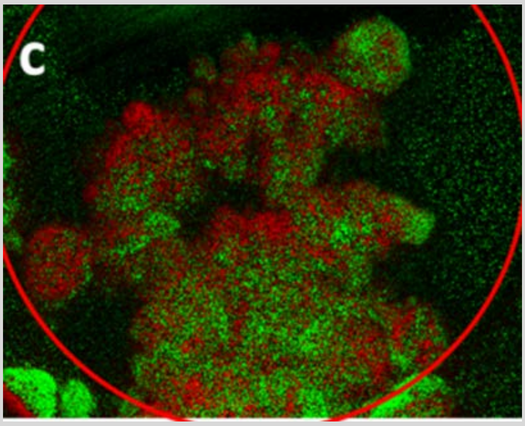
Using high resolution synchrotron X-ray powder diffraction for *in situ* studies of $LiFePO_4$ cathode materials in a specially designed micro battery cell allowed unique structural and microstructural information to be obtained during charge and discharge conditions. The *in situ* experiments were performed at the high resolution powder diffractometer at ID31 and ID22 at the European Synchrotron Radiation Facility, ESRF, in Grenoble. Due to the extreme angular resolution it was possible to investigate small deviations from





High resolution synchrotron X-ray powder diffraction data for structural and *in situ* studies collected at ESRF stoichiometry of the phases involved during charge/discharge and to investigate anisotropic strain and peak shape development.

Initial *ex situ* studies of intracrystalline interfaces have been performed on partially lithiated $LiFePO_4$ materials. Using advance electron microscopy techniques, the domain structure and phase distribution within single particles will be investigated.

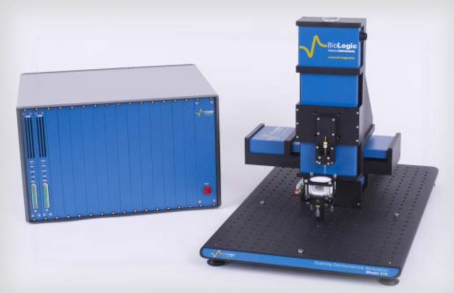


Color representation of distribution of $FePO_4$ (red) and $LiFePO_4$ (green)

SEI formation and interfaces:

New development of equipment for *in situ* characterization of e.g. SEI layer formation during charge/discharge conditions is ongoing. This includes establishment of facilities for TERS (tip enhanced Raman spectroscopy) and SECM (scanning electrochemical microscopy), which are presently being installed and equipped for operation under inert conditions.

Studies on SEI design using electrolyte additives are ongoing, focusing on anode materials, e.g. Si and graphite.



The M470 Scanning Probe Electrochemical Workstation from Uniscan Instruments

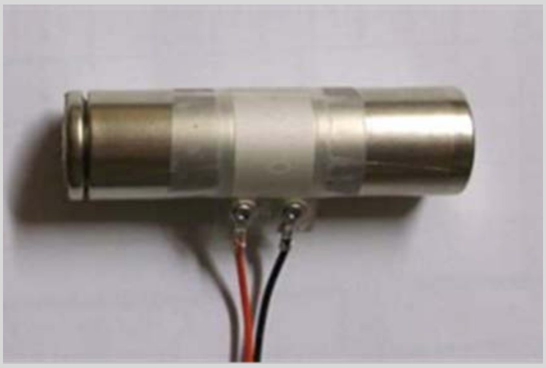
TERS setup (Tip Enhanced Raman Spectroscopy): (a) Raman spectroscope (b) AFM unit (white) and the coupling arm connecting the Raman spectroscope and AFM unit (black) to a TERS. The parts are placed in a glovebox, visible in the background.

In operando monitoring

For *in operando* monitoring of battery cells, advanced methods will be developed to follow internal behavior through the monitoring of non-electrochemical signals arising from matter changes and constraints. The aim is to develop utilization of non-invasive methods, coupled to electrochemical characterizations and thermal sensing, that could record data related to material and interfacial modifications. These *in operando* methods will form the base for embedded sensors for the next generation of Li-ion or super capacitor systems.

Three different types of sensors were evaluated. The most suitable sensors have been selected, regarding their sensitivity, reliability and integration into light devices. Validation tests were conducted on commercial cylindrical batteries (18650 and 26650-type).

The use of these *in operando* monitoring methods could lead to a better understanding of the ageing mechanisms occurring during battery operation. It could be possible to prevent some phenomena regarding performance degradation and have relevant indicators for safety issues, increasing the batteries lifetime and promoting a safer use.



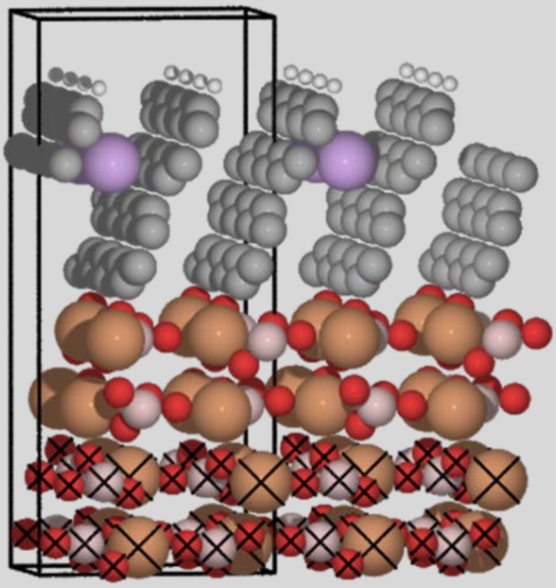
In operando monitoring of an 18650 cell.

Transport and interfaces

Computational methods and DFT calculations have been employed to investigate electronic and ionic transport across interfaces in relevant battery materials. As an example, a computational study of the structure and ionic transport of lithium ions through carbon coatings on $LiFeBO_3$ crystallites was performed.

For electrode materials with low electronic conductivity, nano-structuring and carbon coating is essential for optimal performance in a battery. Therefore, the electronic transport through the interface between particle and coating as well as the ionic resistance of the coating must be understood.

Computational investigations into different graphite and graphene structures and the angular orientation of the graphene/graphite coating have been investigated, as well as the role of defects in the carbon coating on the lithium transport mechanisms, e.g. the formation energy and lithium transport through di-vacancies. Based on the calculations, it is therefore concluded that large structural defects and/or significant misalignments between the carbon coatings and the $LiFeBO_3$ nano-particles are required in order to reduce the overpotentials for charge and discharge, and achieve fast charge/discharge kinetics.



A non-parallel configuration of the carbon-$FeBO_3$ interface for the configuration just prior to the onset of lithiation in $FeBO_3$.