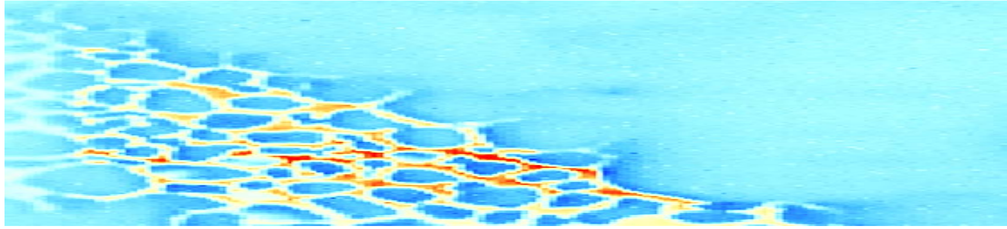

The Hi-C project

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

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Technical University of Denmark

DTU Energy
Department of Energy Conversion and Storage

Hi-C

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

www.hi-c.eu

Project number 608575

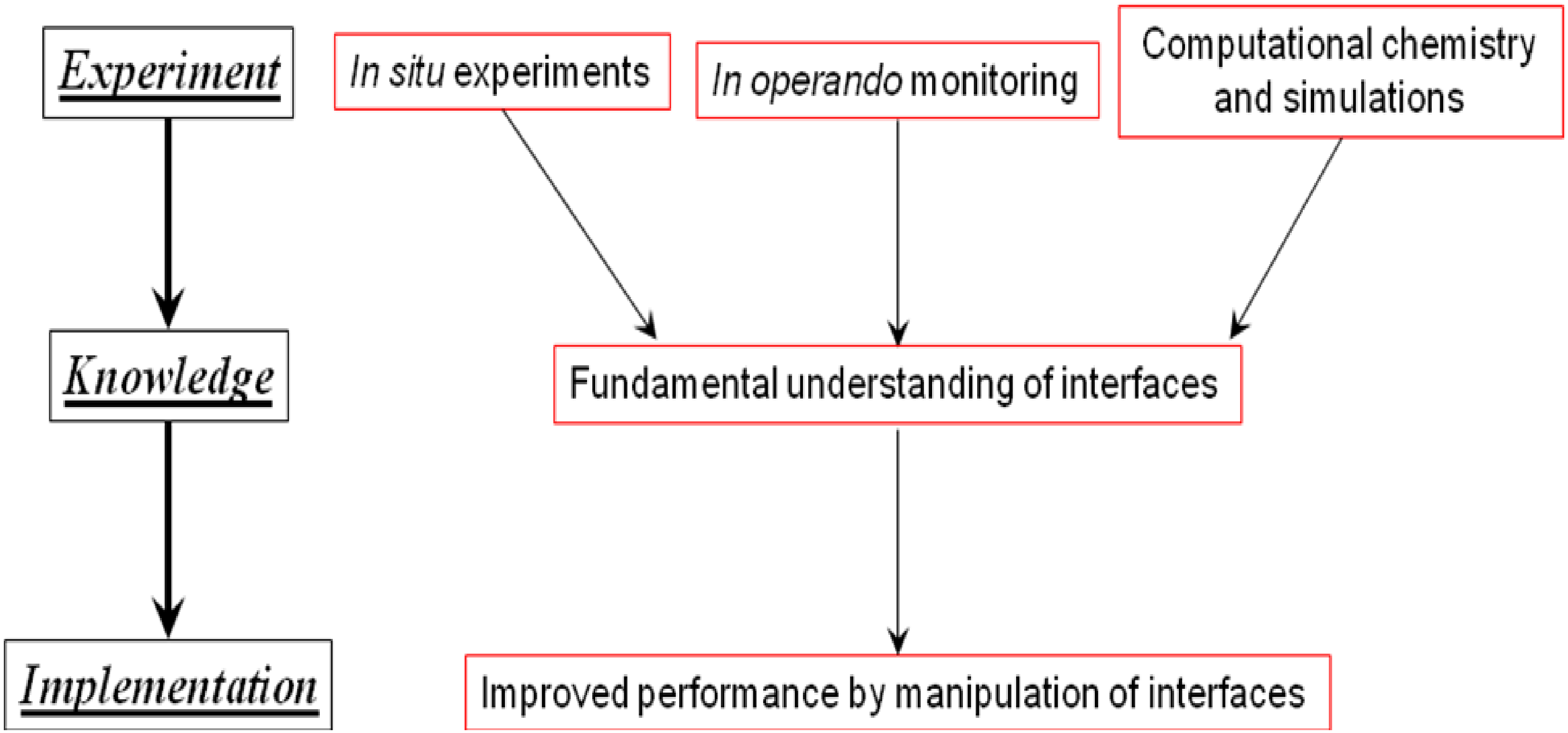
FP7-ENERGY-2013-1

Call: ENERGY.2013.7.3.3:
Understanding interfaces in rechargeable batteries and super-capacitors through *in situ* methods

Hi-C partners

Partner	Organisation name	Short	Country
1	Technical University of Denmark	DTU	Denmark
2	University of Tours	UT	France
3	Commissariat à l'Energie Atomique et aux Energies Alternatives	CEA	France
4	Karlsruhe Institute of Technology	KIT	Germany
5	Uppsala University	UU	Sweden
6	Haldor Topsøe A/S	TOP	Denmark
7	Uniscan	UNI	UK
8	Varta Microbattery GMBH	VM	Germany

- Month 1-6: **initiation phase**
- Month 7-30: ***In situ* development phase**
- Month 31-42: **Testing phase**



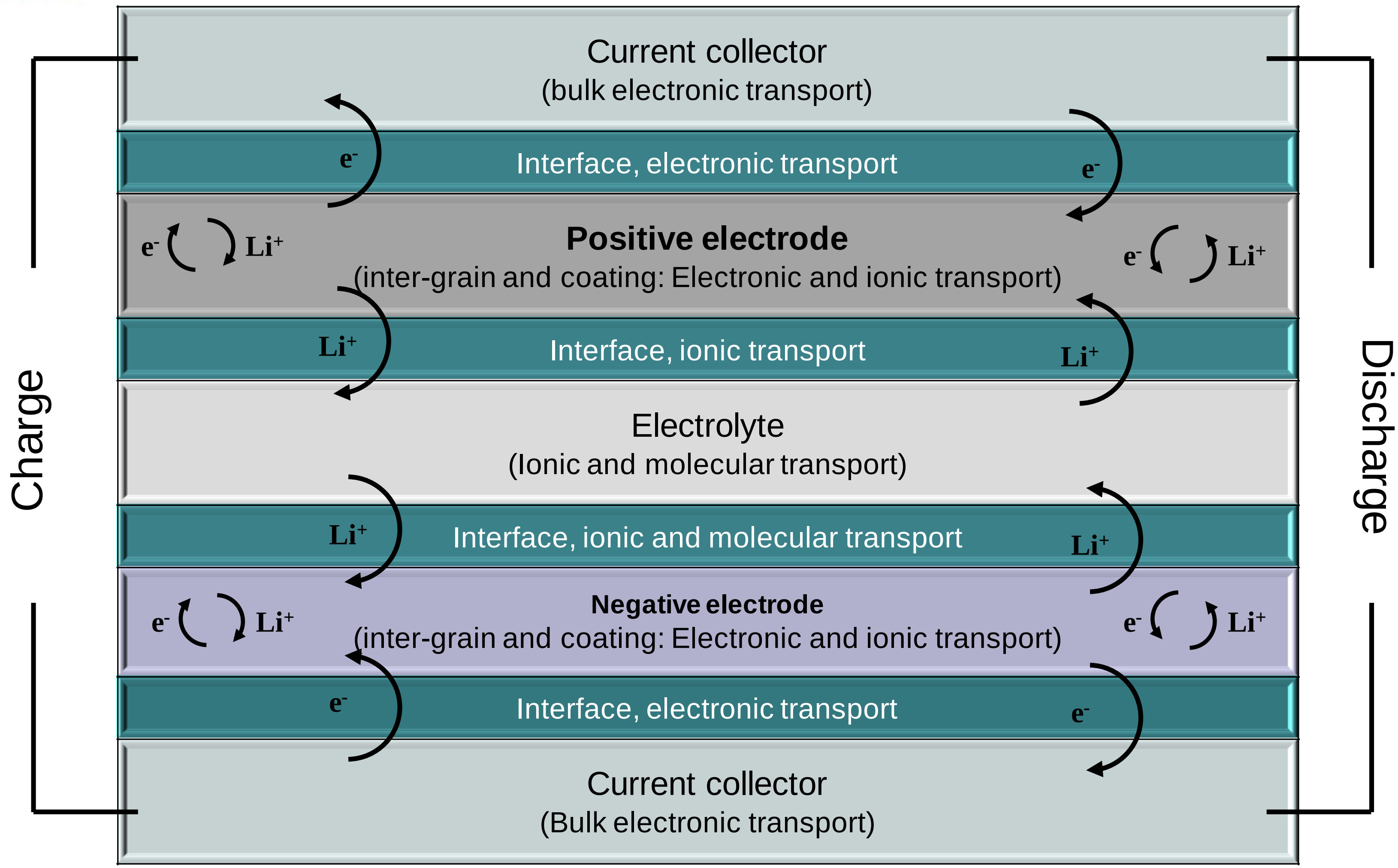
Aim: Improving electrochemical storage systems (lithium batteries and super capacitors)

Means: improve understanding of interface formation, structure, dynamics and transport properties

Combining information from:

- *In situ* studies of interfaces during operation
- Theoretic calculations and modelling (from atomic to components scale)
- Experimental studies of formation of artificial and spontaneous solid-electrolyte interface layers.
- In operando monitoring of batteries.

A Battery seen as a series of interfaces.

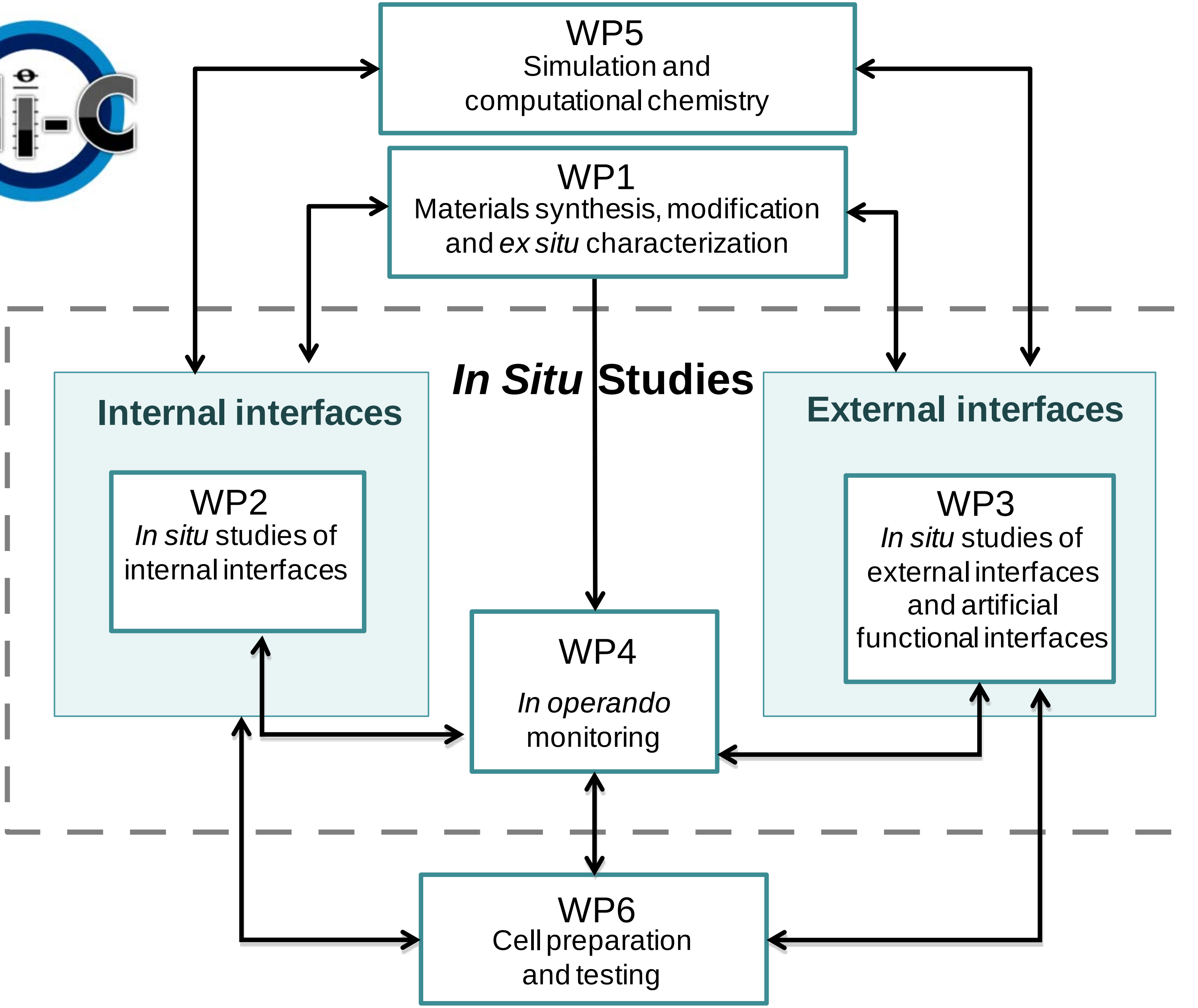


Examples of potential implementation for improving batteries:

Information about intra-particle interfaces, domain structure and interface dynamics with DFT calculations of transport and electronic properties of interfaces→ morphology control of active materials, doping and design of conductive coating.

Multifunctional Solid-electrolyte interface formation: Combining information on inter-particle and solid-electrolyte interface formation and properties with DFT calculations and synthetic efforts → Tailoring additives for SEI formation combined with active and functionalized particle coating.

WP1	**KIT**	Synthesis and modification of electrode materials
WP2	**DTU**	*In situ* studies of internal interfaces
WP3	**Univ. Tours**	*In situ* studies of external interfaces and artificial functional interfaces
WP4	**CEA**	*In operando* monitoring
WP5	**DTU**	Simulation and computational chemistry
WP6	**KIT**	Cell preparation and testing
WP7	**Topsøe**	Dissemination
WP8	**DTU**	Project Coordination


WP5
Simulation and computational chemistry
WP1
Materials synthesis, modification and *ex situ* characterization
In Situ Studies
Internal interfaces
WP2
In situ studies of internal interfaces
External interfaces
WP3
In situ studies of external interfaces and artificial functional interfaces
WP4
In operando monitoring
WP6
Cell preparation and testing

Some results from the Hi-C project:

Materials optimization by interface manipulation:

$LiFeBO_3$

Li_2VO_2F → **Li-rich FCC project (Max Fichtner)**

New devices and methods for in situ studies of interfaces:

In situ SECM cell → **being commercialized by Uniscan / Biologic**

In situ TERS (Tip Enhanced Raman Spectroscopy) **(Developed by KIT/HIU)**

Operando monitoring of lithium batteries and supercapacitors (**Devel. by CEA**)

In situ synchrotron X-ray diffraction **(Micro battery cell developed by DTU)**

"In situ" and high pressure XPS (X-ray Photoelectron Spectroscopy) **(Developed at Univ. of Uppsala)**

Interfaces and SEI:

Development of new additives for SEI formation

Theoretical calculations of transport across interfaces and conductive coatings.

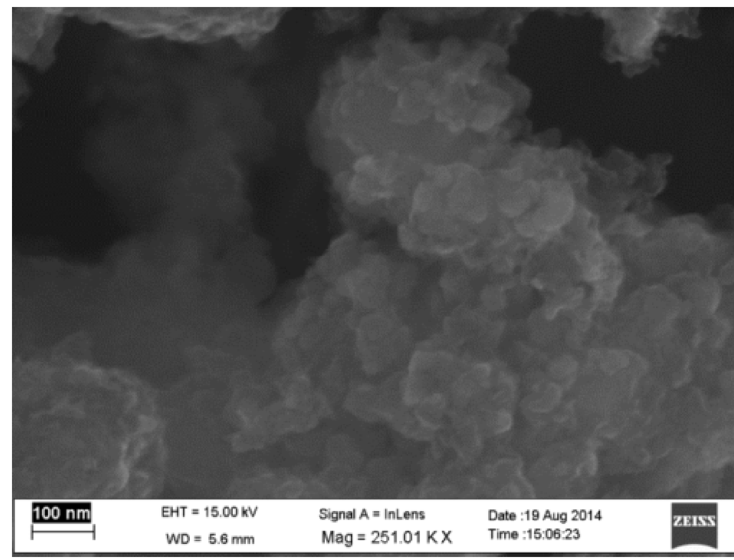
Synthesis and materials distribution

Materials selected for the Hi-C project were distributed among the partners. New and optimized synthesis methods for Hi-C materials have been developed.

A new synthesis method for preparation of optimized **$LiFeBO_3$/C** cathode materials with unprecedented electrochemical performance. New **Li_2VO_2F** materials as well as materials for conversion batteries have been synthesized and characterized.

Nanometer sized materials and efficient conducting coatings are essential for improving energy density, cycle stability and rate capability.

The materials were investigated using e.g. TEM, high resolution synchrotron X-ray powder diffraction and XPS.

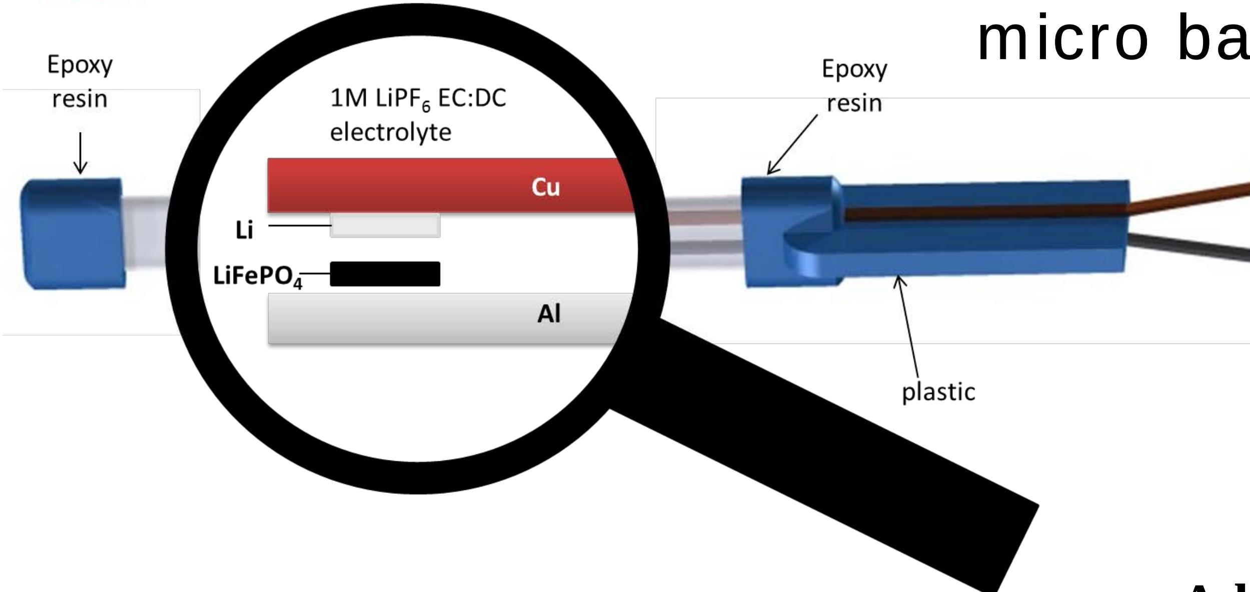


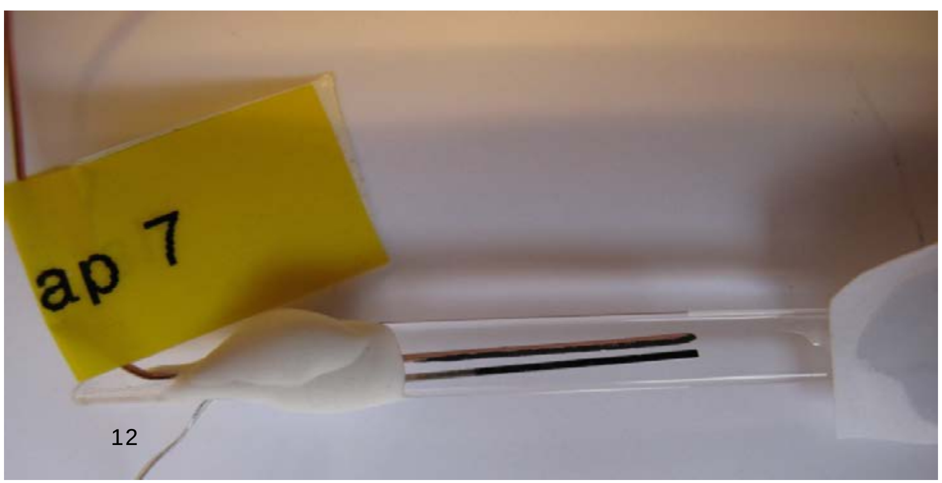
SEM image of one of the synthesized $LiFeBO_3$ materials.

R. Chen, S. Ren, M. Yavuz, A.A. Guda, V. Shapovalov, R. Witter, M. Fichtner, H. Hahn, *Phys. Chem. Chem. Phys*. **17** (2015) 17288-17295 S.
Ren, R. Chen, E. Maawad, O. Dolotko, A.A. Guda, V. Shapovalov, D. Wang, H. Hahn, M. Fichtner, *Adv. Sci.* (2015) 1500128
R. Chen, S. Ren, M. Knapp, D. Wang, R. Witter, M. Fichtner, H. Hahn, Advanced Energy Materials,1401814 (2015)

In situ synchrotron X-ray studies of interfaces between lithiated and non lithiated phases

The capillary based *in situ* micro battery cell





Advantages

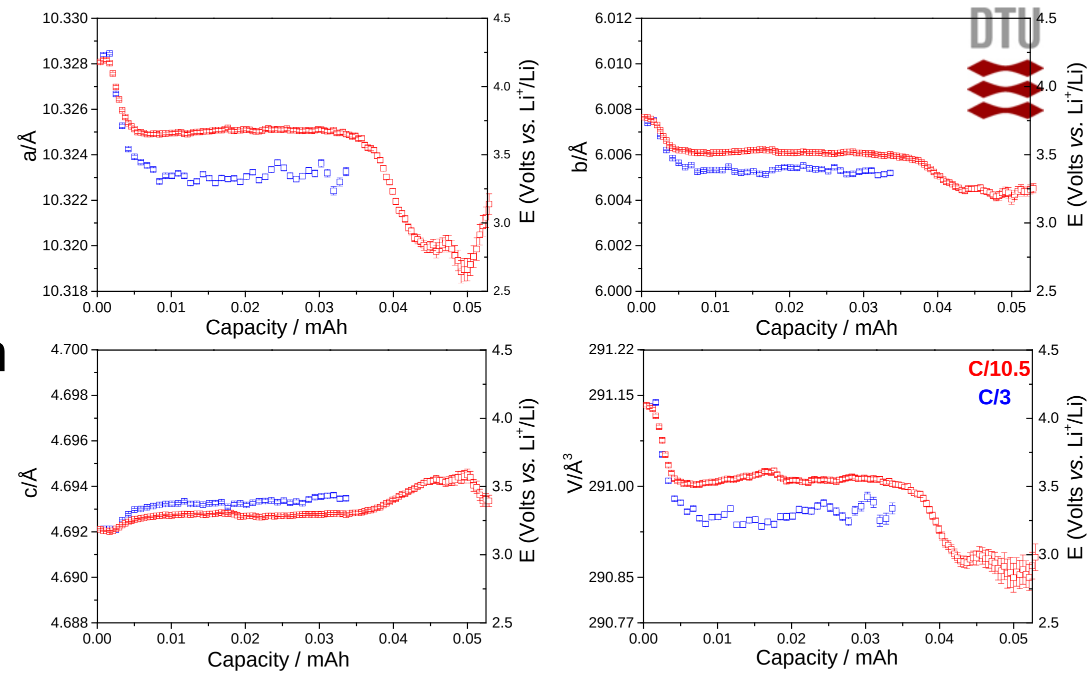
- Diffraction from pure electrode phases
- Time resolved and spatial resolution: Follow evolution of chemical gradients, inhomogeneities and fluctuations
- Possibilities for imaging, spectroscopy (Raman, XAS) and visual observation

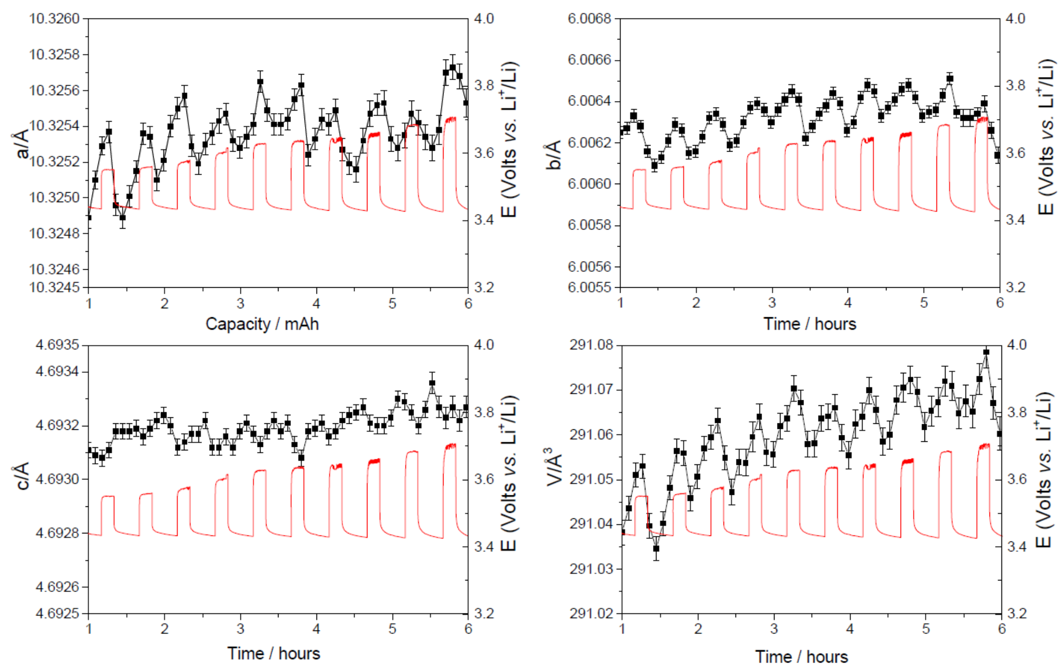
Dynamic effects in $LiFePO_4$. Stoichiometry/solid solution dependence on charging rate.

Unit cell variation for $LiFePO_4$ during charging by C/10 and C/3.

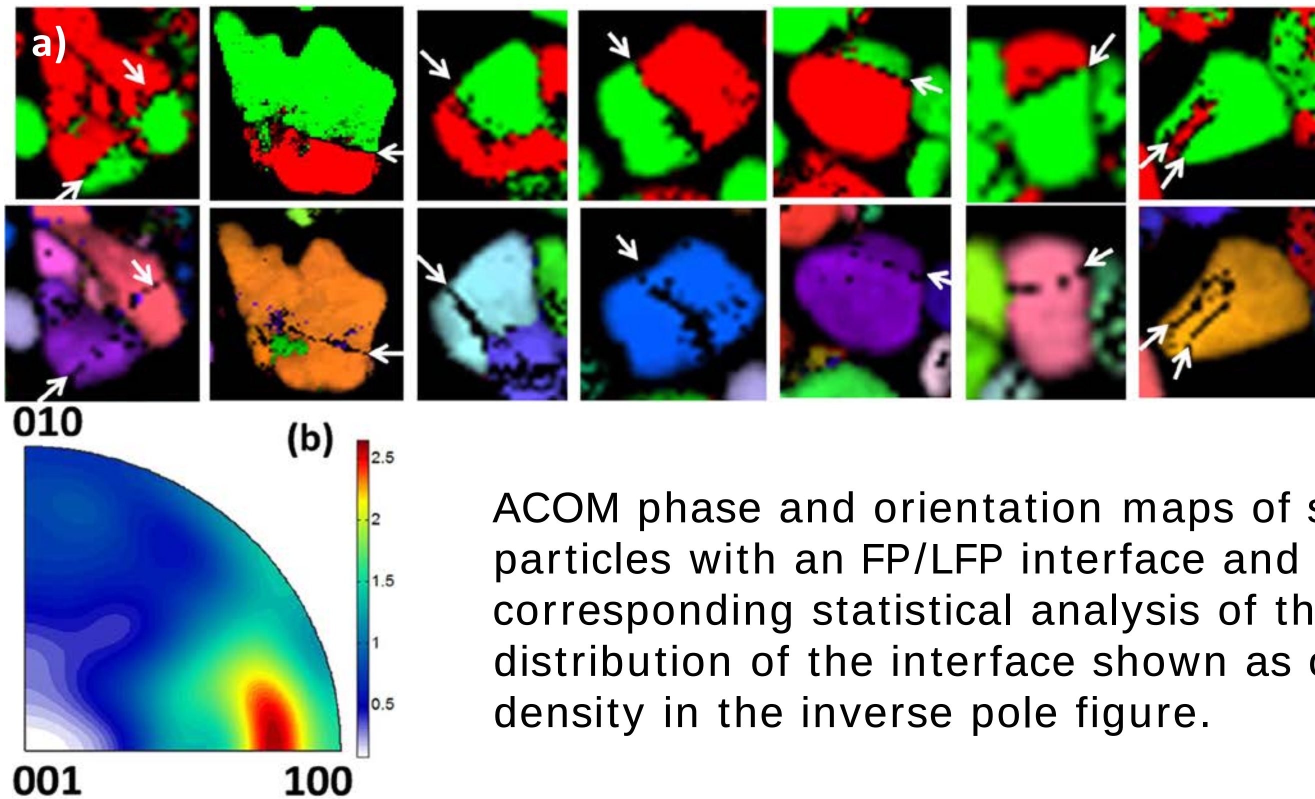
Increased solid solubility by increased current density.

In situ diffraction during GITT (Galvanostatic Intermittent titration technique) conditions. The unit cell parameters are correlated to the current.





Comprehensive analysis of TEM methods for $LiFePO_4/FePO_4$ phase mapping: spectroscopic techniques (EFTEM, STEM-EELS) and STEM diffraction techniques (ACOM-TEM)



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.

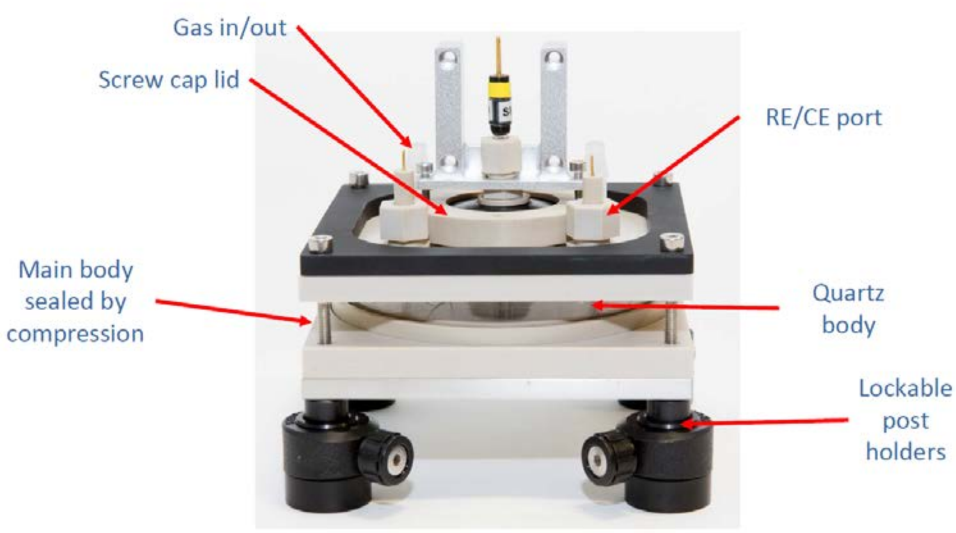
X. Mu, A. Kobler, D. Wang, V.S.K. Chakravadhanula, S. Schlabach, D.V. Szabó, P. Norby, C. Kübel, *Ultramicroscopy*, 2016, **170**, 10-18

SEI formation and interfaces:

UNISCAN Instruments (now Biologic)

New in situ cell for development of equipment for *in situ* SECM (scanning electrochemical microscopy) for characterization of e.g. SEI layer formation during charge/discharge conditions.

The M470 Scanning Probe Electrochemical Workstation from Uniscan Instruments



TERS setup (Tip Enhanced Raman Spectroscopy)

Local spectroscopic information at you AFM tip.

Developed at KIT.

Makes it possible to follow SEI formation in lithium batteries *in situ under inert conditions.*

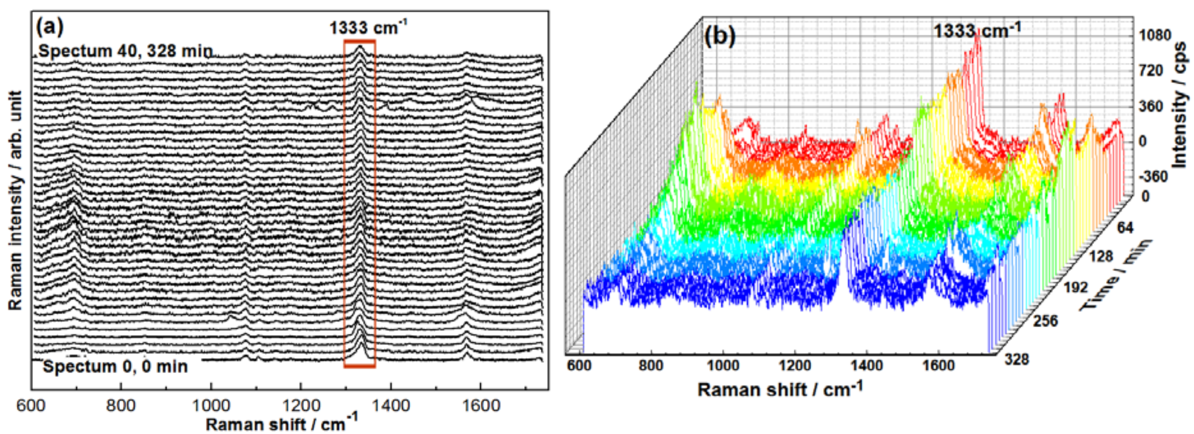
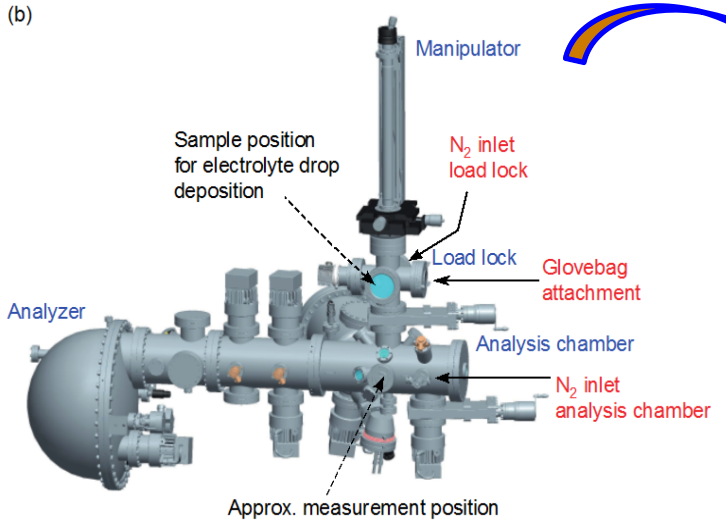


Figure 3 TERS spectra of p-NTP recorded in about 5.5 hours in two different formats **(a)** 2 dimensions and **(b)** 3 dimension showing the stability of the TERS instrument.

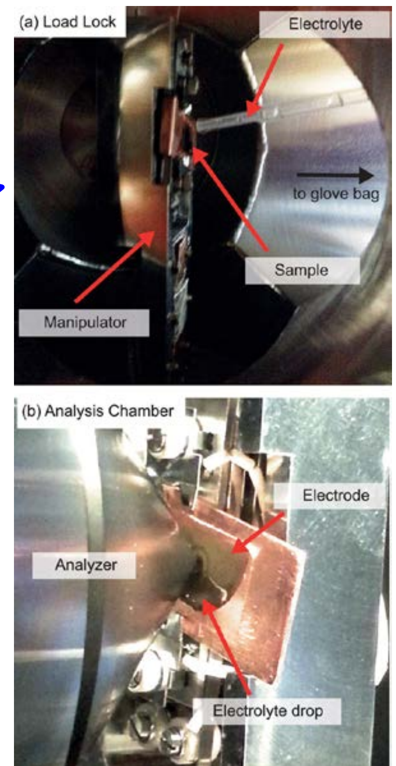
In-situ XPS

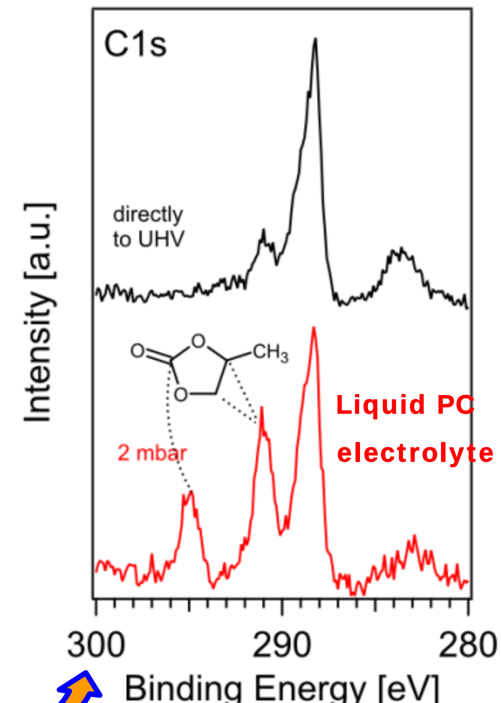
New sample transfer technique without UHV step developed

In situ XPS equipment is being tested at the synchrotron (Maxlab, Sweden)



In-house NAP-XPS @ VG Scienta, Uppsala





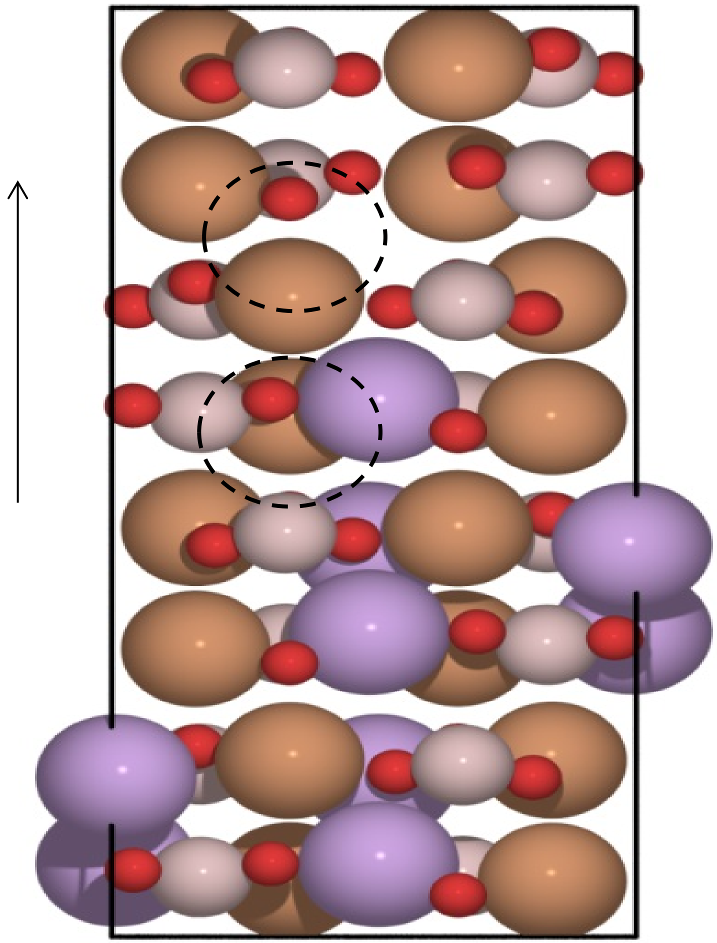
XPS characterization of liquid electrolyte achieved!

S. Eriksson et al., Rev. Sci. Instrum. **85**, 075119 (2014)

J. Maibach et al., Rev. Sci. Instrum. **86**, 044101 (2015)

Transport and interfaces

Computational methods and DFT calculations are employed to investigate electronic and ionic transport across interfaces in relevant battery materials. E.g. computational studies of the structure and ionic transport of lithium ions through carbon coatings on $LiFeBO_3$ crystallites.



Yedilfana S. Mekonnen, Juan M. Garcia-Lastra, Jens S. Hummelshøj, Chengjun Jin, and Tejs Vegge, J. Phys. Chem. C, 2015, 119 (32), pp 18066–18073

Loftager, Garcia-Lastra, Pochet, Vegge (2015)

1. *What challenge is the project tackling? (What is the <u>problem</u>?)*

Interfaces are crucial for battery operation: SEI, Conducting coatings, interfaces inside individual crystallites of active electrode materials.

But how do we study interfaces inside an operating battery?

2. What technological solution is the project developing? (What is the <u>solution</u>?)

In the Hi-C project we have developed a number of new *in situ* methods and devices for obtaining information about interfaces. Especially the *in situ* SECM is close to commercialization.

- What is the starting TRL (state of the art) and the end TRL?

Difficult to say; some methods will be exploited mainly in further research products, other are being commercialized and patented.

- What are the technology risks?

- How the consortium is progressing versus the KPI's/milestones of the project?

Good

3. What will be the impact if the project is successful? (What is the impact?)

New methods for research and development of batteries and supercapacitors.

- What is the market for the technology?

Scientific research and product development. New instrumentation and methods for in situ studies.

- What are the market risks? (what could go wrong in terms of technology adoption by the market? How solid are the market forecasts?)

- How will Europe-based industry (in particular manufacturers of advanced materials) benefit from the technology?

New insight in materials performance in real batteries.

4. What is potentially missing to take the project results from the lab to the market with a manufacturing of the advanced materials &/or batteries in Europe? (What do you recommend to the European Commission in terms of future R&I orientations and policies?)

Focus on low TRL levels as well as on the higher TRL. E.g. methods and materials development.