New insight from X-ray diffraction studies of materials under operative conditions

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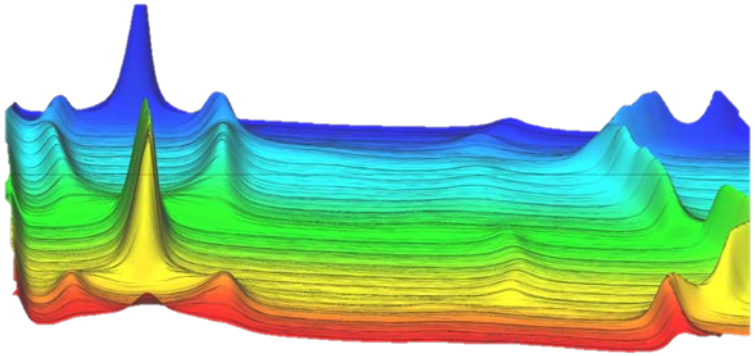

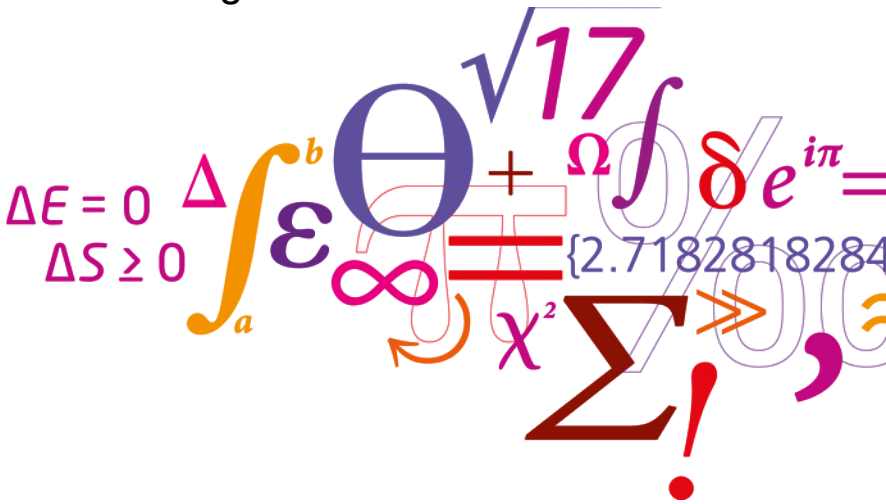

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In situ or *operando* experiments

In *in situ* or *operando* experiments materials are characterized at actual operating conditions or during operation of an actual device.

- *Ex situ* studies, i.e. characterization of materials before and after operation, do not necessary reflect the state of the material at operating conditions

- Often a combination of complementary *in situ* techniques must be used, either in a combined experiment or separately, if the techniques cannot be used together without compromise. For instance diffraction together with:

    - X-ray absorption spectroscopy
    - Raman spectroscopy
    - Small angle scattering
    - Thermal analysis
    - Dynamic light scattering

Examples of *in situ* synchrotron X-ray powder diffraction studies

- **Hydrothermal synthesis:** zeolites, aluminophosphates, microporous sulfides, mesoporous materials, layered phosphates…
- Chemical reactions: Hydrolysis, carboxylation, solid state synthesis…
- Solid/gas reactions: high temperature oxidation/reduction
- Ion exchange
- Intercalation
- Dehydration and dehydroxylation
- Adsorption/desorption
- Thermal transformations
- **Microporous catalysts at operating conditions**
- Fischer-Tropsch catalysts
- **Rechargeable batteries**

Information obtained from *in situ* powder diffraction experiments.

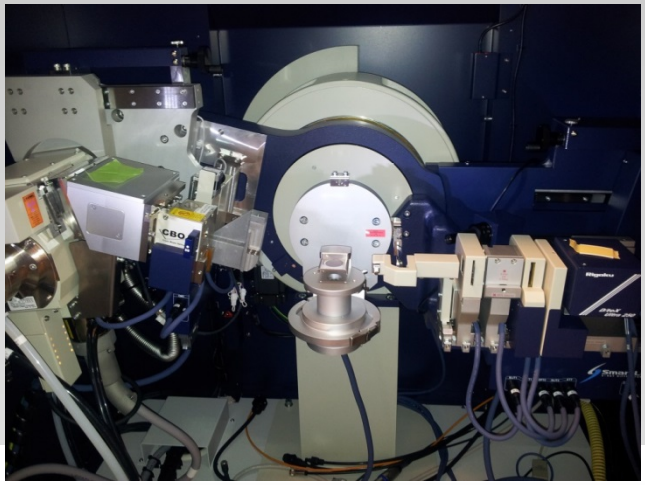
- Identification of intermediate and transient phases
- Quantitative analysis/phase distribution during operation
- Changes in crystallite size and size distribution
- Development or annealing of strain, defects, disorder and stacking faults
- Variations in unit cell and symmetry
- Thermal expansion/phase transition
- Crystal structure refinement at process conditions
- Texture development

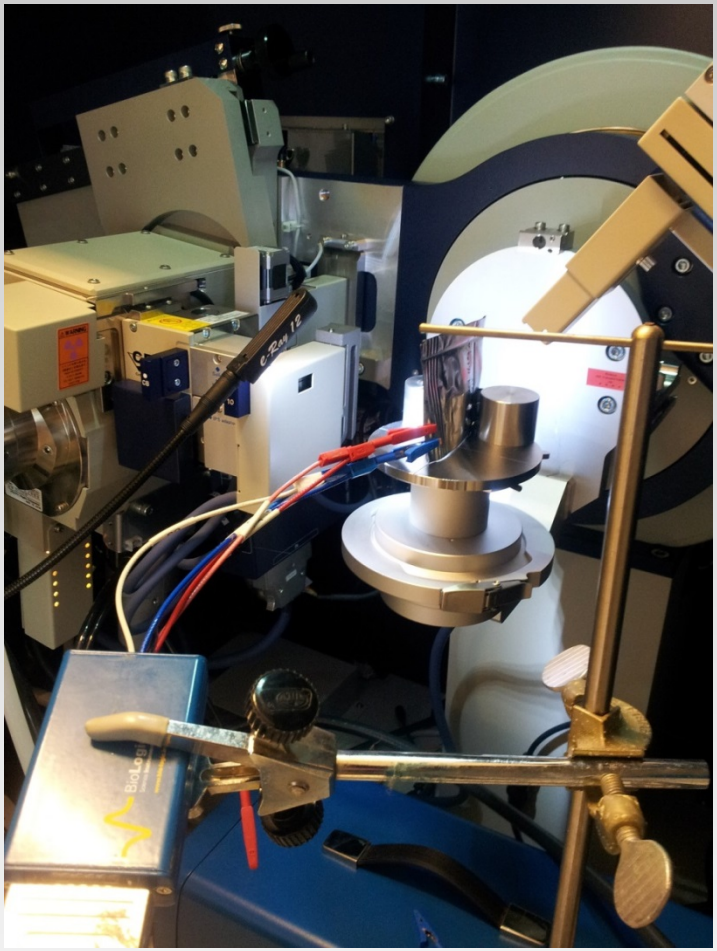
In-house *in situ* X-ray diffraction

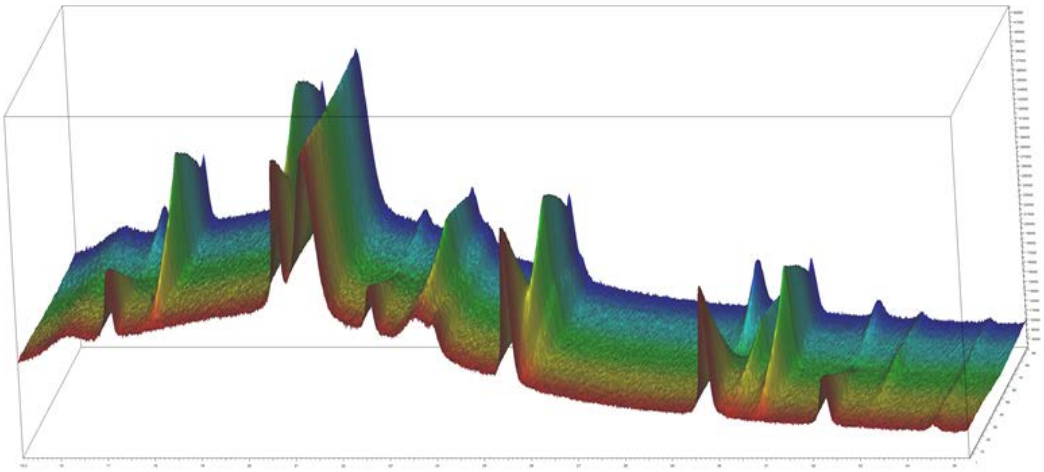
Rigaku Smartlab Diffractometer

9kW rotating anode X-ray source, Cu radiation, theta-theta geometry

In situ study of a $LiFePO_4$ battery in a coffee-bag cell







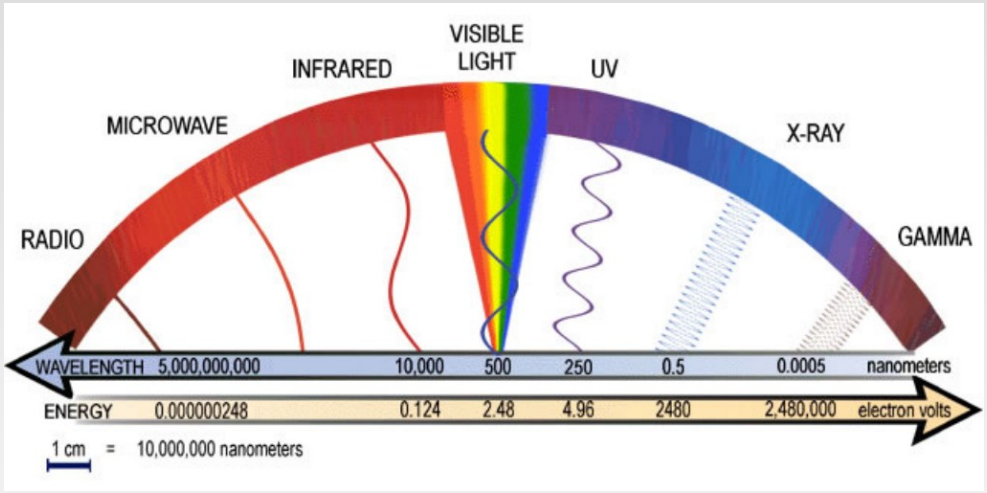
Why use synchrotron X-ray radiation?

Development of powerful synchrotron X-ray sources has been one of the most important contributors to the explosive development in *in situ* and *operando* diffraction experiments.

Using synchrotron X-ray radiation has several advantages:

- Very intense X-ray radiation allows good time resolution
- The tuneable X-ray energy allows for using very hard radiation (penetrating containers and sample holders) or using e.g. anomalous scattering for element specific analysis.
- Due to low emittance of the beam, very high angular resolution can be obtained.
- Use of micro beams allow spatially resolved *in situ* diffraction and micro diffraction

Synchrotron sources are large facilities providing very intense electromagnetic radiation over a broad spectrum.




ALBA
APS
Petra III
Diamond
NSLS
MAX IV
SLS
ESRF

Neutron diffraction for *in situ* studies

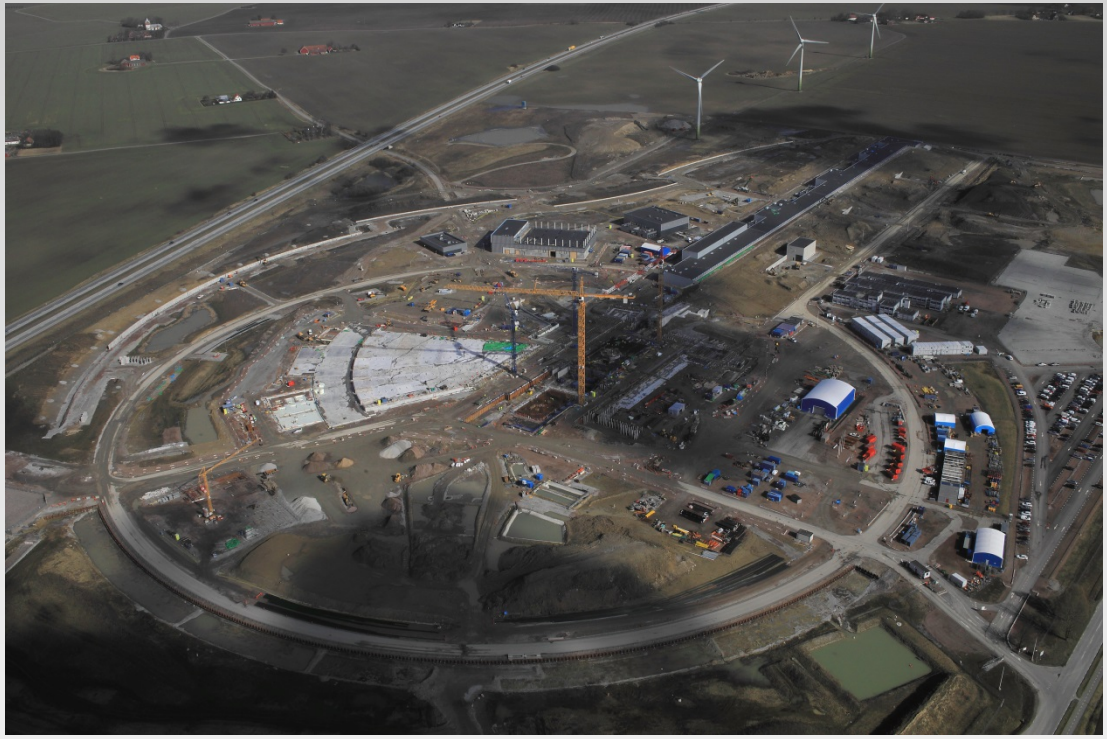
EUROPEAN SPALLATION SOURCE

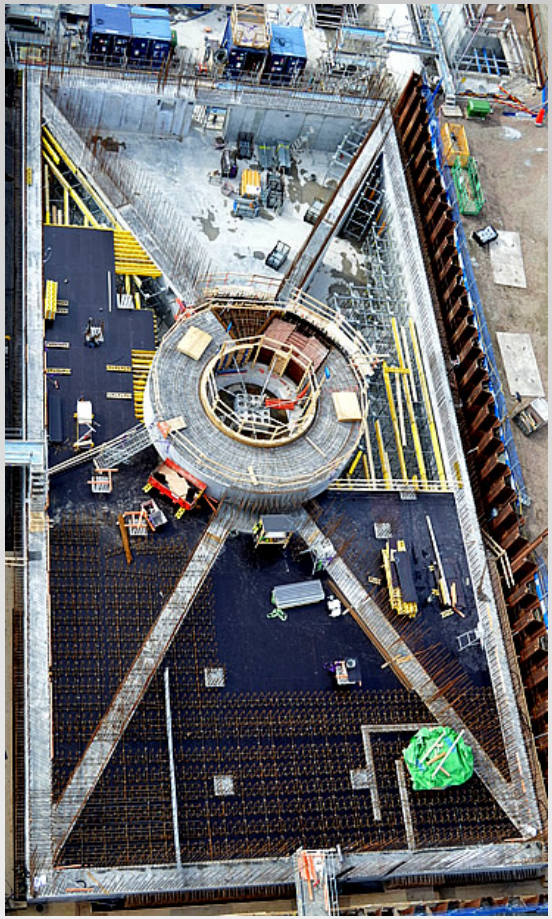
ESS is being built in Lund

The new spallation source next door.

Powerful technique for *in situ* studies.

Especially combined with X-ray diffraction



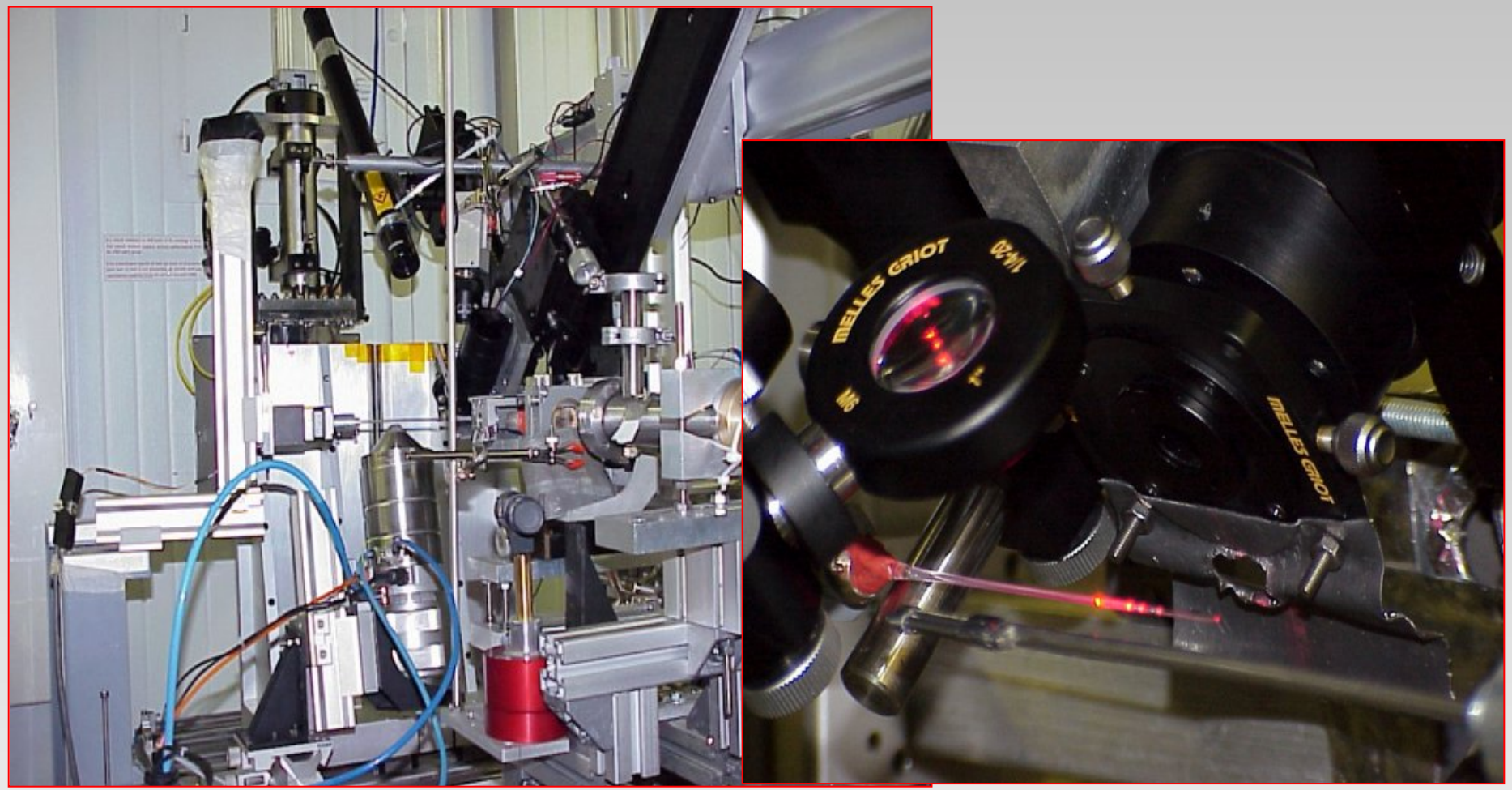


Studies of materials live and kicking:

A few examples of *in situ* studies.

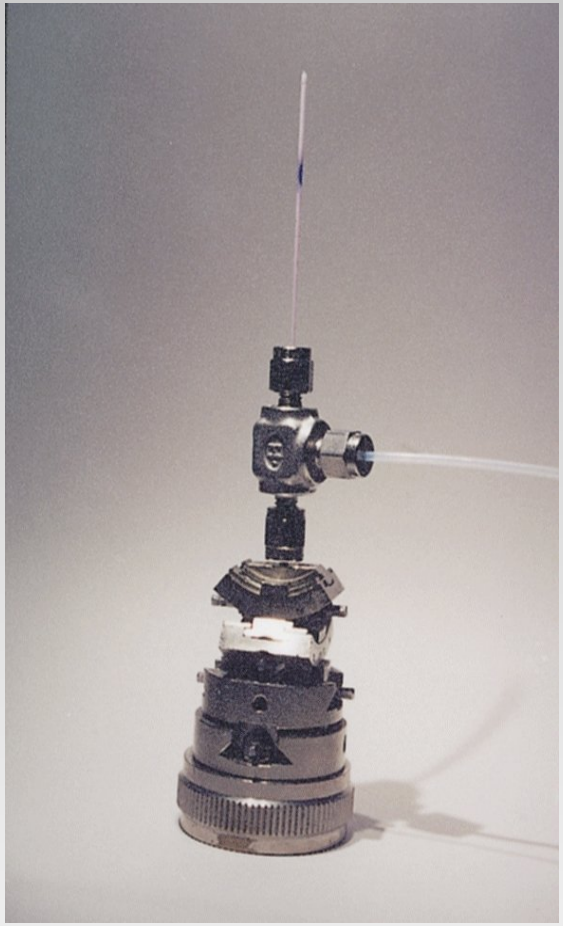
- Hydrothermal synthesis in capillaries
- Catalysts at work
- Batteries; structure and interfaces during operation.

In situ studies of hydrothermal synthesis of microporous materials



Example of a combined XRD/SAXS/DLS *in situ* experiment of zeolite synthesis

Micro Reaction Cell for *in situ* studies of Hydrothermal Synthesis using Synchrotron X-ray Powder Diffraction

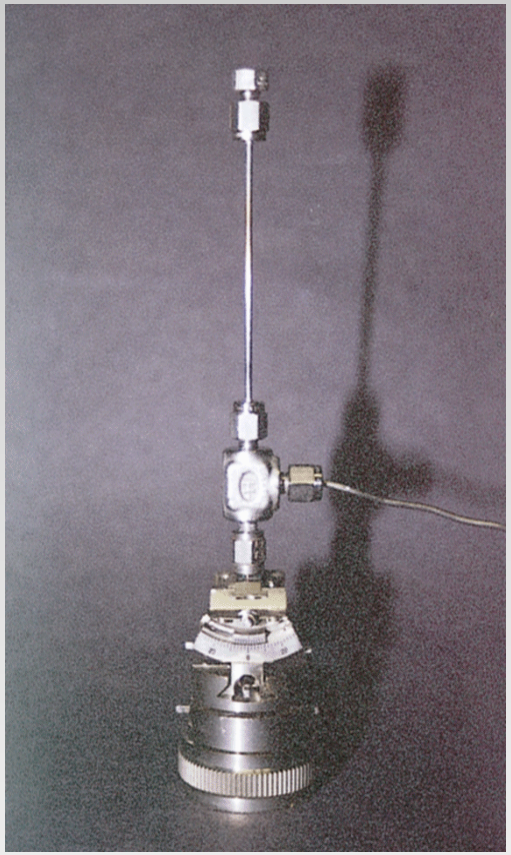


Capillary based Micro Reaction Cell

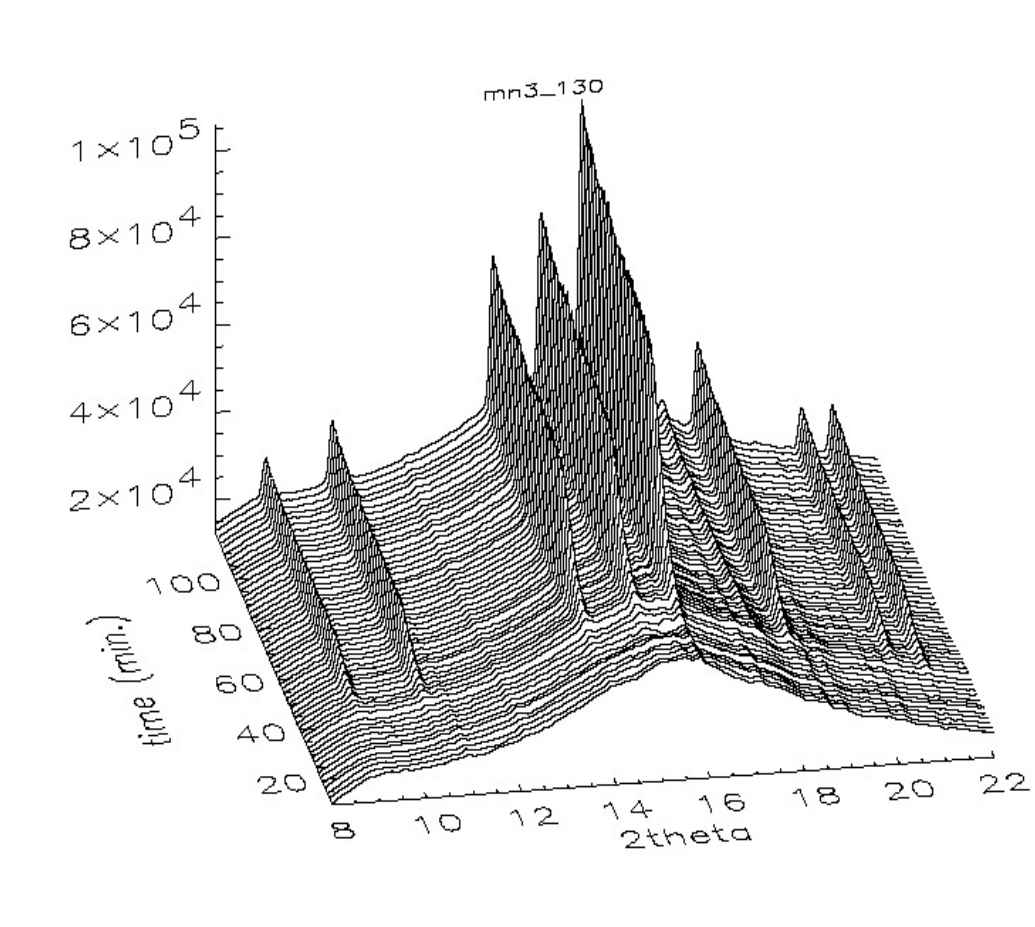
←

Cell for studies of hydrothermal synthesis at high temperatures (>350 °C) →

NSLS, National Synchrotron Light Source at Brookhaven National Laboratory



Synthesis of transition metal substituted microporous alumino-phosphates from non-aqueous media.

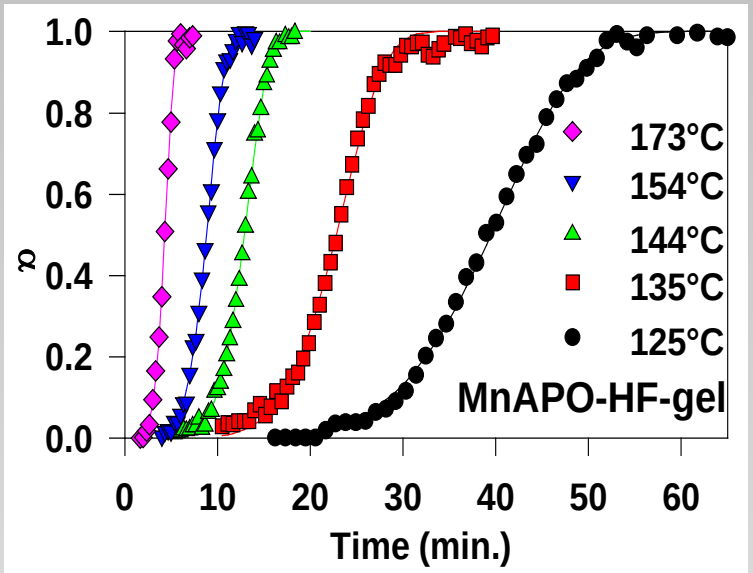


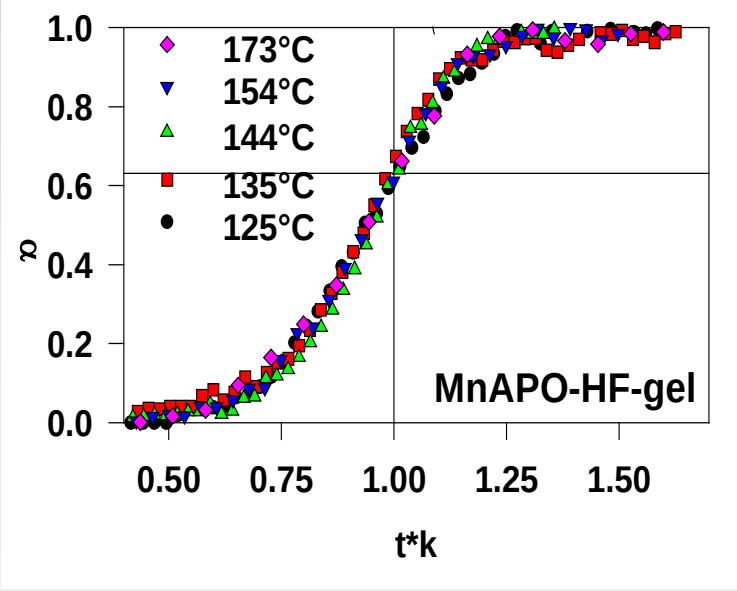
Studies of the effect of mineralizers in the solvothermal synthesis of MAPO-5, M=Mn, Co in ethylene glycol.

E.g.: P. Norby *J. Amer. Chem. Soc.* **119** (1997) 5215 5221.

P. Norby, A. Nørlund Christensen and J.C. Hanson *Inorg. Chem.* **38** (1999) 1216-1221

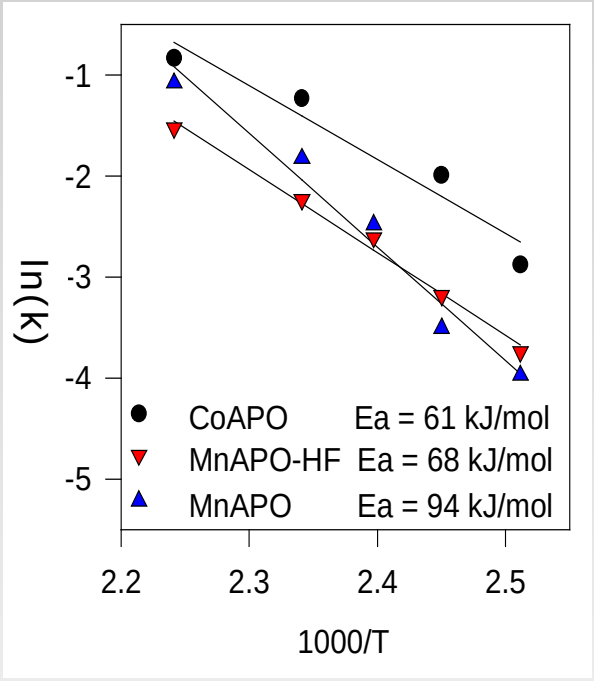
Kinetics analysis from isothermal experiments





Analysis using an Avrami type expression:

$$\alpha = 1 - \exp(-(k(t-t_0))^n)$$



Catalysts at real/realistic conditions.

Pioneering work by Bjerne S. Clausen, Haldor Topsøe A/S, using *in situ* EXAFS and XRD.

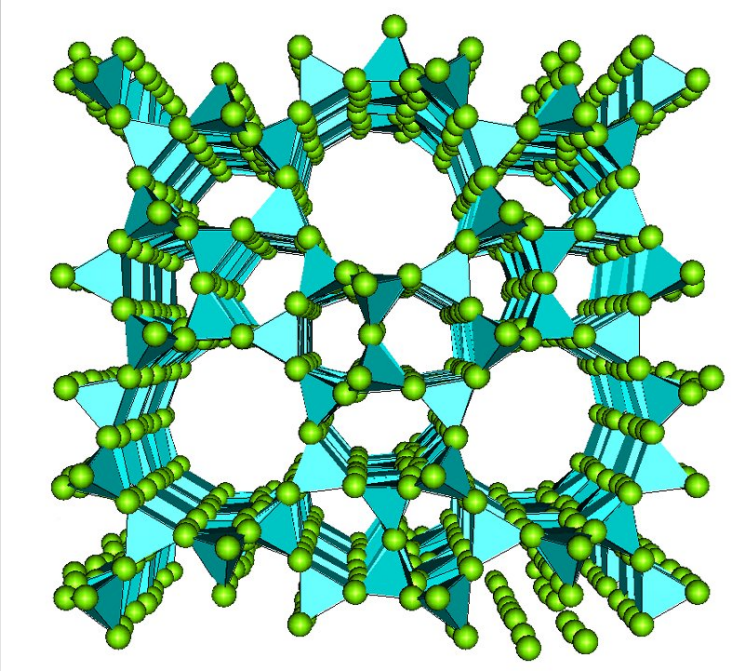
It is all about surface; how can diffraction be interesting for catalysis?

Often a combination of e.g. spectroscopy and diffraction is very efficient in studying catalysts at work.

Especially one class of catalysts are very well suited for diffraction studies; the microporous materials, zeolites and zeolite-like materials.

Microporous catalysts

Microporous materials have well ordered porosity with access to the inner surface on a molecular scale. Catalytic reactions may take place inside pores and voids in the crystalline structure, giving a high active area and at the same time giving strict limitations on product distribution.



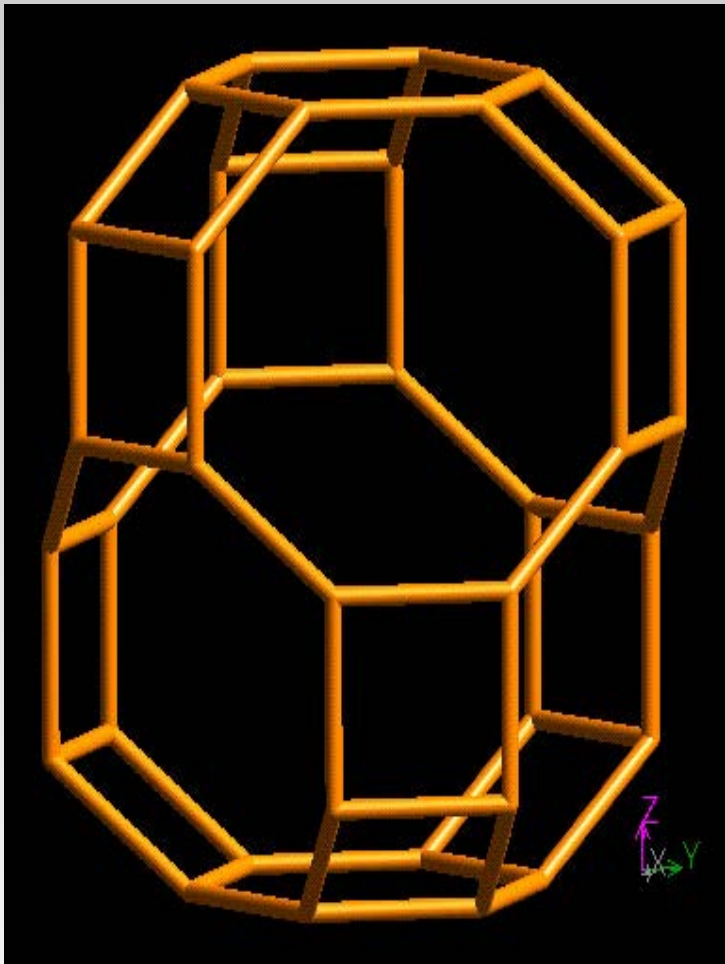
The catalytic active sites are often ions coordinated to the framework structure. The position and distribution of ions in the material is influenced by e.g. temperature and interaction with guest molecules. It is therefore not possible to extrapolate from room-temperature or ambient conditions to predict properties at operating conditions.

MTO (Methanol-to-olefin) catalyst under operative conditions

In situ XRD/Raman/MS experiments

Conversion of methanol to light olefins, e.g. ethylen and propylen, over a microporous catalyst.

Silicon substituted microporous aluminophosphate: HSAPO-34 (CHA-type)



Wragg, D.S., Johnsen, R.E., Balasundaram, M., Norby, P., Fjellvåg, H., Grønvold, A., Fuglerud, T., Hafizovic, J., Vistad, O.B., Akporiaye, D., *J. Catal.* **268** (2009) 290-296.

Wragg, D.S., Johnsen, R.E., Norby, P., Fjellvåg, H., Microporous *Mesoporous Mater.* **134** (2010) 210-215.

Wragg, DS; Gronvold, A; Voronov, A; Norby, P; Fjellvag, H. *Microporous Mesoporous Mater.* **173** (2013) 166-174

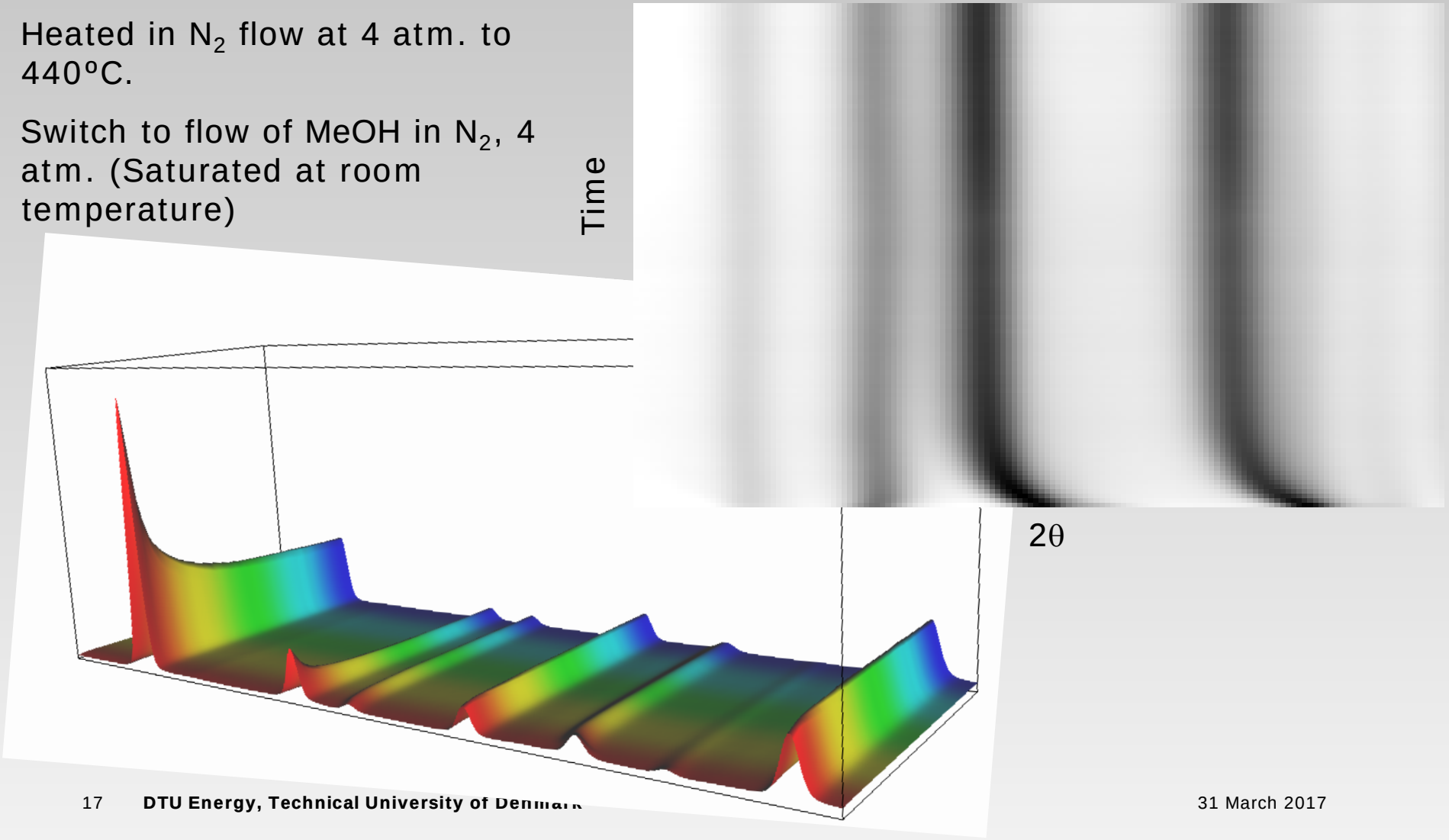
Methanol conversion

Reaction conditions:

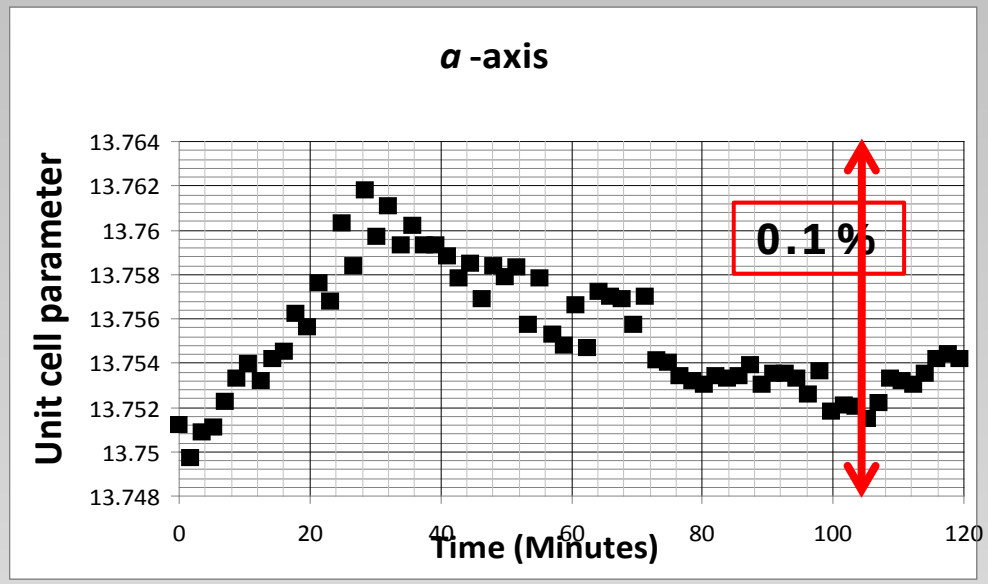
Calcined HSAPO-34

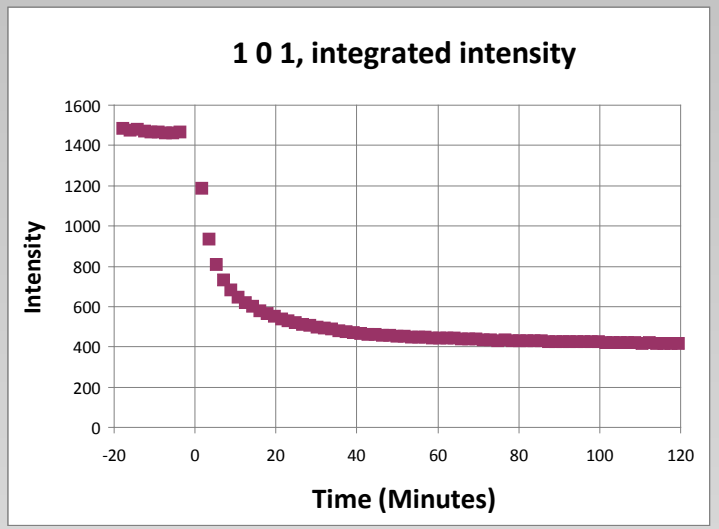
Heated in N_2 flow at 4 atm. to 440ºC.

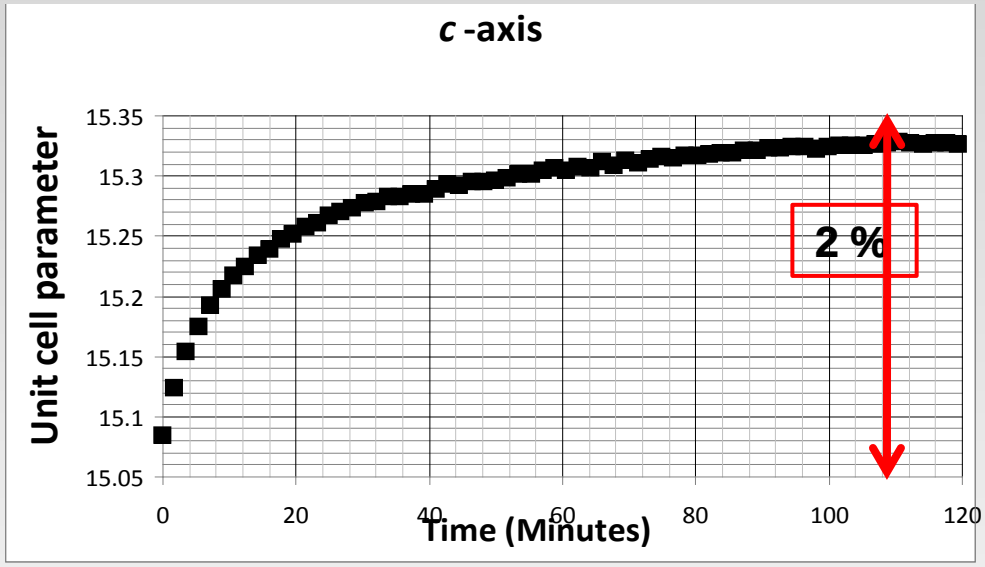
Switch to flow of MeOH in N_2, 4 atm. (Saturated at room temperature)

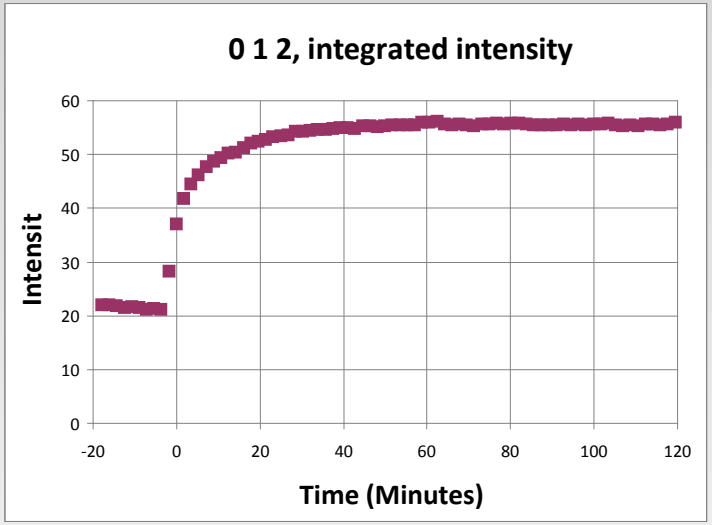


Unit cell parameter changes during the MTO process.

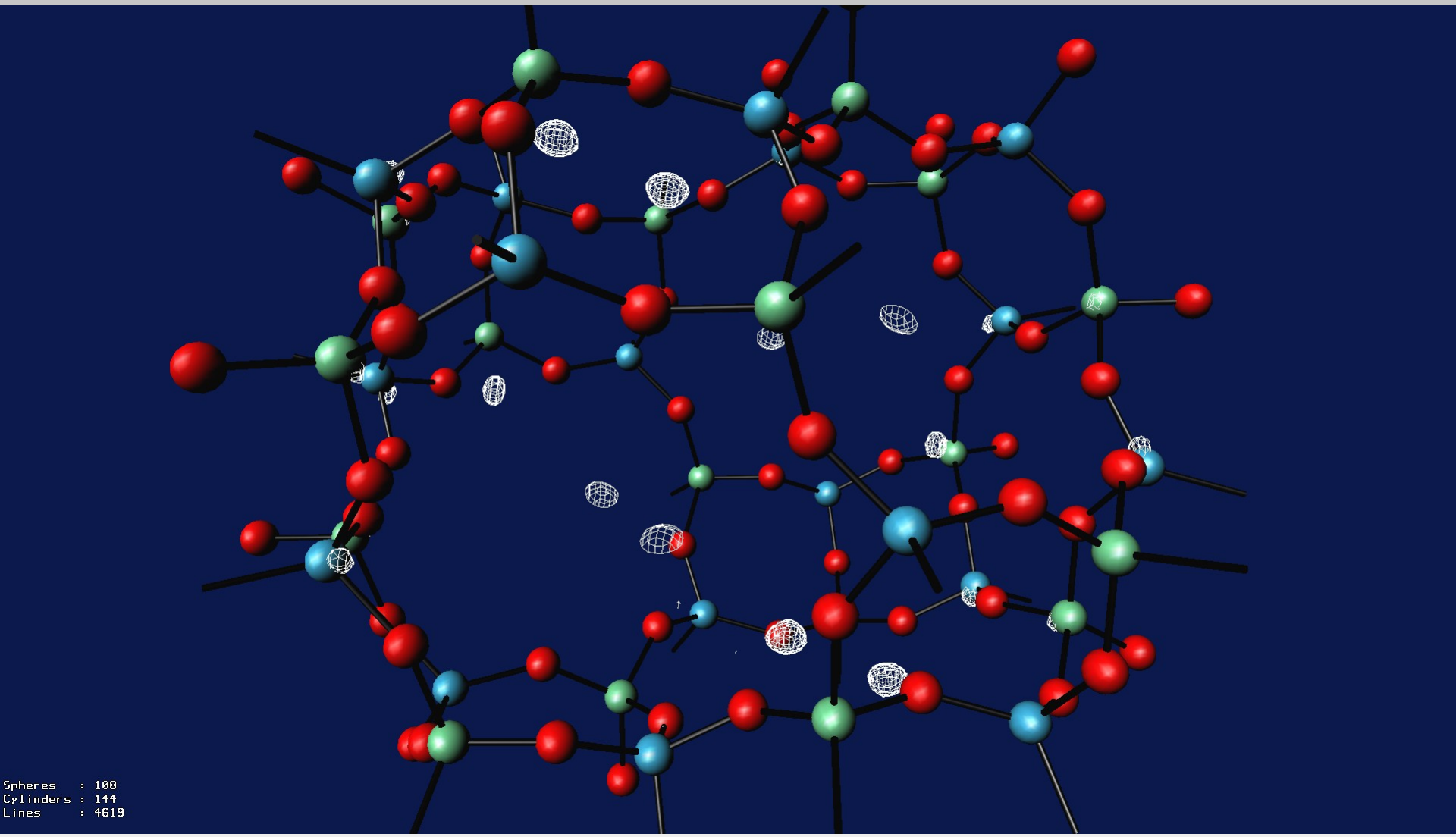




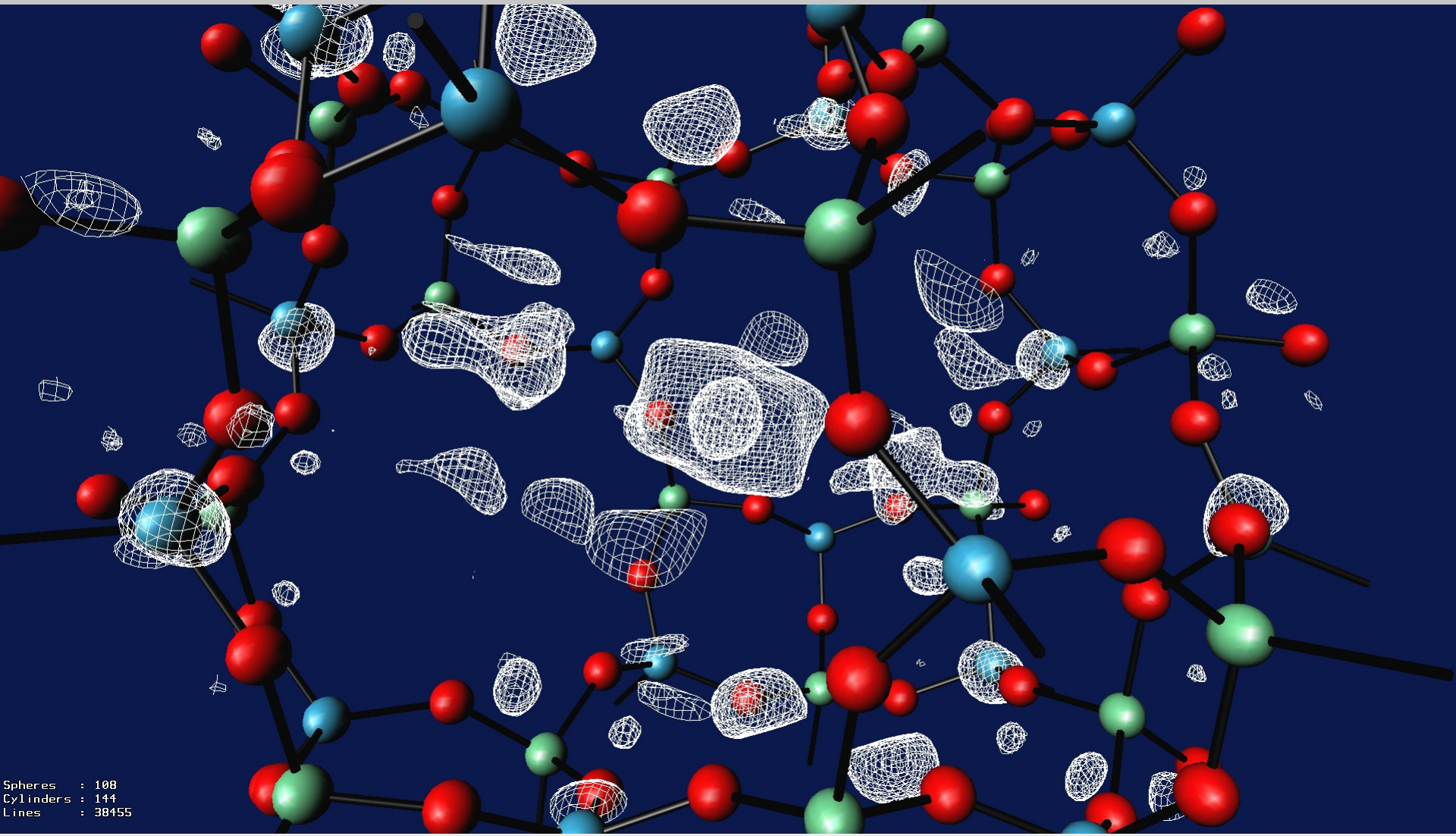




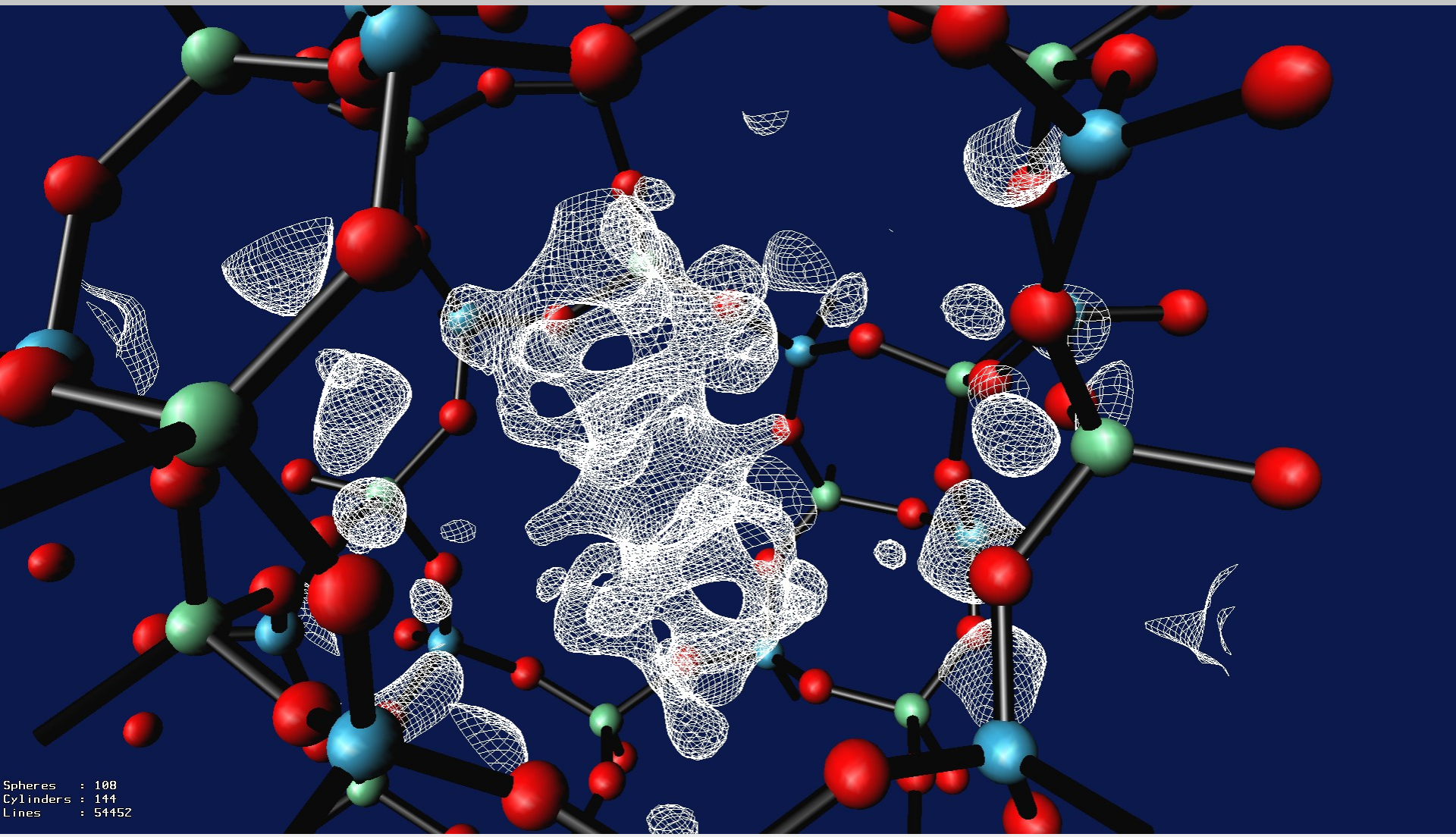
Electron density contours (Difference Fourier map) in SAPO-34 before MTO reaction.



Electron density contours (Difference Fourier map) in SAPO-34 after 3 minutes.



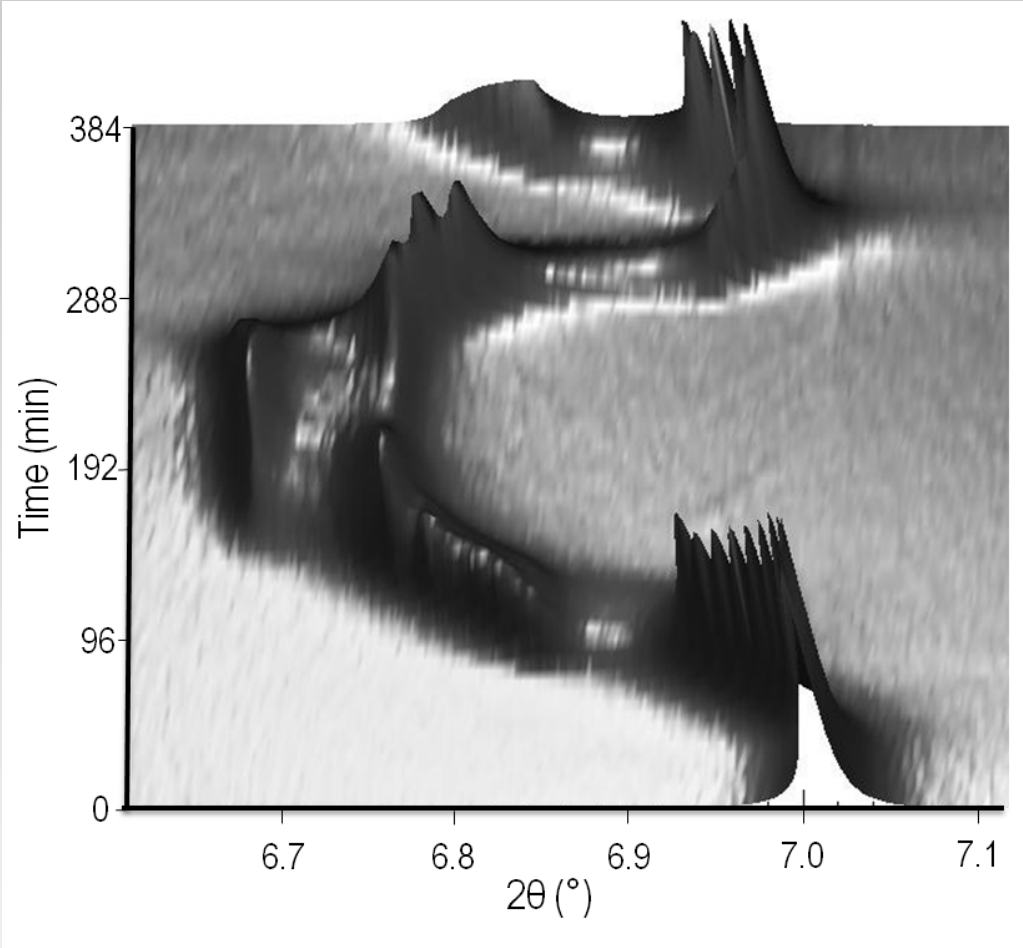
Electron density contours (Difference Fourier map) in SAPO-34 after 20 minutes.

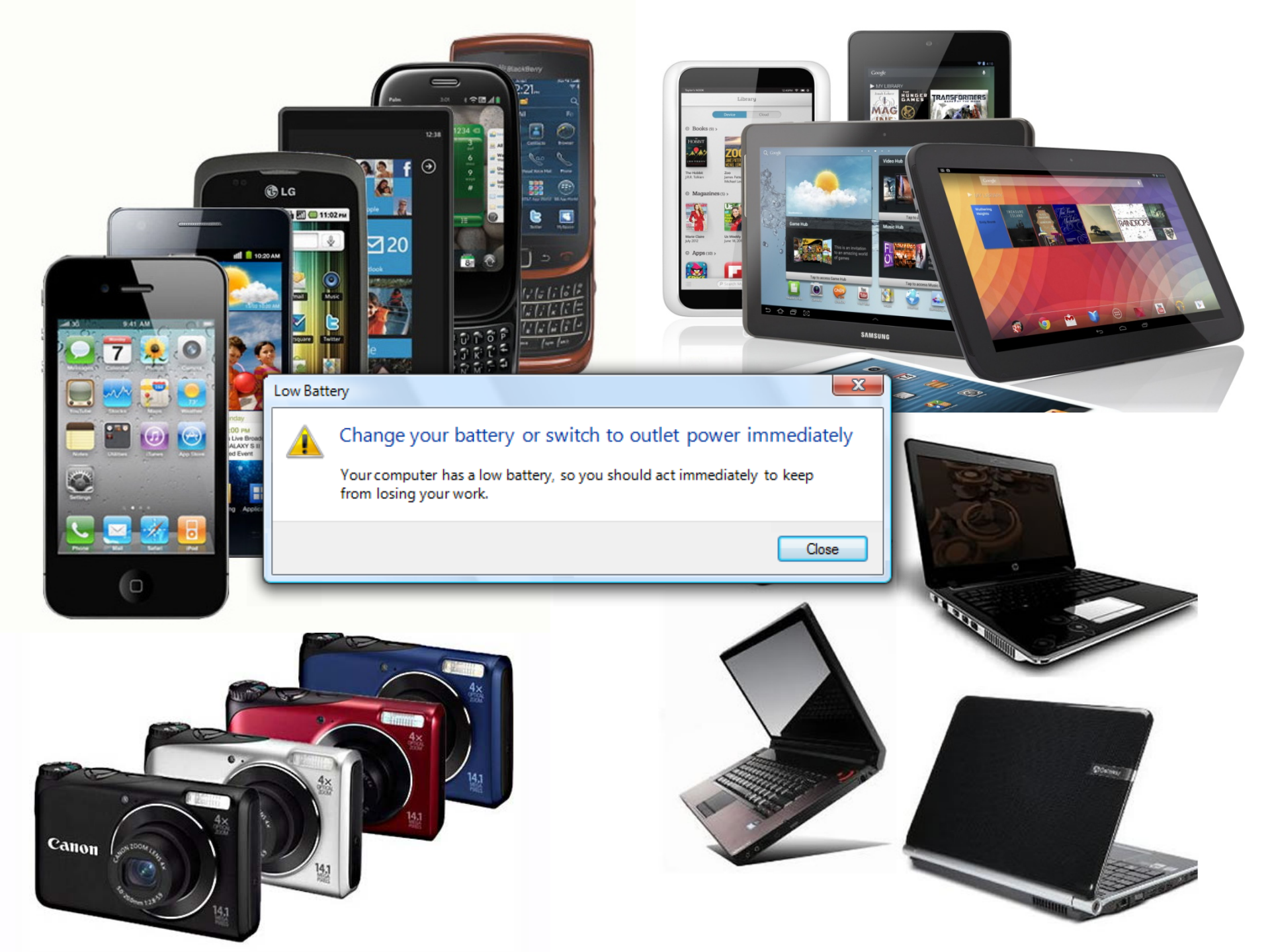


Electrochemistry live;
in situ diffraction studies of battery cells.

Some battery types we have studied *in situ*:

- Lithium-ion
- Sodium-ion
- Lithium-air (Li-O_2)
- Zinc-air (Zn-O_2)
- Dual-carbon
- Aluminium-"ion"
- Conversion batteries




LG
SAMSUNG
Low Battery
Change your battery or switch to outlet power immediately
Your computer has a low battery, so you should act immediately to keep from losing your work.
Close
Canon


Poul Norby

UltraFire BRC 18650

3.7V 5000mAh

Rechargeable battery

Rechargeable battery cells at operating conditions

We would like to understand the mechanisms during charge, discharge as well as failure mechanisms and degradation. Therefore we need to be able to look inside the battery and to study structural and microstructural changes during operation.

We are interested in:

- *Structural changes in electrode materials during charge/discharge*

In situ diffraction is a very powerful tool for this and has been used in numerous *in situ* studies involving development of various electrochemical *in situ* cells. Conventional and synchrotron X-ray diffraction as well as neutron diffraction is used.

Could we also get information about for instance:

- *Chemical and temperature gradients in real operating batteries?*
- *Interface formation and reactions in operating batteries?*
- *Microstructural and morphological information e.g. related to degradation?*

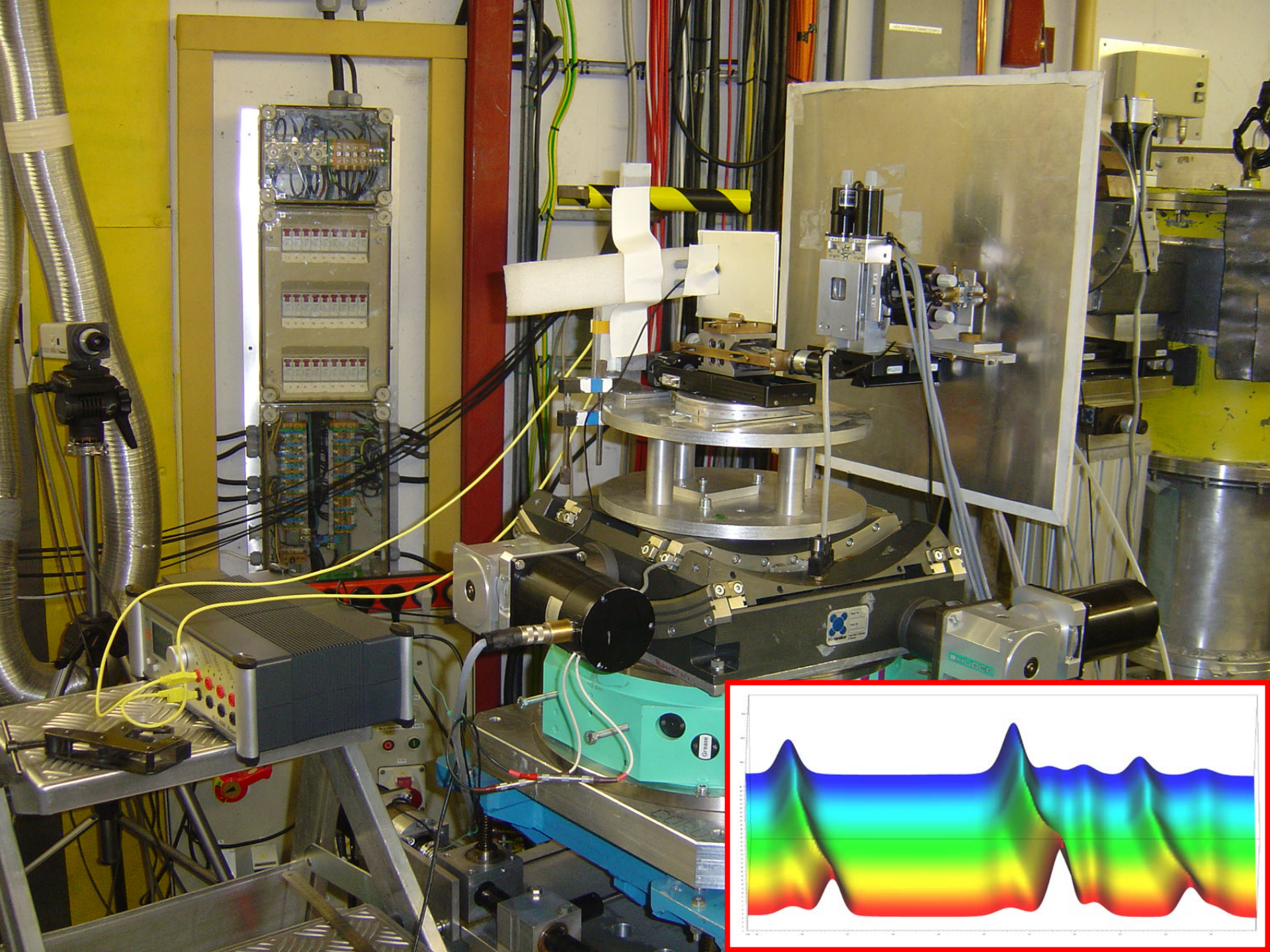
In situ battery cells from 10Ah to 1nAh

Some in situ studies of batteries require real commercial batteries.

In order to study fundamental reactions and detailed structural changes a dedicated in situ battery cell is needed.

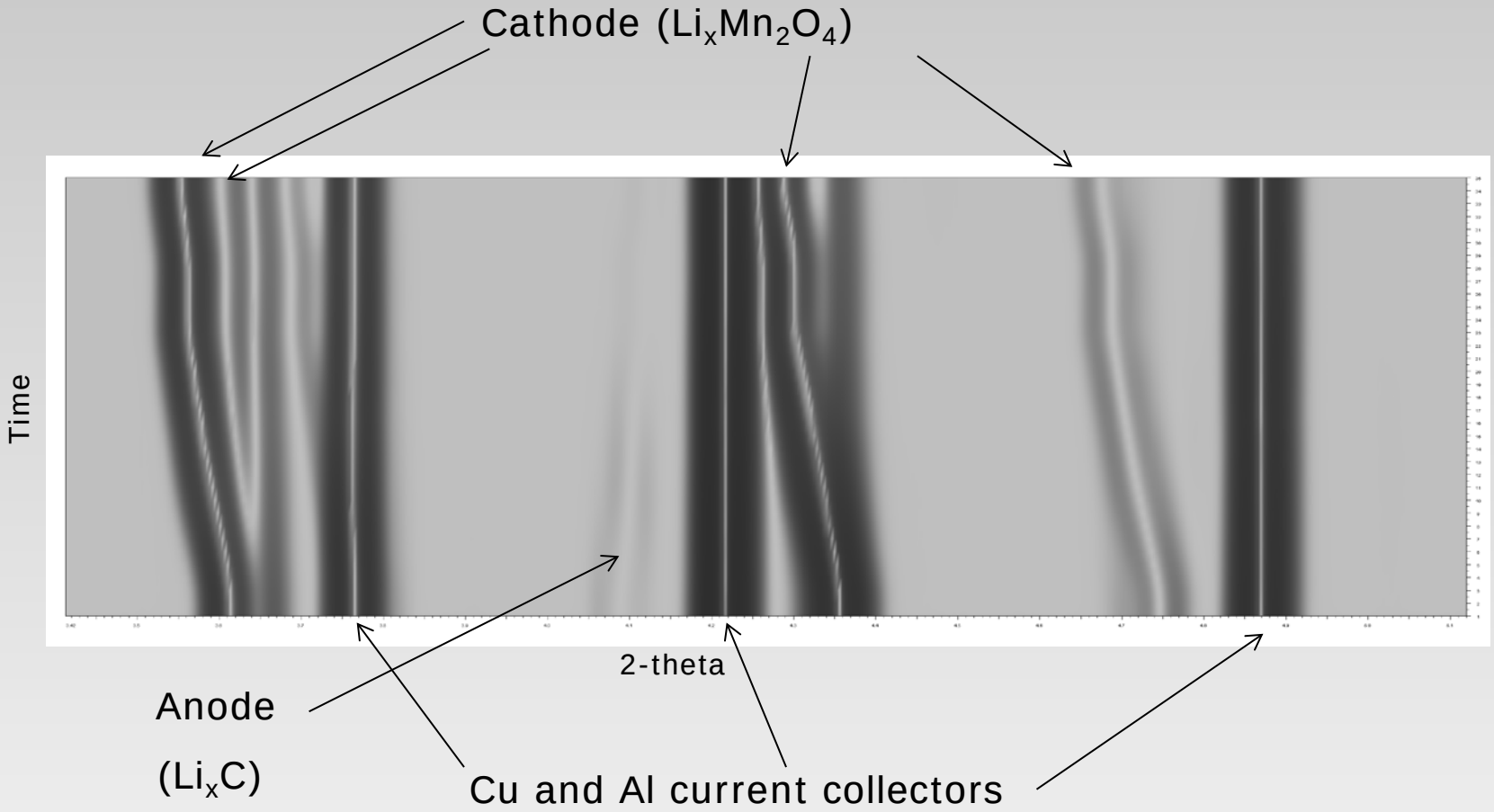
Advantages of synchrotron X-ray radiation:

- Hard radiation (40-100keV) for large and absorbing samples and devices.
- Medium hard radiation (10-40keV) for smaller samples and custom built *in situ* cells.
- Micro diffraction for spatial resolution and chemical gradients.

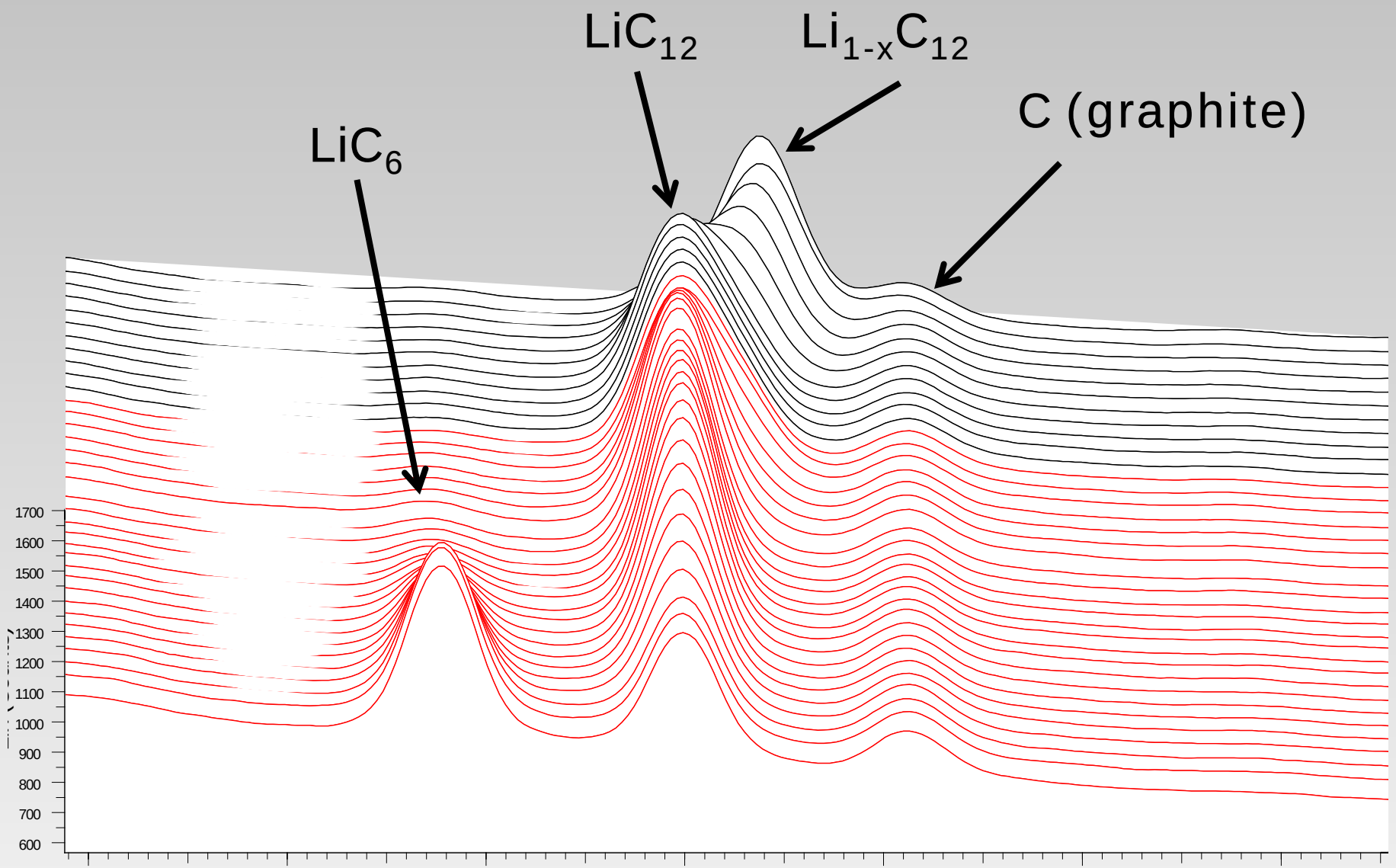


High energy synchrotron X-ray diffraction during discharge of a 7.5Ah Amita lithium ion battery

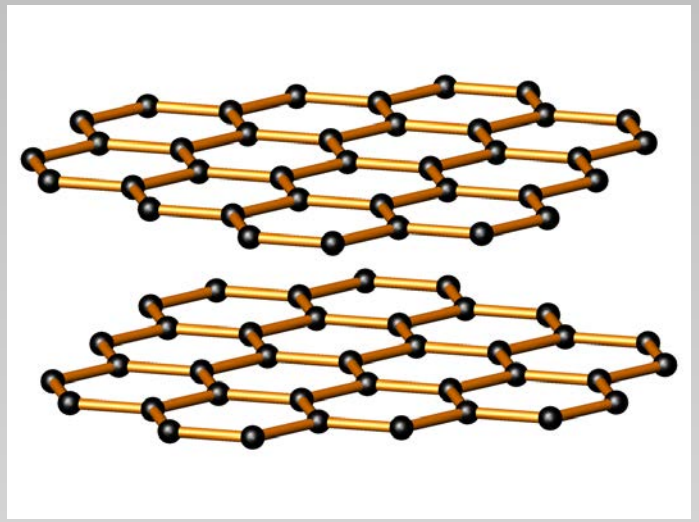
Diffraction from all active and inactive components

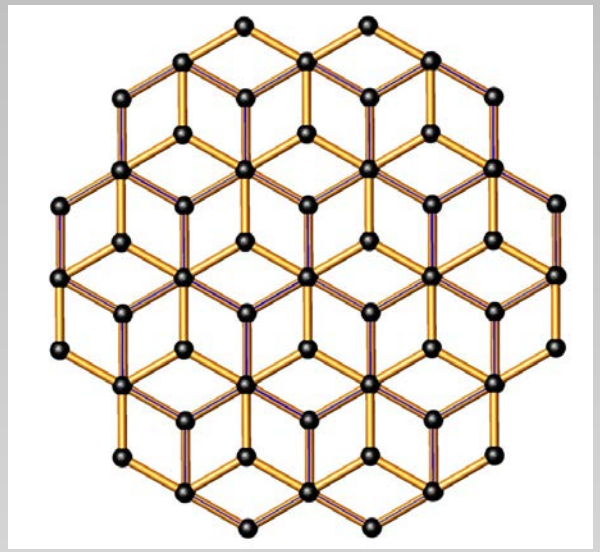


Discharge Amita lithium battery: Anode

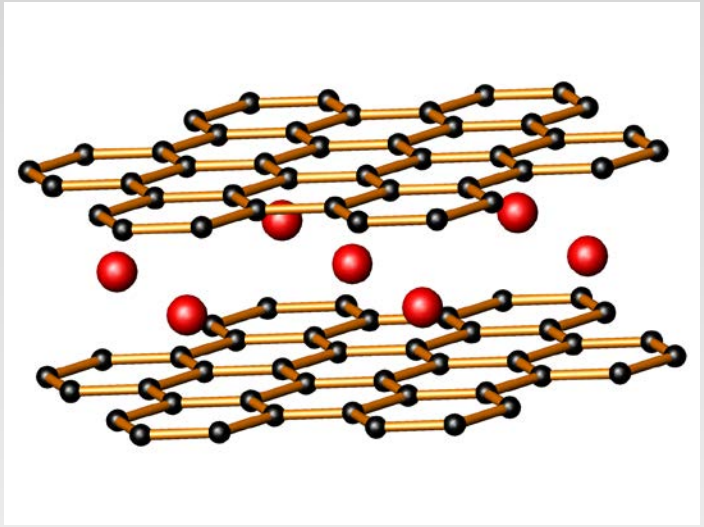


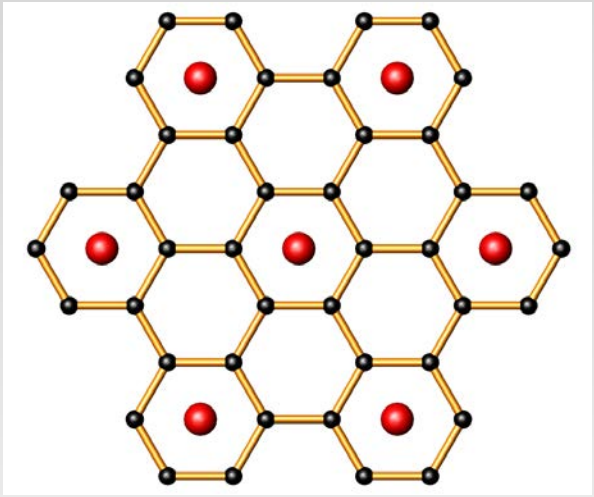
Graphite: ABAB stacking





LiC_6: $\alpha A \alpha A$ stacking





$a(LiC_6) = \text{sqrt}(3) * a(\text{graphite})$

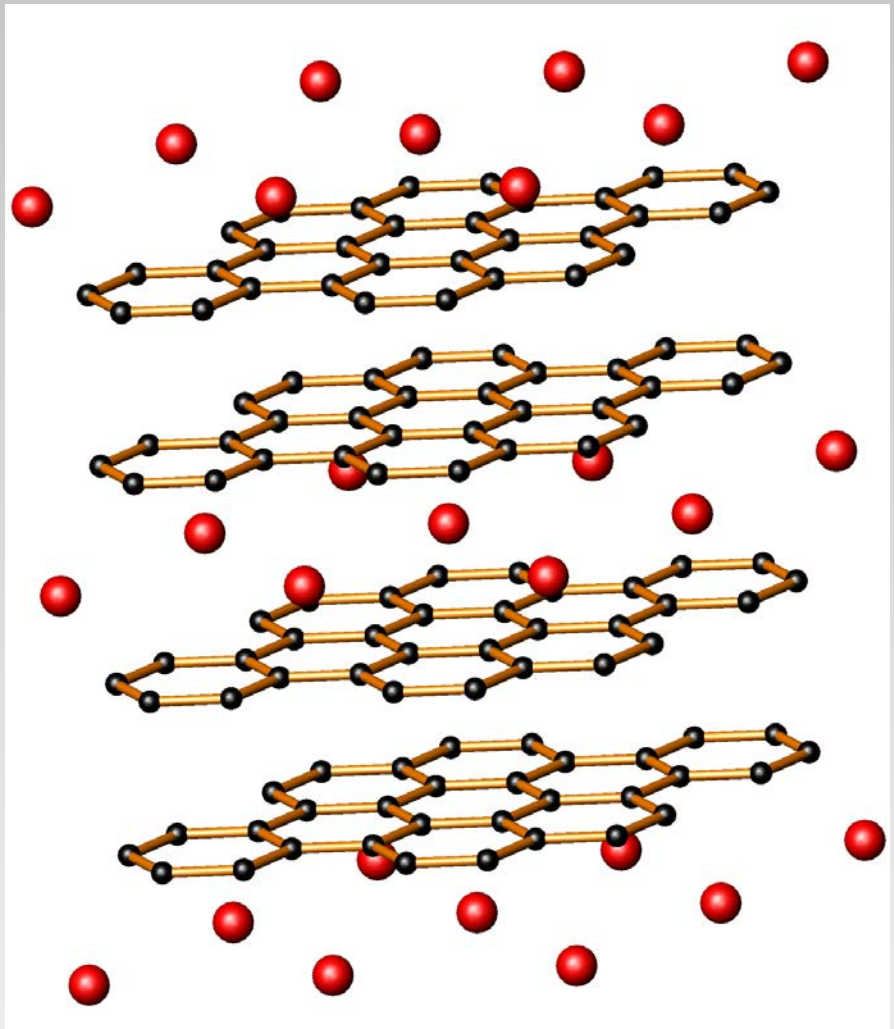
$c(LiC_6) = c(\text{graphite})$

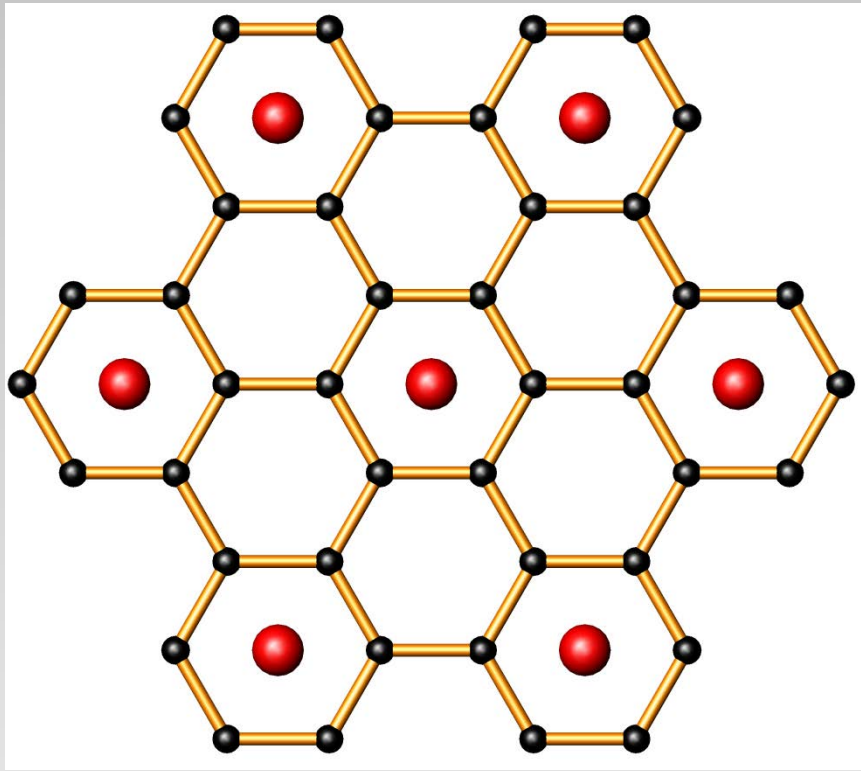
LiC_{12} : αAAαAA stacking

(or αABαAB stacking)

$a(LiC_{12}) = \text{sqrt}(3) * a(\text{graphite})$

$c(LiC_{12}) = 2 * c(\text{graphite})$

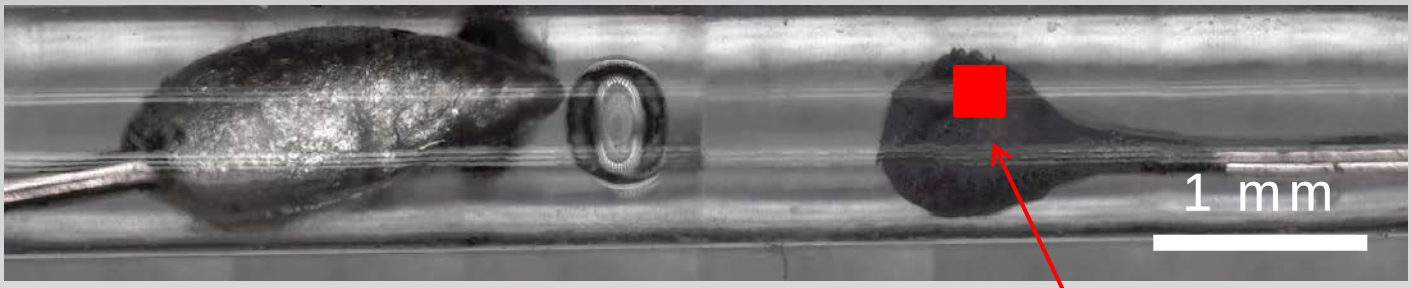


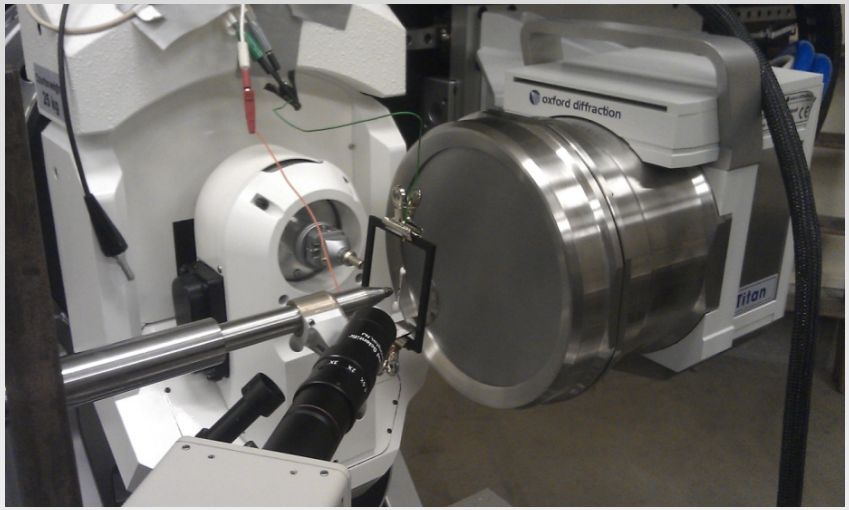


Our first capillary based micro battery for *in situ* studies

Detailed structural information be selective diffraction from a single phase.

Anode: Lithium metal Cathode: Graphite





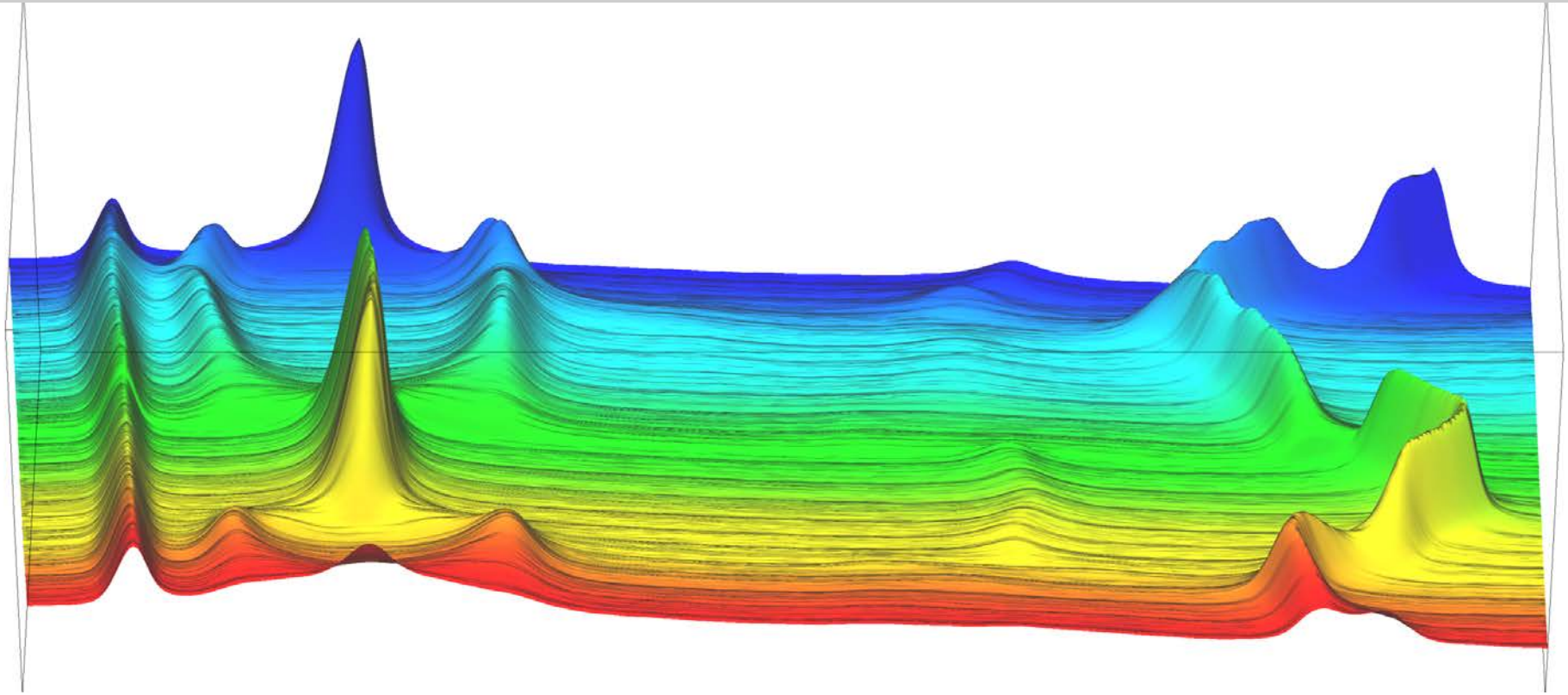
The capillary battery cell at beamline I711, Maxlab

Initial stages in the lithiation of graphite.

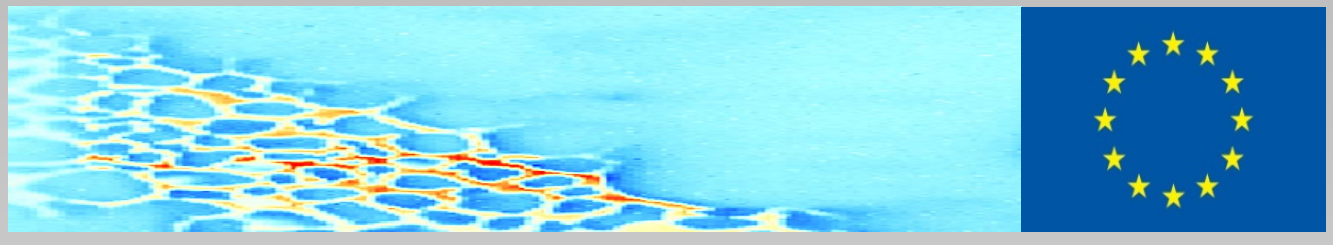
Detailed information about disorder and stacking faults

The micro battery cell allows *in situ* diffraction and scattering data to be obtained from only one of the components (e.g. electrode material) in the battery.

Diffraction patterns of graphite during intercalation/de-intercalation of lithium



Johnsen, Rune E.; Norby, Poul *J. Appl. Cryst*. **46** (2013) 1537-1543



The Hi-C project

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

www.hi-c.eu

FP7 project, 2013-2017.

Coordinator: DTU

Partners: KIT, University of Tours, CEA, Uppsala University, Haldor Topsøe A/S, Varta Microbatteries, Uniscan

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KIT Karlsruhe Institute of Technology

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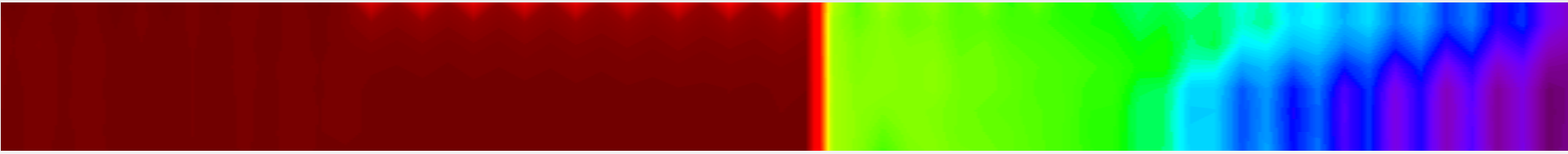
CATALYZING YOUR BUSINESS

VARTA

uniscan instruments



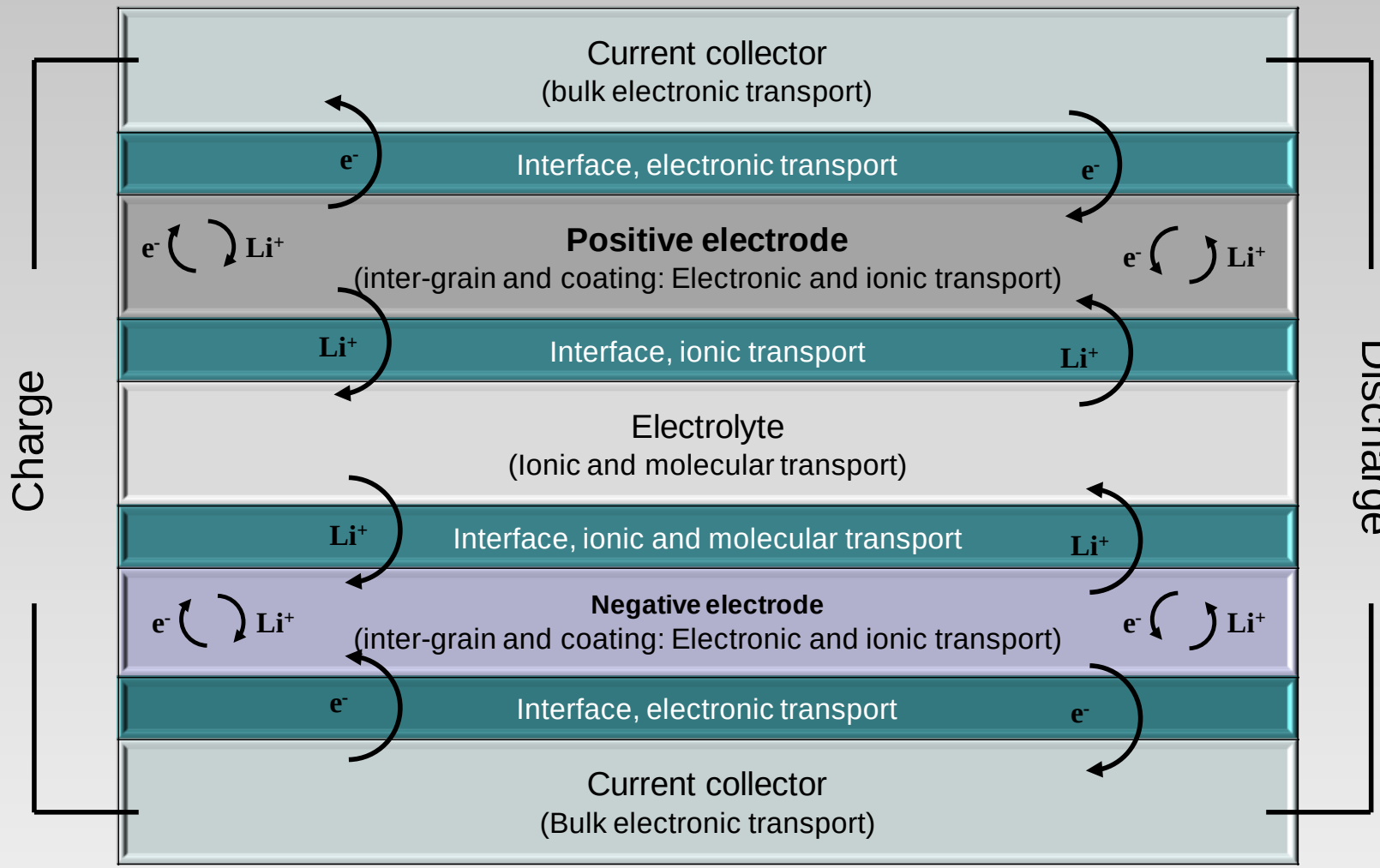
Using *in situ* powder diffraction to study interfaces in operating battery cells.

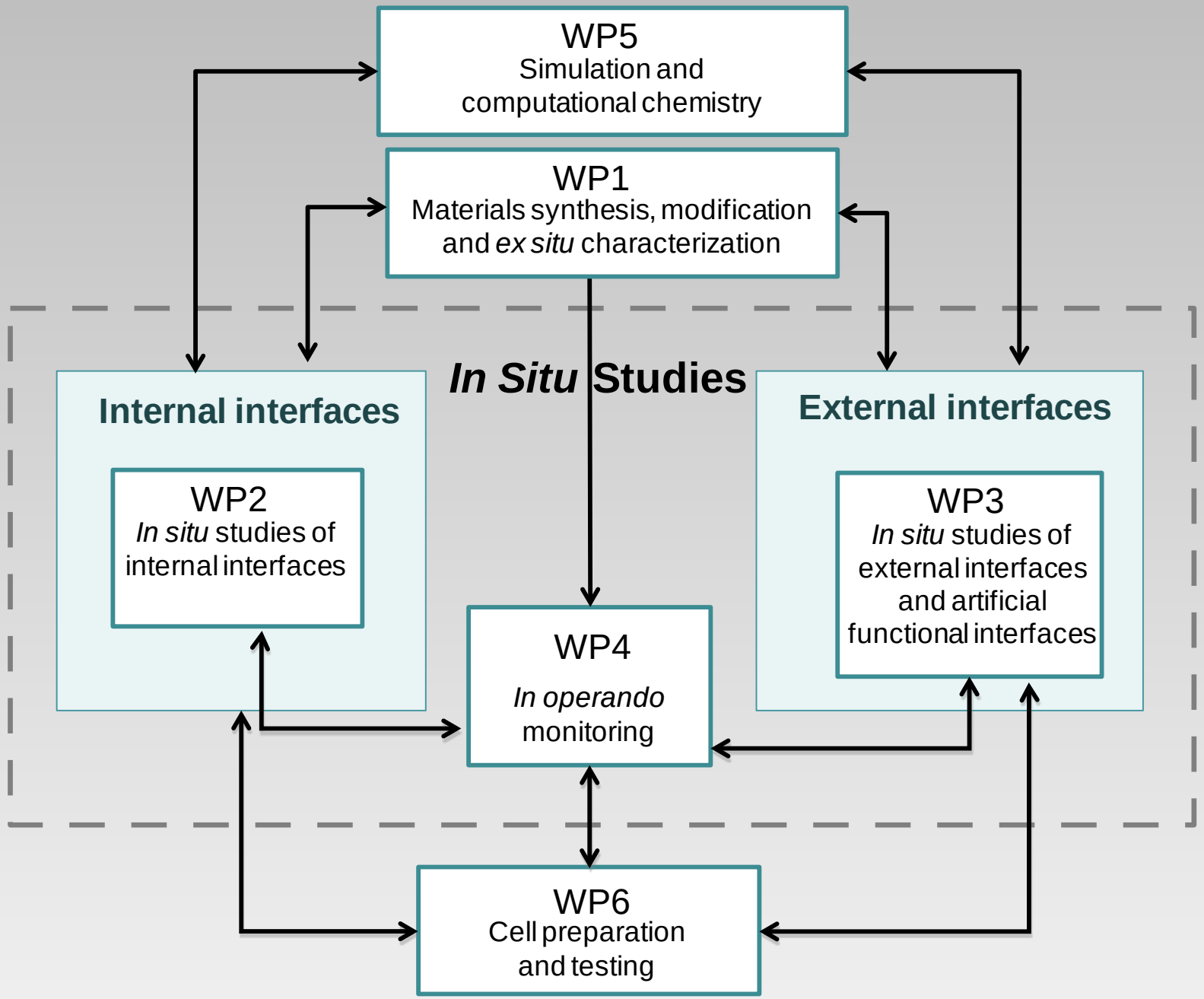
Main focus points:

- Intracrystallite interfaces in e.g. the cathode materials $LiFePO_4$ and $LiFeBO_3$.
- Nucleation and growth of nanomaterials in conversion type batteries.
- Chemical gradients in electrodes during battery operation.

- Using high resolution powder diffraction to reveal details about interface regions and non-stoichiometry inside single crystallites, e.g. between lithiated and non-lithiated domains.
- Using microdiffraction with capillary based micro battery cells to study development of chemical gradients in battery electrodes.

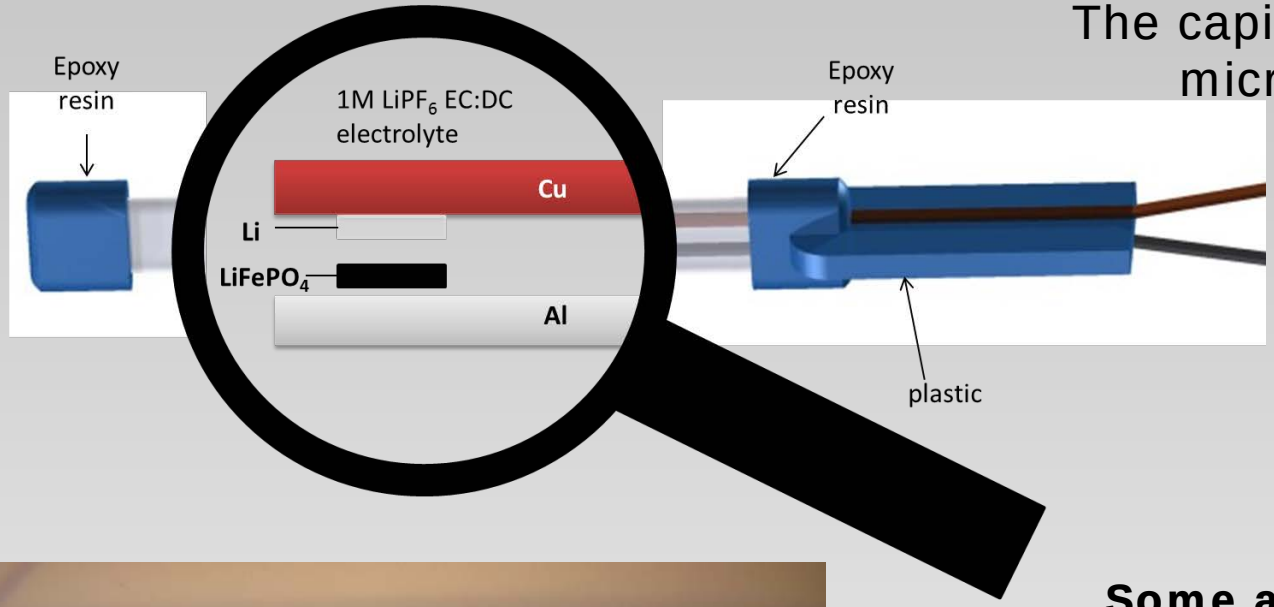
An electrochemical cell may be viewed as a series of interfaces

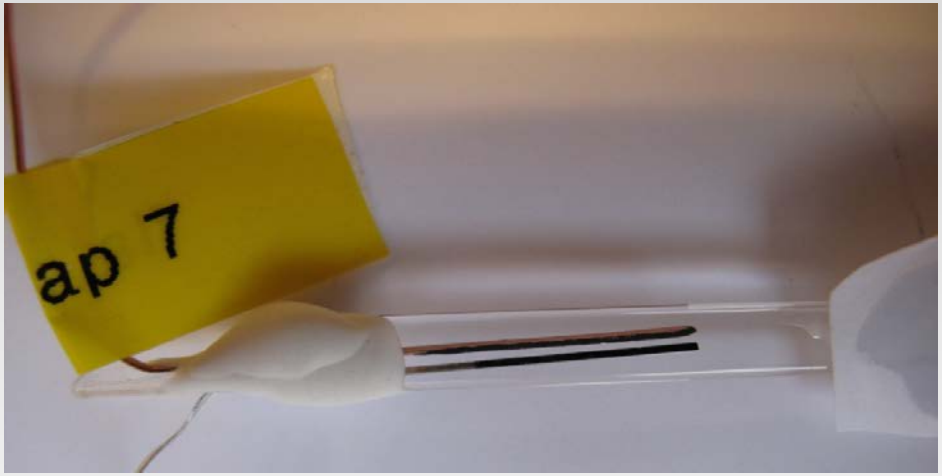



WP5
Simulation and computational chemistry
WP1
Materials synthesis, modification and *ex situ* characterization
In Situ Studies
Internal interfaces
WP2
In situ studies of internal interfaces
External interfaces
WP3
In situ studies of external interfaces and artificial functional interfaces
WP4
In operando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

In situ synchrotron X-ray studies of interfaces between lithiated and non lithiated phases in $LiFePO_4$ based lithium ion batteries

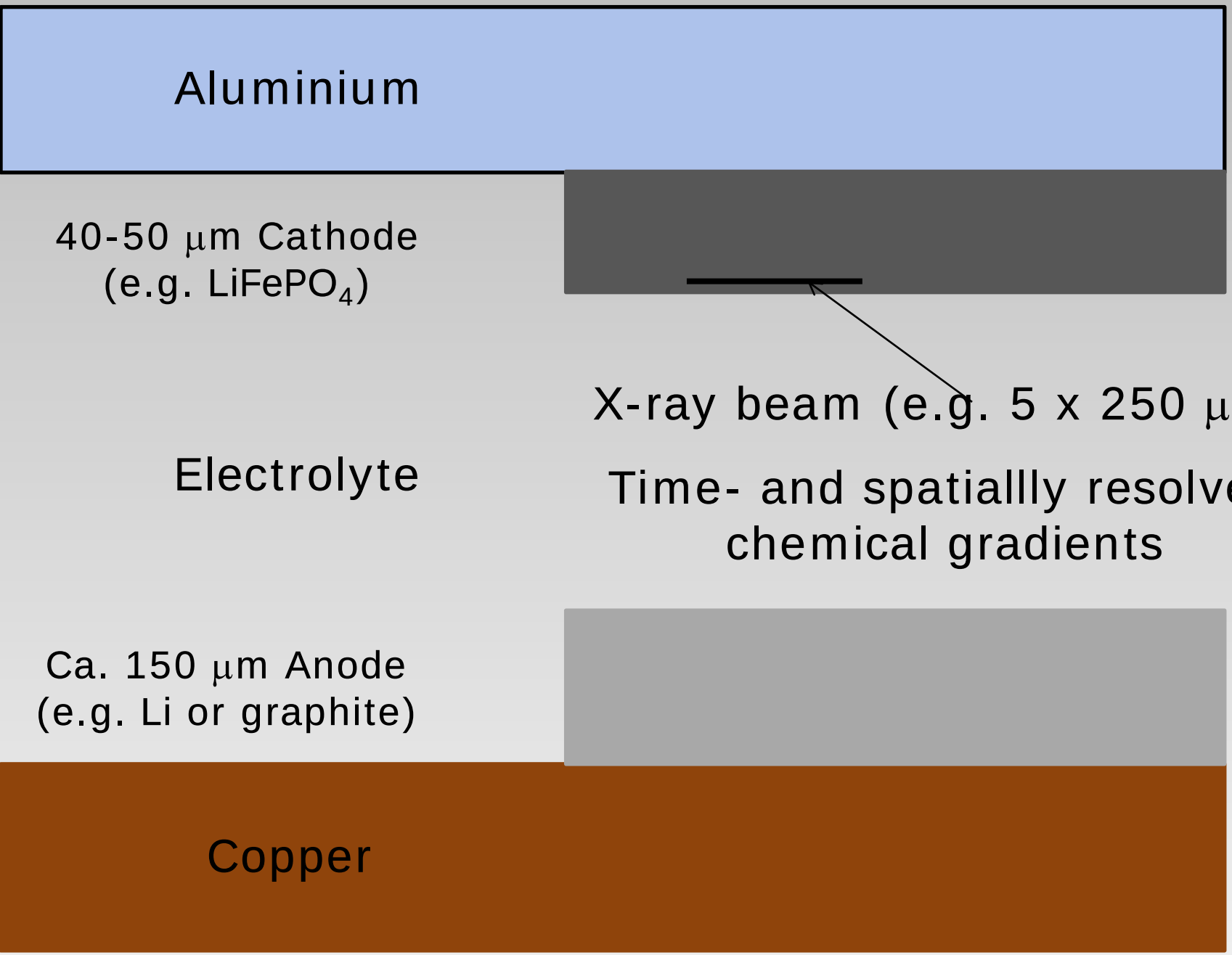
The capillary based *in situ* micro battery cell





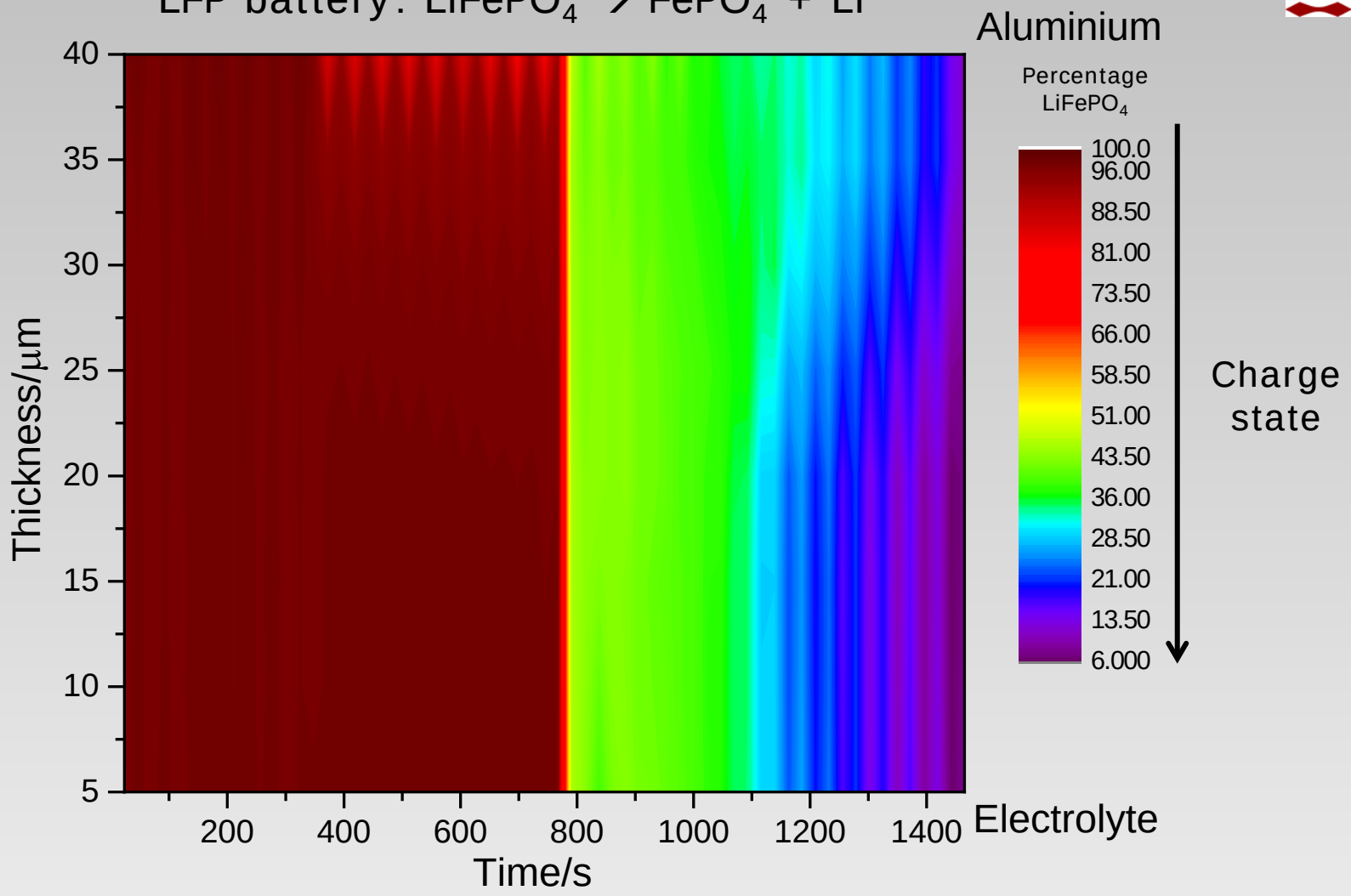
Some advantages

- 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


Aluminium
40-50 μm Cathode
(e.g. $LiFePO_4$)
X-ray beam (e.g. 5 x 250 μm)
Electrolyte
Time- and spatiallly resolved
chemical gradients
Ca. 150 μm Anode
(e.g. Li or graphite)
Copper

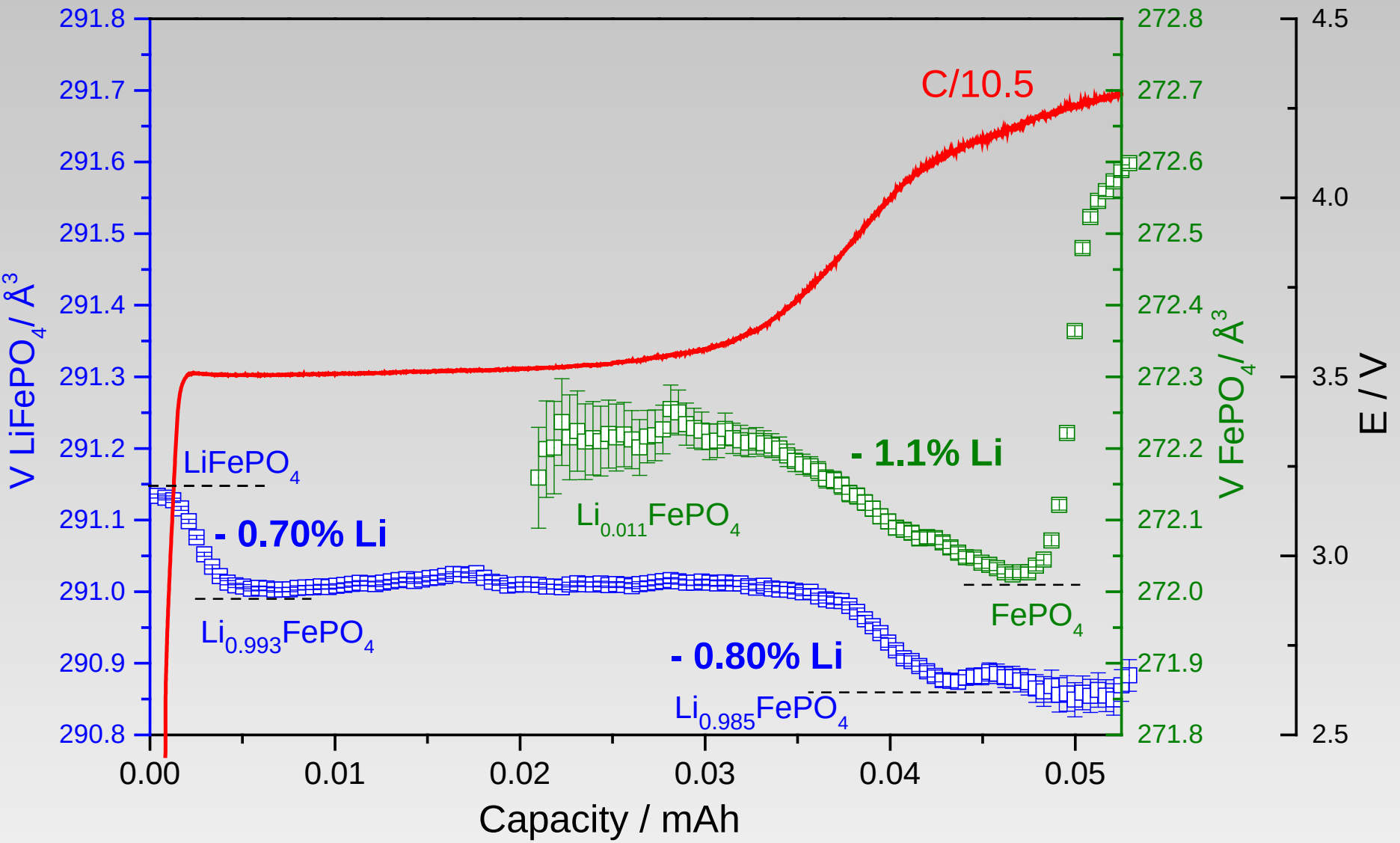
Investigating chemical gradients in electrolyte layers

LFP battery: $LiFePO_4 \rightarrow FePO_4 + Li$

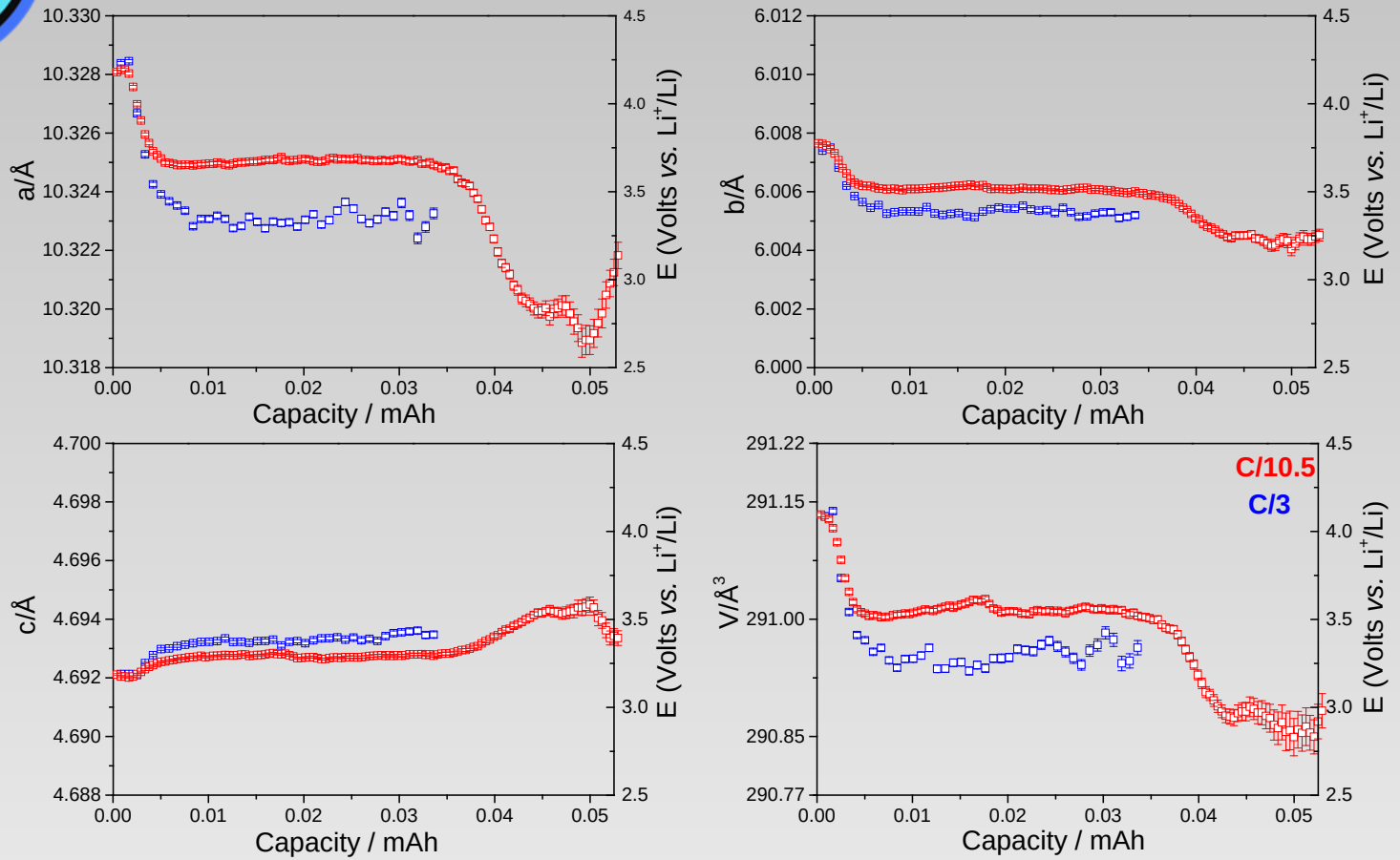


Gradient development during fast charge of $LiFePO_4$ battery cell determined by Rietveld refinement

Variation of unit cell volume for $LiFePO_4$ and $FePO_4$ determined from Rietveld analysis during battery charge



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

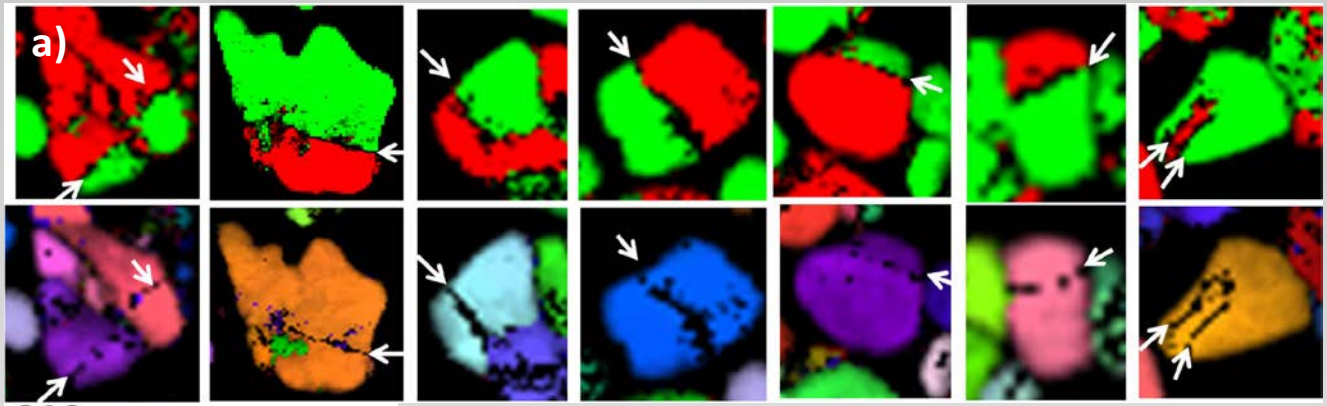


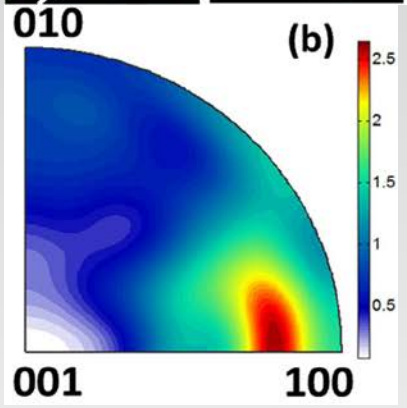
Unit cell variation for $LiFePO_4$ during charging by C/10 and C/3.

Increased solid solubility by increased current density.

Comprehensive analysis of TEM methods for $LiFePO_4/FePO_4$ phase mapping.

Spectroscopic techniques (EFTEM, STEM-EELS) and STEM diffraction techniques including automated crystal orientation mapping (ACOM-TEM)



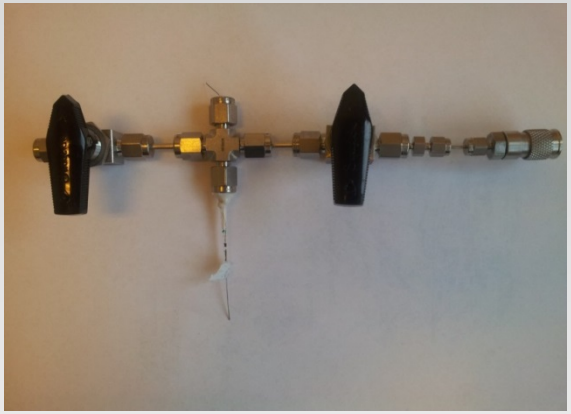


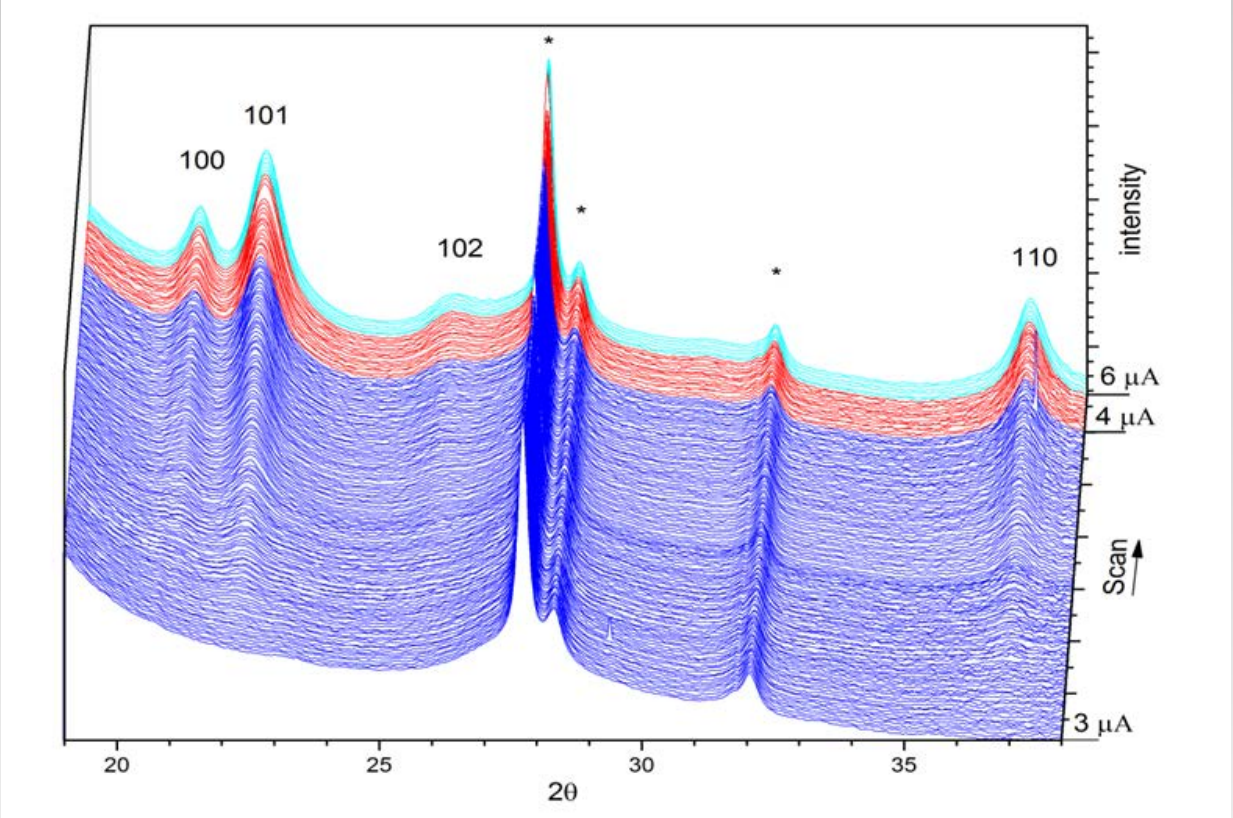
ACOM phase and orientation maps of single crystalline particles with an FP/LFP interface and the corresponding statistical analysis of the orientation distribution of the interface shown as orientation density in the inverse pole figure.

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

Beyond lithium-ion batteries

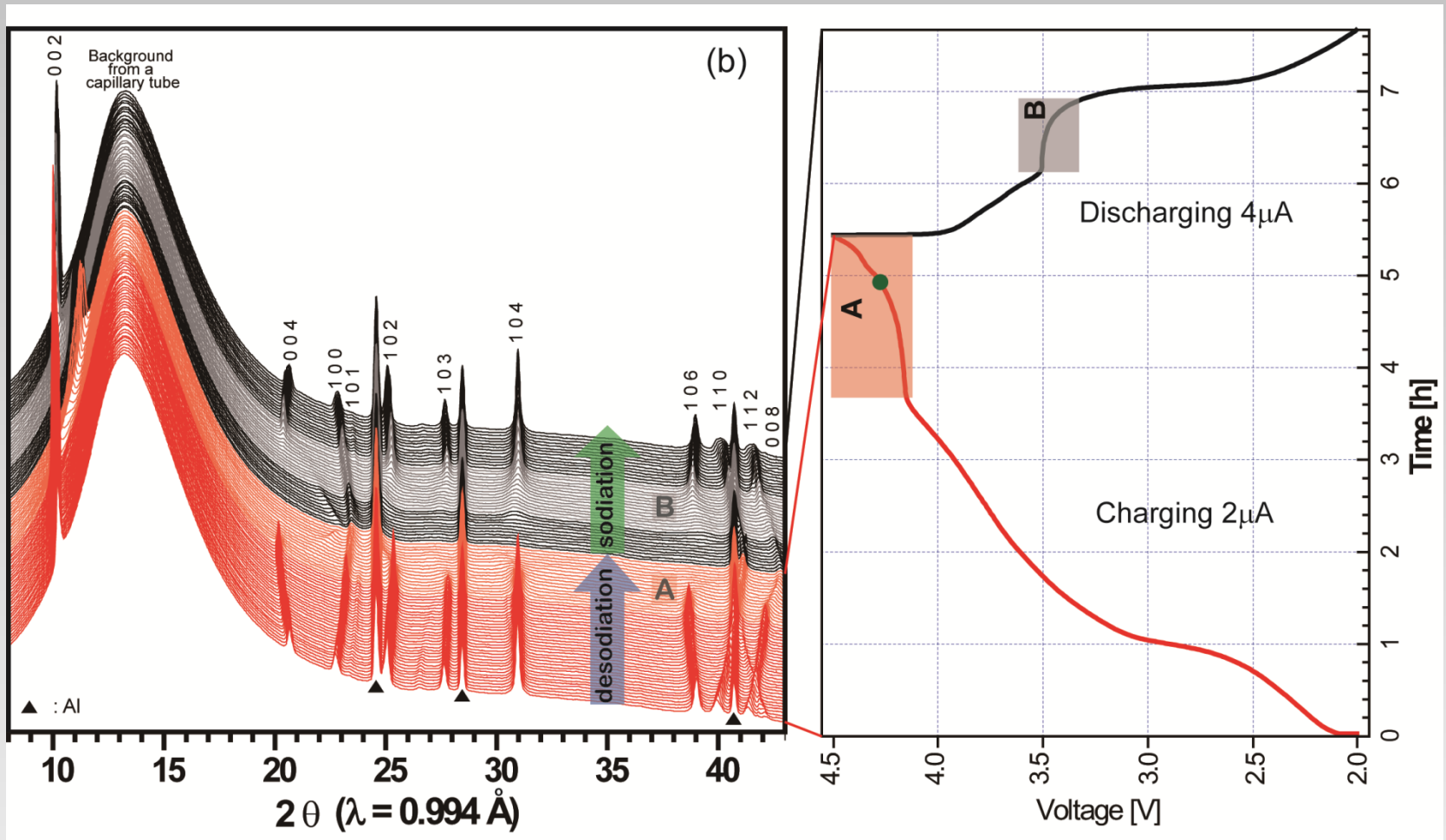
- Lithium-sulphur batteries
- Sodium ion batteries
- Magnesium ion batteries
- Lithium-air batteries
- Zn-Air batteries





Lithium peroxide formation in a lithum-air (O_2) battery during discharge

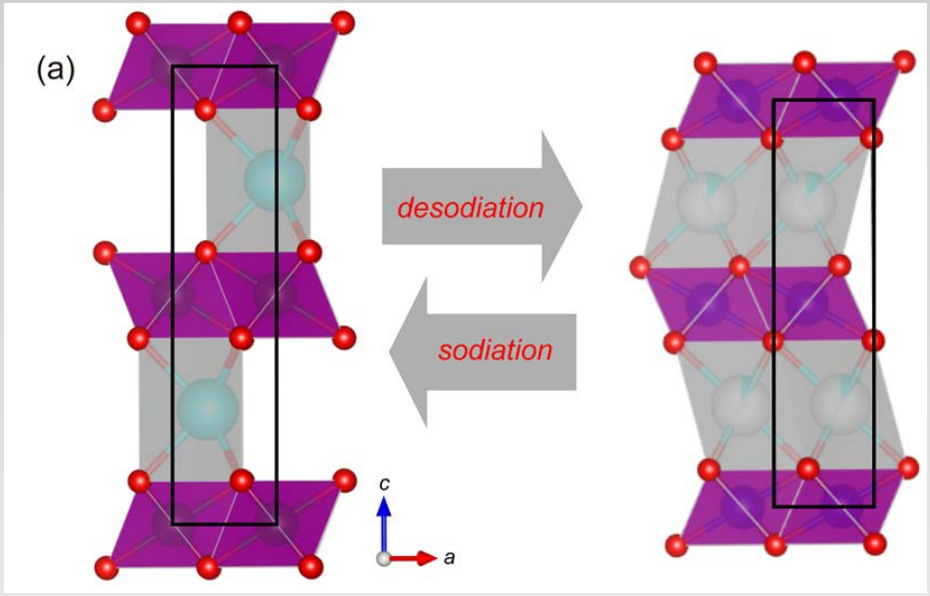
In situ studies of sodium ion batteries.
Sodiation/desodiation in positive electrode materials.



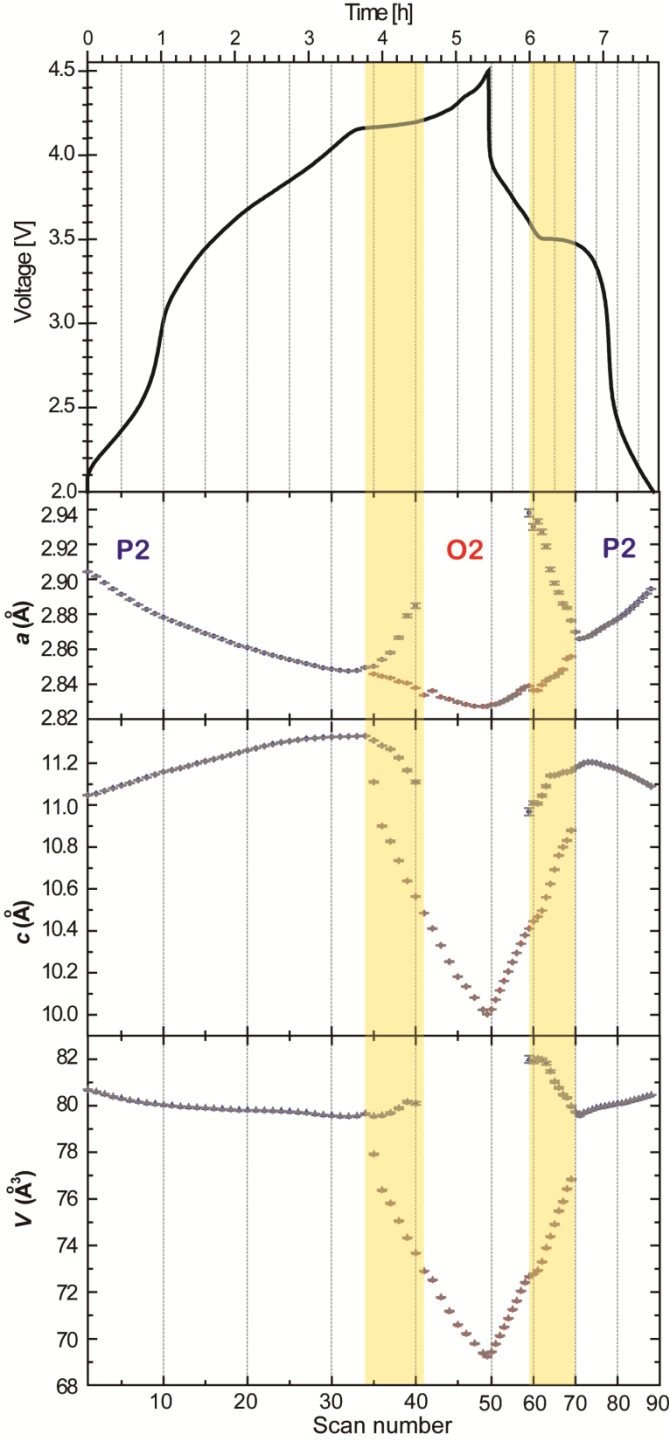
In situ synchrotron XRD patterns of the P2-$Na_{0.7}Fe_{0.4}Mn_{0.4}Co_{0.2}O_2$ electrode while a sodium ion battery capillary cell was charged at a current of 2 μA to 4.5 V and discharged at a current of 4 μA to 2.0 V.

Structural changes during sodiation/de-sodiation

Variation in unit cell parameters and phase evolution of P2-$Na_{0.7}Fe_{0.4}Mn_{0.4}Co_{0.2}O_2$ electrode from *in situ* synchrotron XRD patterns.



Crystal structures of the P2 and O2 phases



Young Hwa Jung , Ane S. Christiansen , Rune E. Johnsen , Poul Norby , and Do Kyung Kim *Adv. Funct. Mater.* **25** (2015) 3227-3237

Future research directions

Building better batteries; strengthen the battery research at DTU.

Go smaller… Micro batteries. *In situ* diffraction and ptychography tomography studies of single (or few) electrode crystals.

Develop methods for *in situ* neutron diffraction studies.

Contribute to the development of the DANMAX beamline at MAX IV.

Utilizing NANOMAX and other new research facilities at MAX IV.

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SEVENTH FRAMEWORK PROGRAMME