Probing the lithium/electrolyte distribution in Li-ion batteries by diffraction techniques

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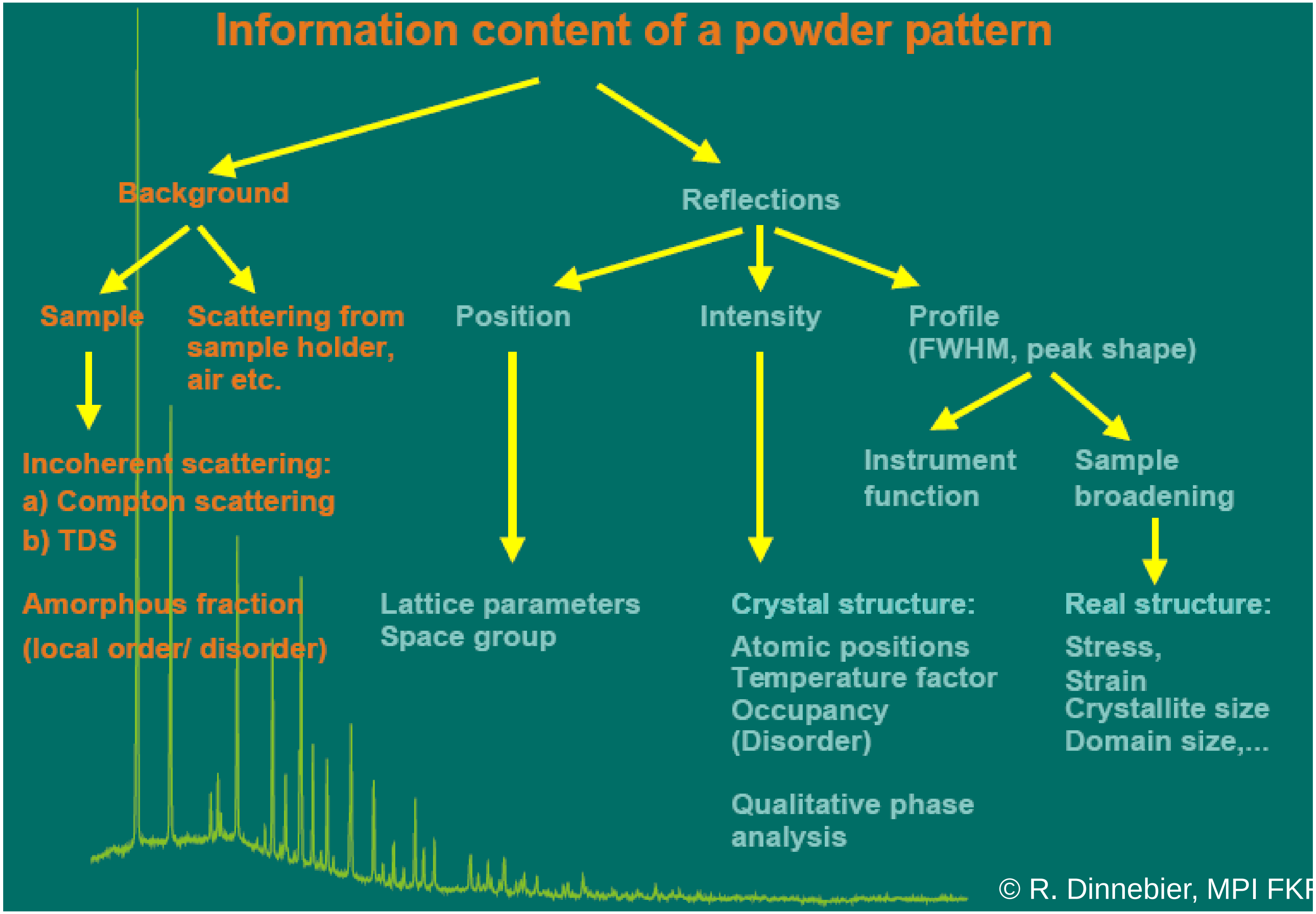
Information content of a powder pattern
Background
Reflections
Sample
Scattering from sample holder, air etc.
Position
Intensity
Profile (FWHM, peak shape)
Instrument function
Sample broadening
Incoherent scattering:
a) Compton scattering
b) TDS
Amorphous fraction
(local order/ disorder)
Lattice parameters
Space group
Crystal structure:
Atomic positions
Temperature factor
Occupancy
(Disorder)
Qualitative phase analysis
Real structure:
Stress,
Strain
Crystallite size
Domain size,...
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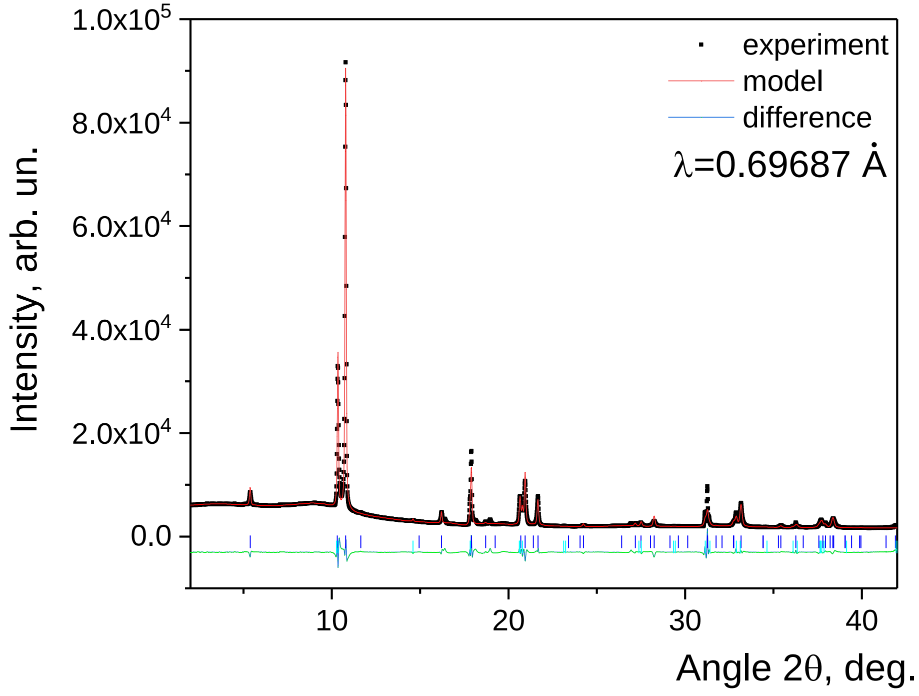
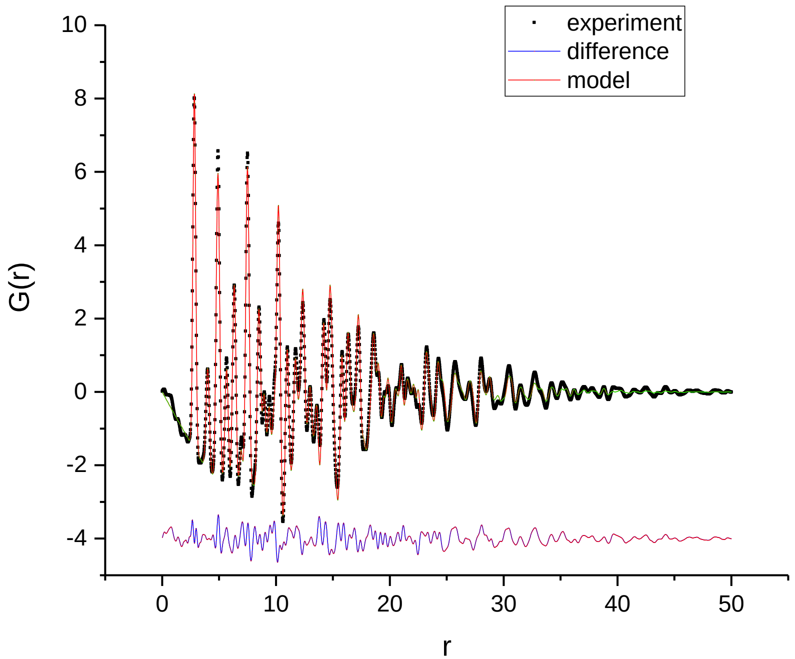
Analysis of diffraction data

Rietveld method

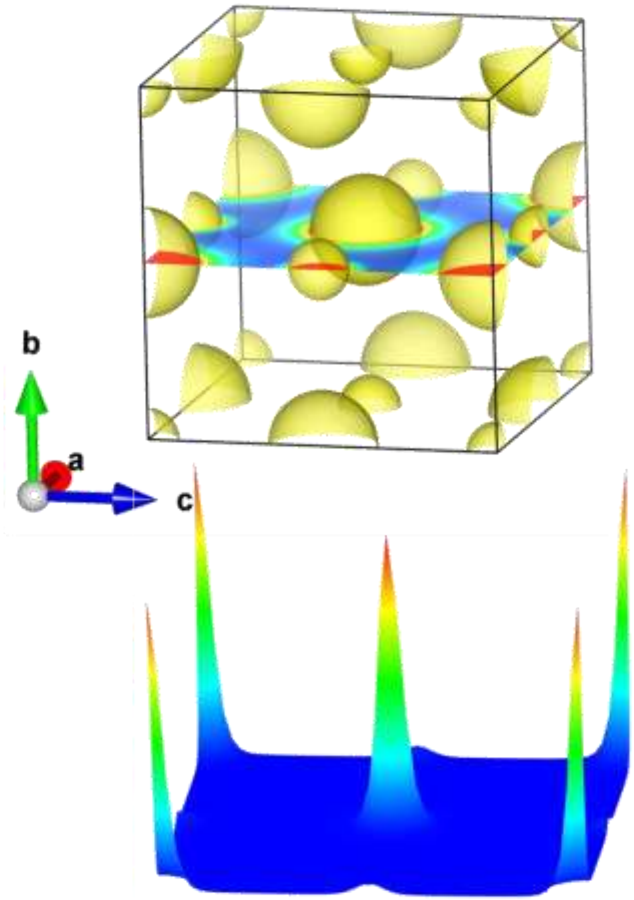


Pair distribution function analysis

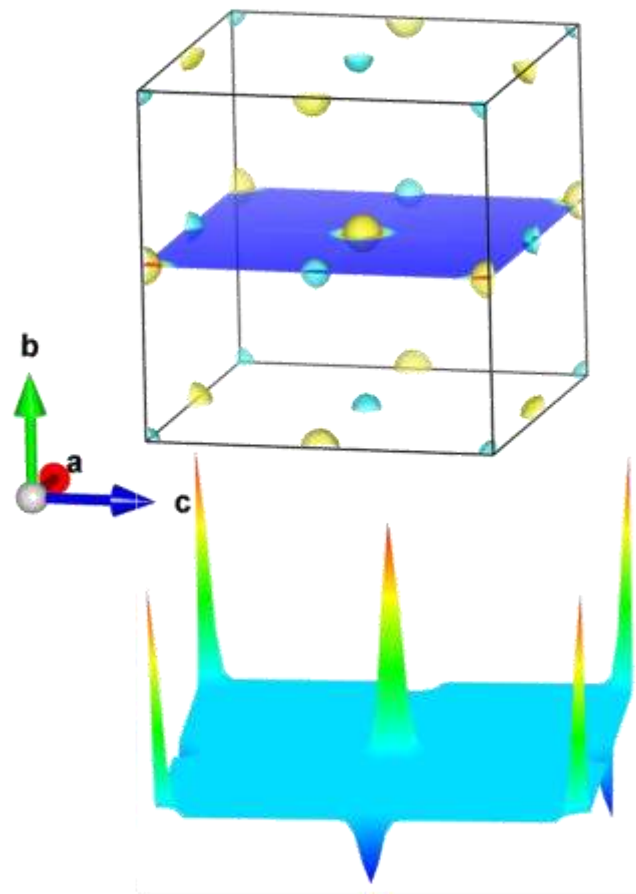


Electron vs. Nuclear densities
(X-ray vs. Neutron diffaction)

Simulated electron densities

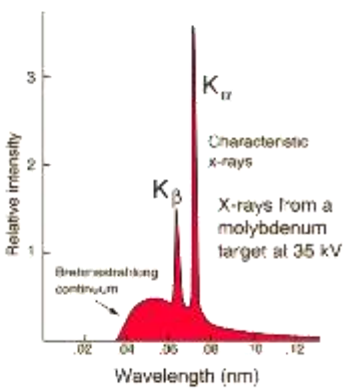


Simulated nuclear densities

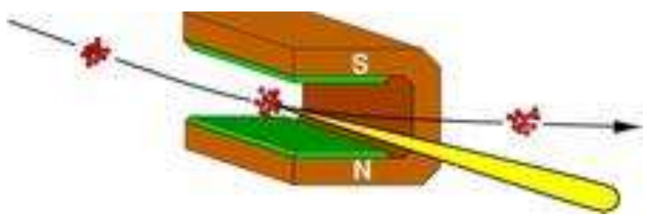


Sources of radiation

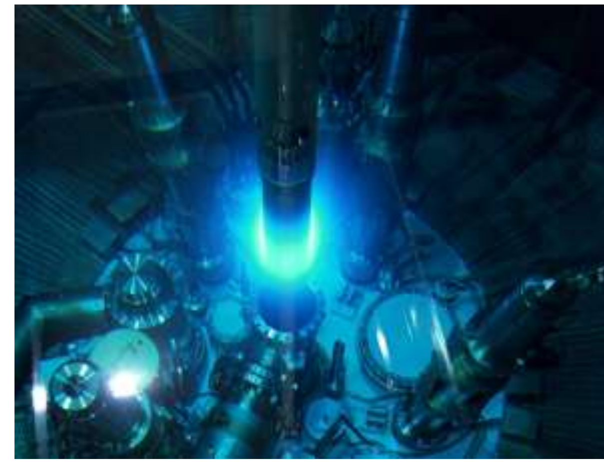
Laboratory X-ray

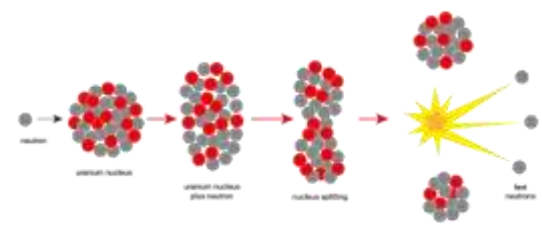


Synchrotron source



Neutron source





Use of X-ray diffraction for battery applications

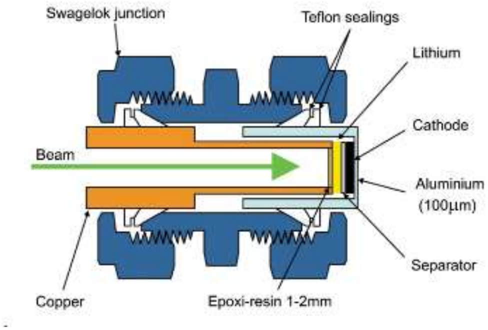
- X-ray diffraction studies of battery materials and components
- In-operando studies of complete batteries

Types of in situ electrochemical cells for X-ray diffraction

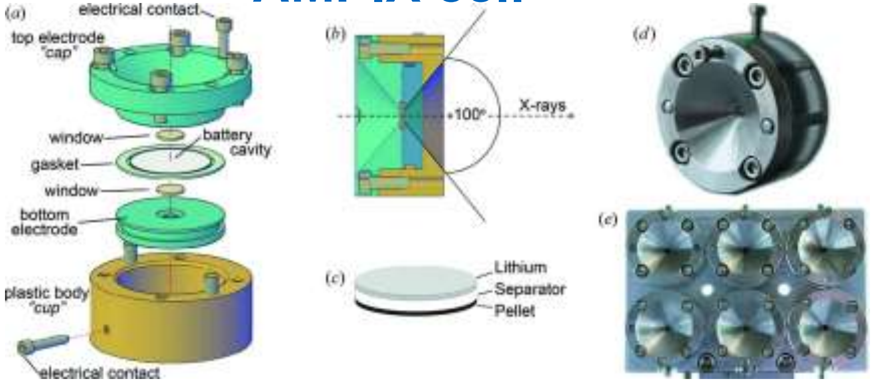
Rigaku – reflection cell

Coin cell with window

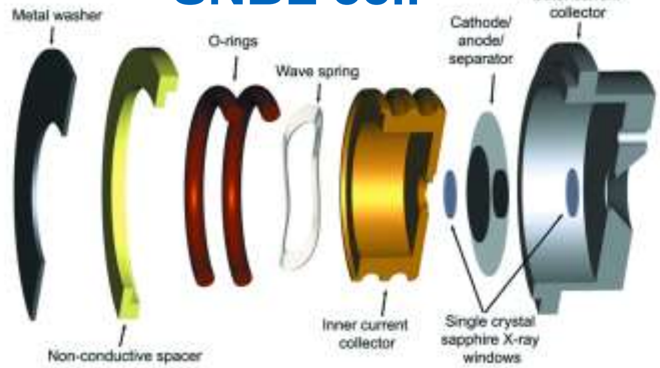
Swagelok cell



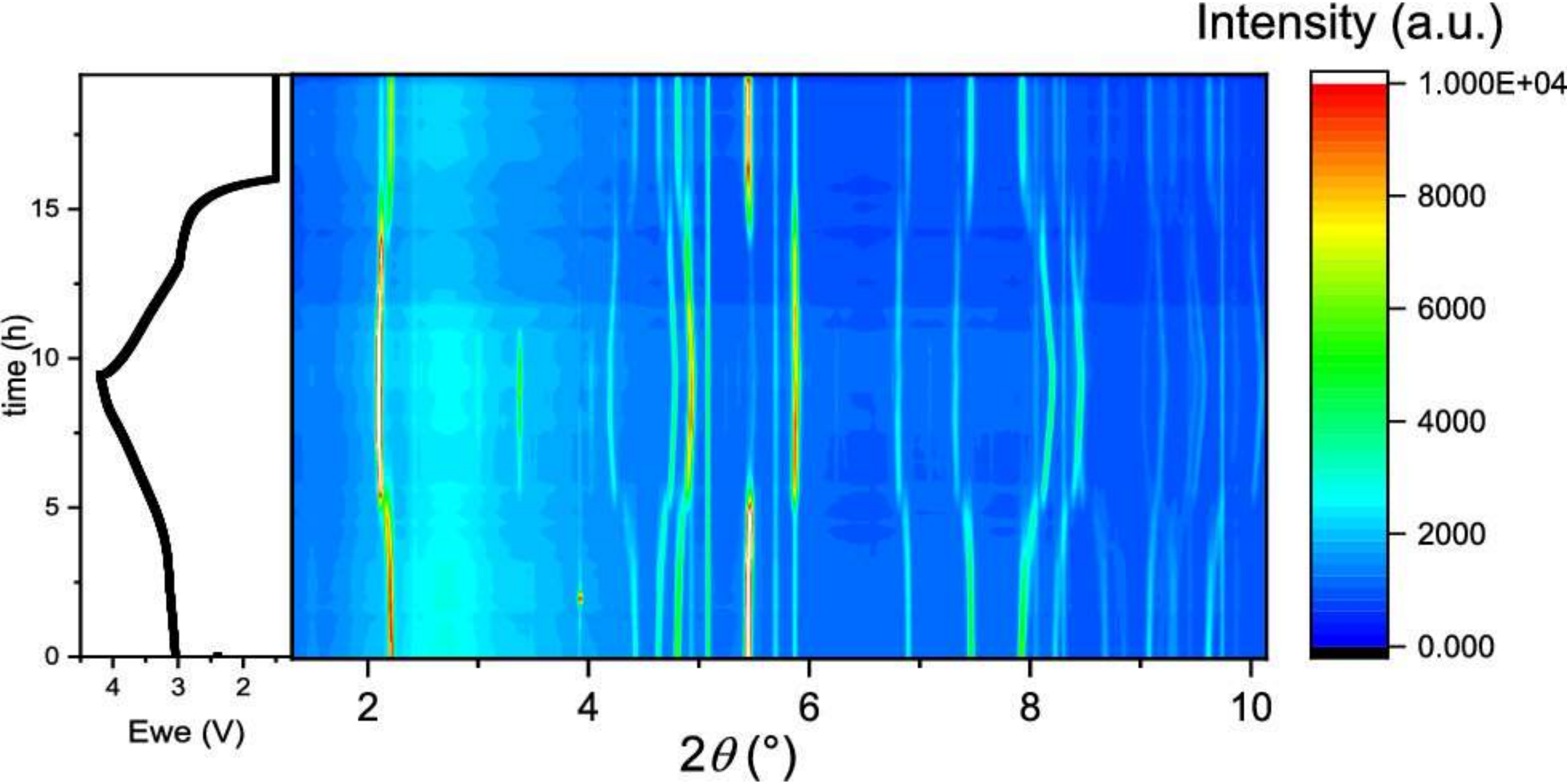
AMPIX cell



SNBL cell



Example of in situ diffraction studies



Courtesy: D. Mikhailova; Evolution of $NaNi_{0.5}Ti_{0.5}O_2$ structure, NNTO+NiO+Na+Al present to pattern

Advantages of neutron scattering

The energy of thermal neutrons is in range of meV → Neutrons weakly perturb the experimental system, i.e. non-destructive.

Neutrons are deeply penetrating into the matter → Studies of bulk samples or processes under realistic conditions (in complex environments).

Neutrons interact with nucleous (strong force interaction) → Neutrons can localize light atoms (e.g. hydrogen, lithium) in the presence of heavier ones and to distinguish isotopes (additional contrast) and neighboring elements from Periodic Table. Accurate Debye-Waller (displacement parameter) determination.

The wavelength of thermal neutrons is similar to interatomic spacings. Neutron scattering length not depending on momentum transfer ($\sin(\theta)/\lambda$). → Details of the crystal structure. Studies of bulky samples – better particle average. Accurate lattice parameters and atomic coordinates, effects of microstructure.

Neutron-based experimental techniques with proven relevance in battery research

Neutron diffraction: detail of crystal structure, localisation and quantification of lithium; microstructural studies; phase analysis.

Neutron imaging: lithium distribution, gas formation, electrolyte dynamics;

Small-angle neutron scattering: in-situ materials morphology and fracturing upon cell fatigue;

Quasielastic neutron scattering: in-situ structure and mobility of electrolytes in Li-ion batteries;

Reflectometry: studies of solid-electrolyte interphase; studies of lithiation in amorphous silicon; solid-liquid interfaces;

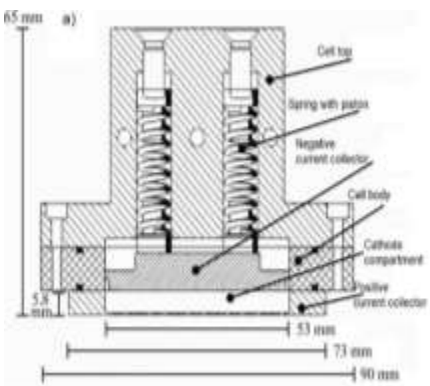
Neutron depth profiling: nanometer sensitive probe of lithium concentration in electrode materials;

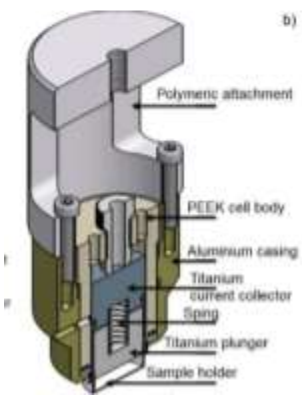
Positron spectroscopy: charge- and fatigue-induced defect formation;

Neutron and Prompt gamma activation analysis: non-destructive and simultaneous elemental/isotope analysis;

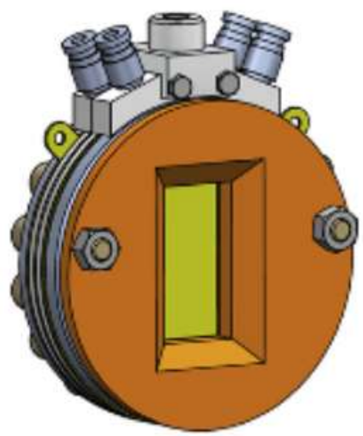
Types of in situ electrochemical cells for neutron diffraction

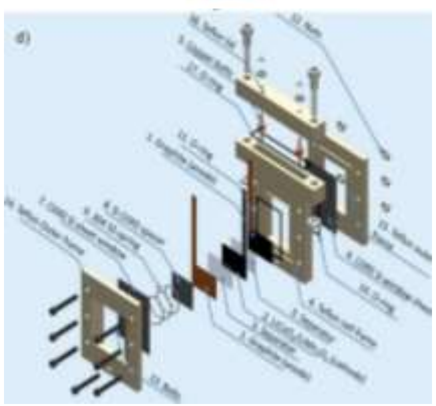
Reflection cells



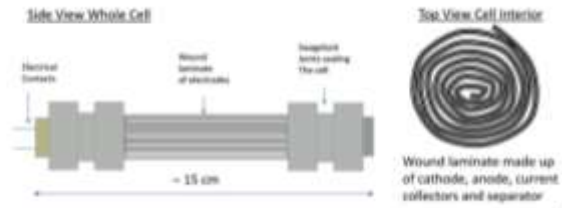


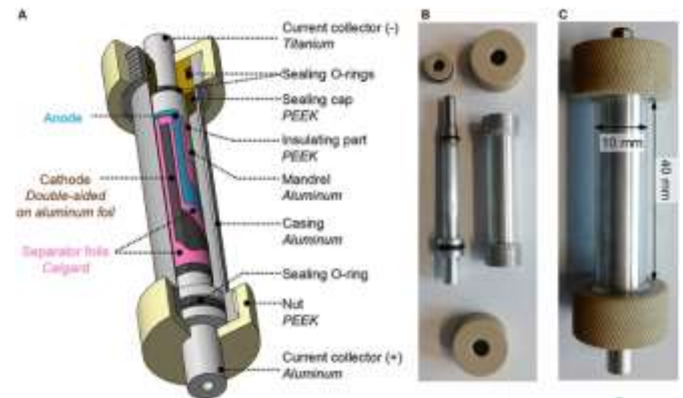
Flat transmission cells



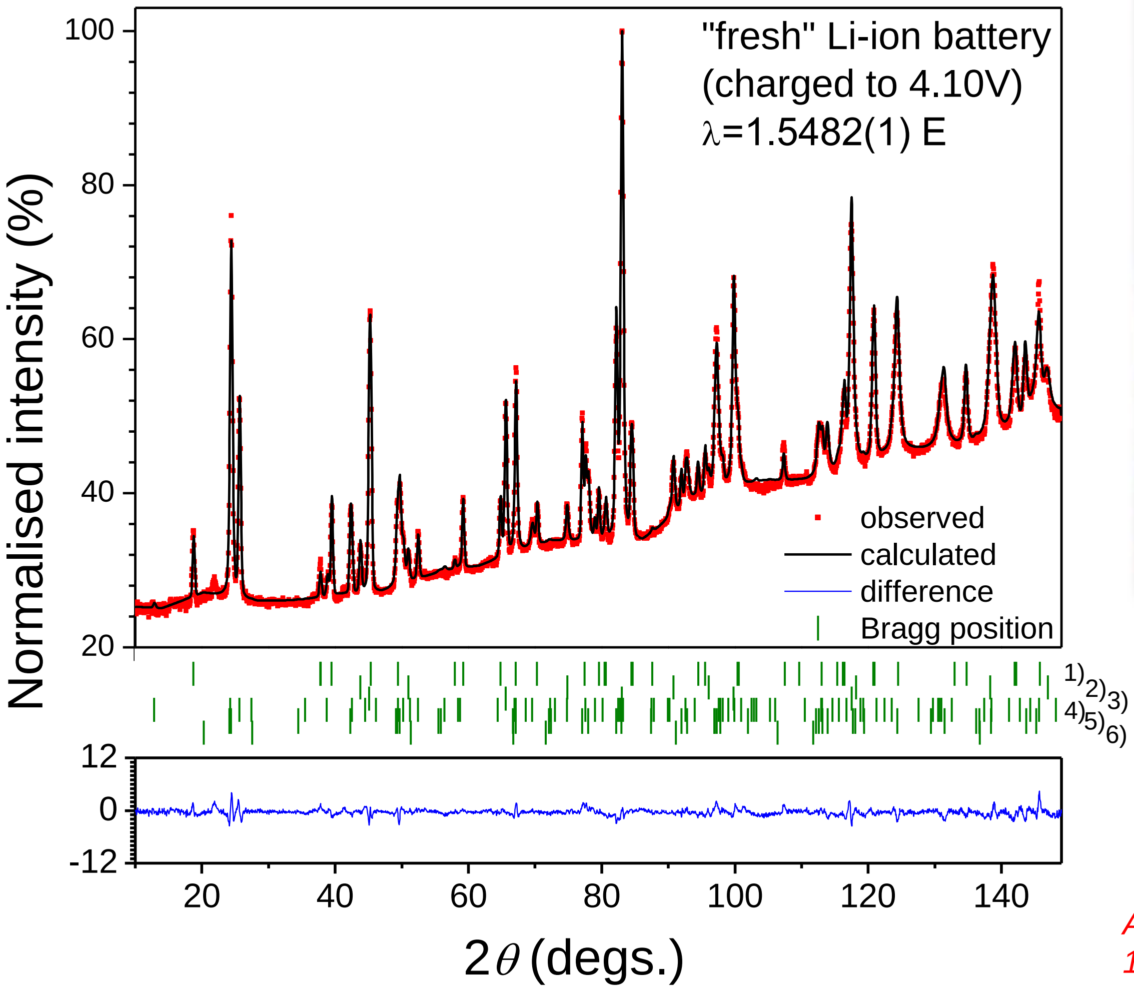


Wound/cylinder cells





Rietveld refinement of typical diffraction pattern for 18650 Li-ion battery

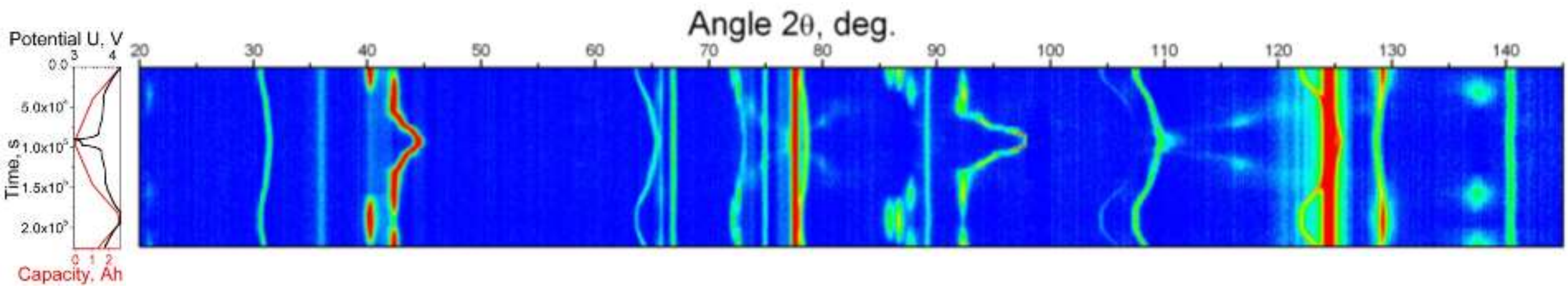


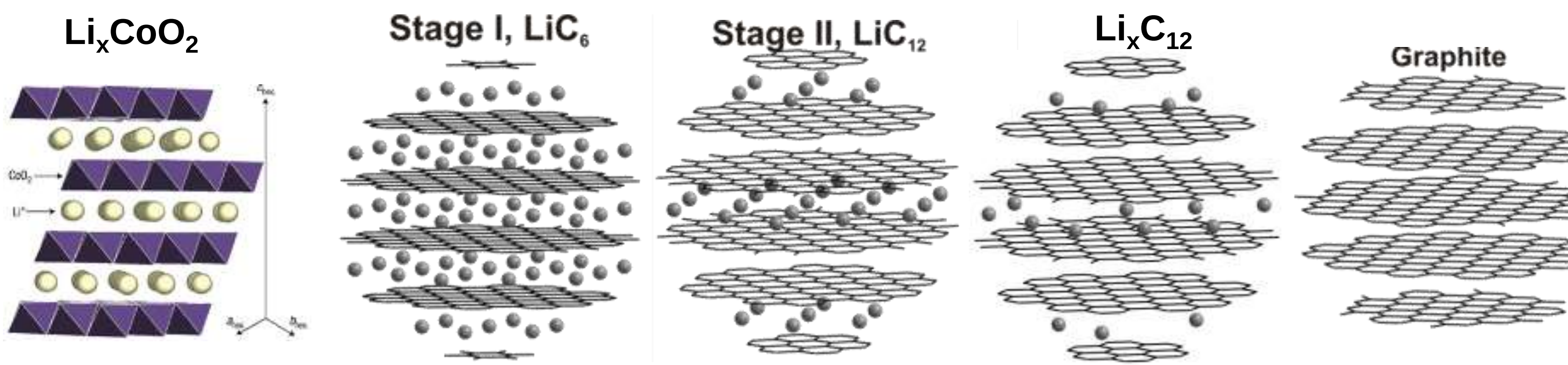
$LiCoO_2$ (1)
Cu (2)
Fe (3)
LiC_{12} (4)
LiC_6 (5)
Al (6)

Beam size:
40x25 mm^2
2θ range:
0-160°

A. Senyshyn et al., J. Power Sources 203 (2012) 126-129.

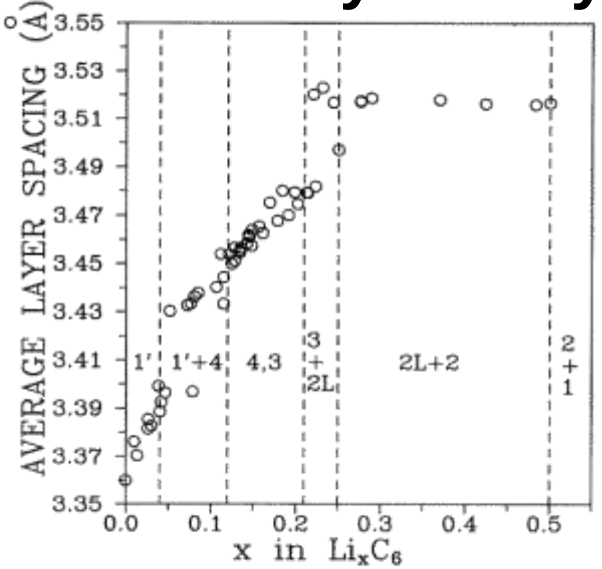
Evolution of diffraction data vs. Electrochemical treatment

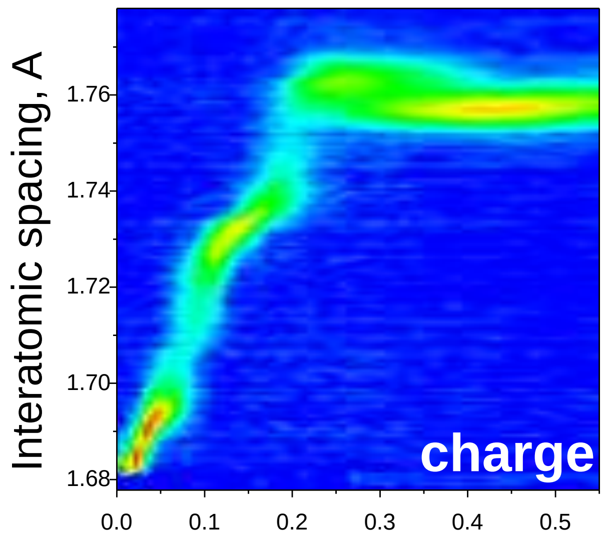


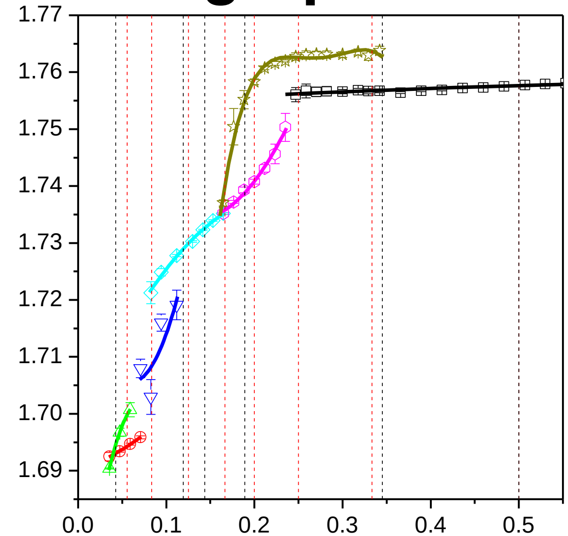


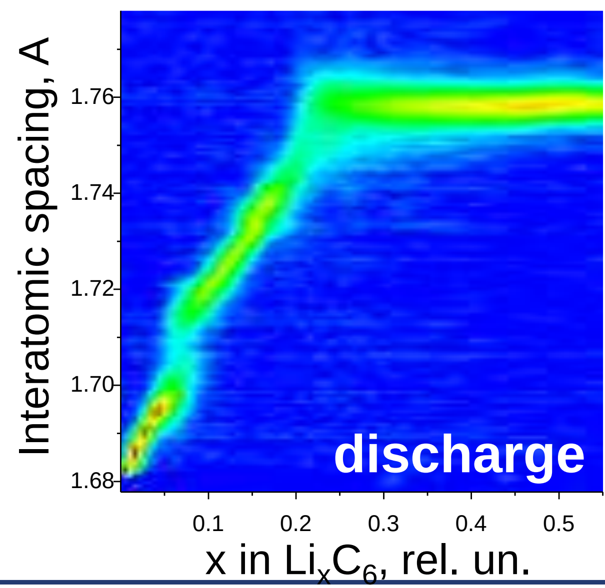
A. Senyshyn et al. J. Electrochem. Soc. 160(5) (2013) A3198-A3205

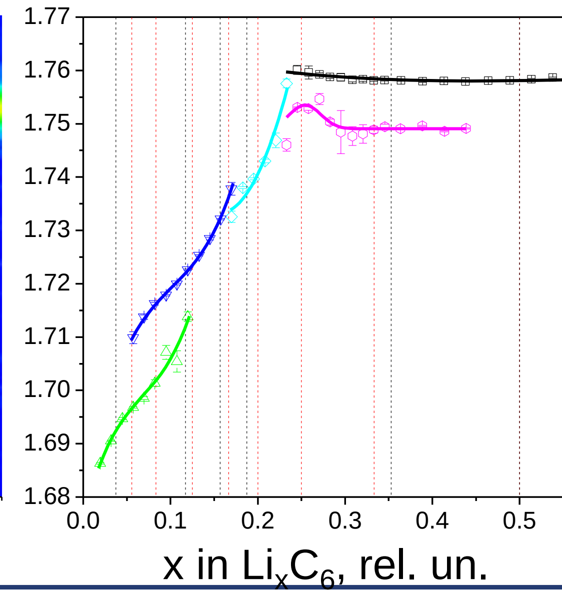
Phase asymmetry in the lithium intercalated graphites











J.R. Dahn, Phase diagram of Li_xC_6, Phys. Rev. B 44(17) 9170-9177 (1991).

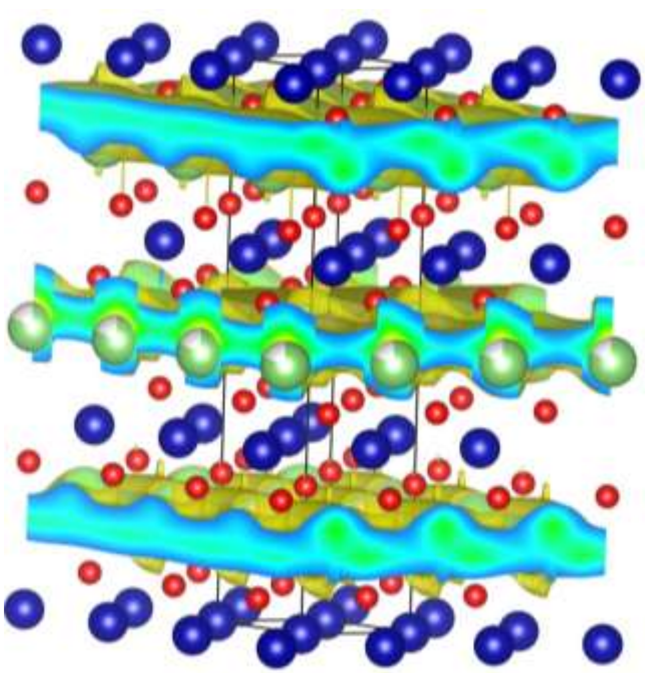
T. Ohzuku, Y. Iwakoshi, K. Sawai, Formation of Lithium-Graphite Intercalation Compounds in Nonaqueous Electrolytes and Their Application as a Negative Electrode for a Lithium Ion (Shuttlecock) Cell , J. Electrochem. Soc., 140(9) 2490-2498 (1993).

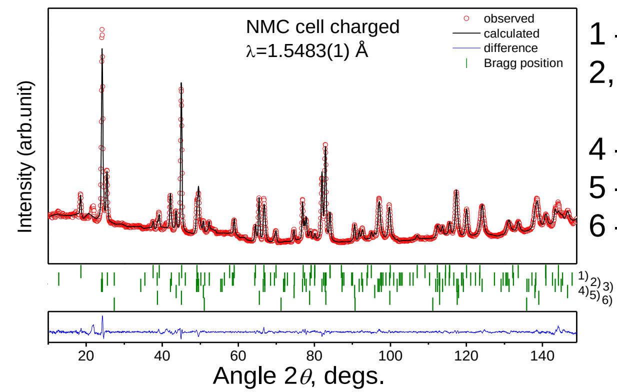
In-situ probe of cation mixing in NMC-type cathode

The $LiCoO_2$ has a high energy density, but cobalt is expensive and reactive …

The NMC materials - $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ or $Li(Ni_{0.5}Mn_{0.3}Co_{0.2})O_2$ are used as an alternative

Distorted rock-salt structure





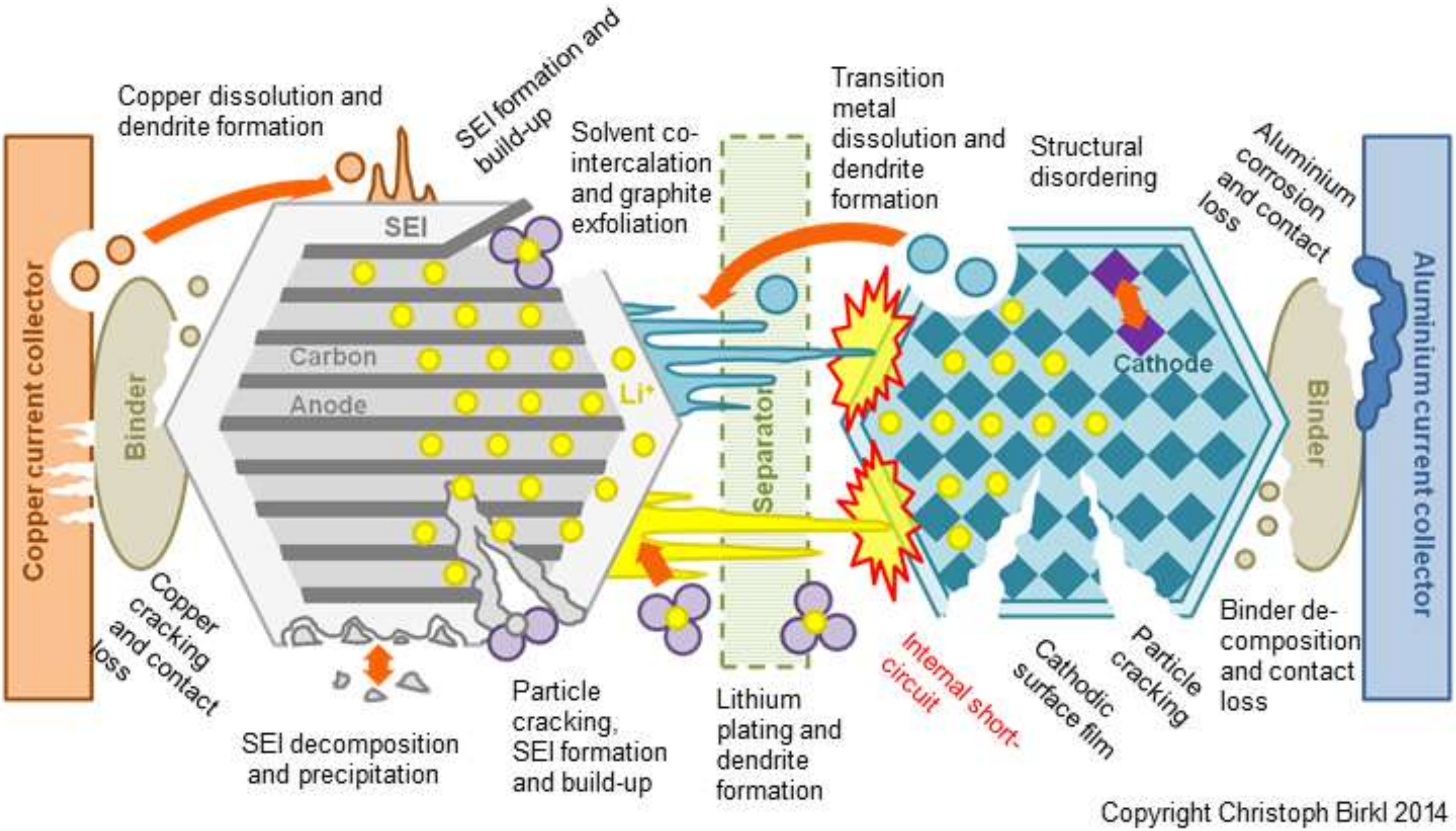
1 – cathode $Li_x(Ni_{0.5}Mn_{0.3}Co_{0.2})O_2$;
2, 3 – lithium intercalated carbons LiC_{12} and LiC_6 respectively;
4 – copper current collector;
5 – aluminum current collector;
6 – steel housing.

O. Dolotko et al., J. Power Sources 255 (2014) 197-203

Obtained structural parameters

Cell capacity, mAh	Li site occupancy x_{Li}, frac. un.		R_p, R_{wp}, χ^2
	Li1 (3a)	Li2 (3b)	
0	0.77(3)	0.054(6)	1.10 1.42 5.70
1200	0.52(5)	0.047(8)	1.10 1.43 5.10
1400	0.48(4)	0.060(8)	1.02 1.36 4.58
1600	0.53(4)	0.063(8)	1.05 1.35 4.00
1800	0.42(4)	–	1.07 1.38 5.35
2000	0.34(4)	–	1.08 1.38 5.34
2237	0.26(3)	–	1.14 1.48 6.01

Different mechanisms of Li-ion battery degradation

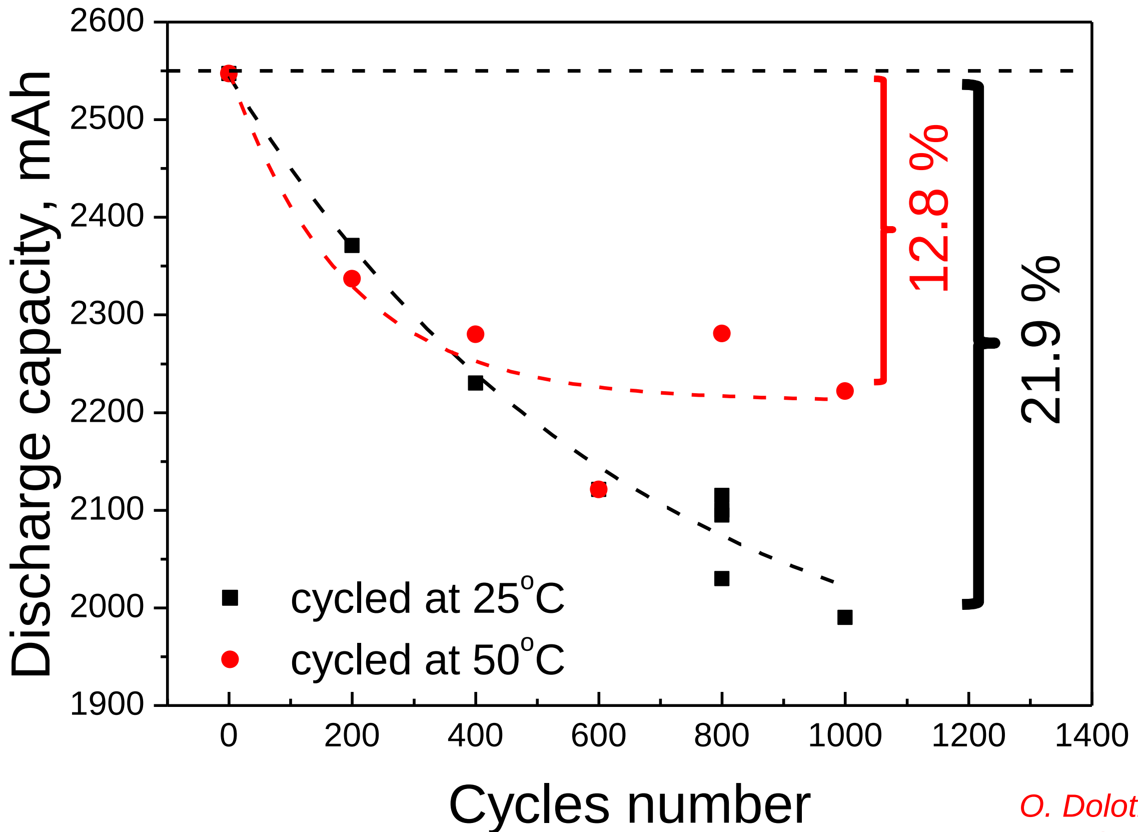


Fatigue Li-ion batteries: an experimental study

Two batches of Li-ion cells purposefully and rapidly cycled (CCCV, 1C)

•„fresh“ – single cycle for testing purposes

•cycled at 25ºC and 50ºC - 200, 400, 600, 800 and 1000 times

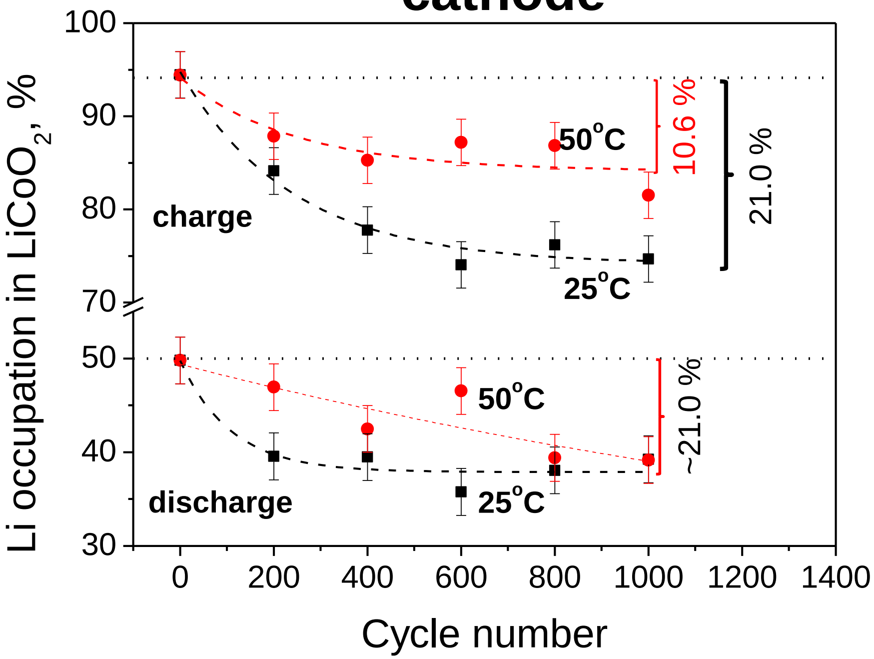


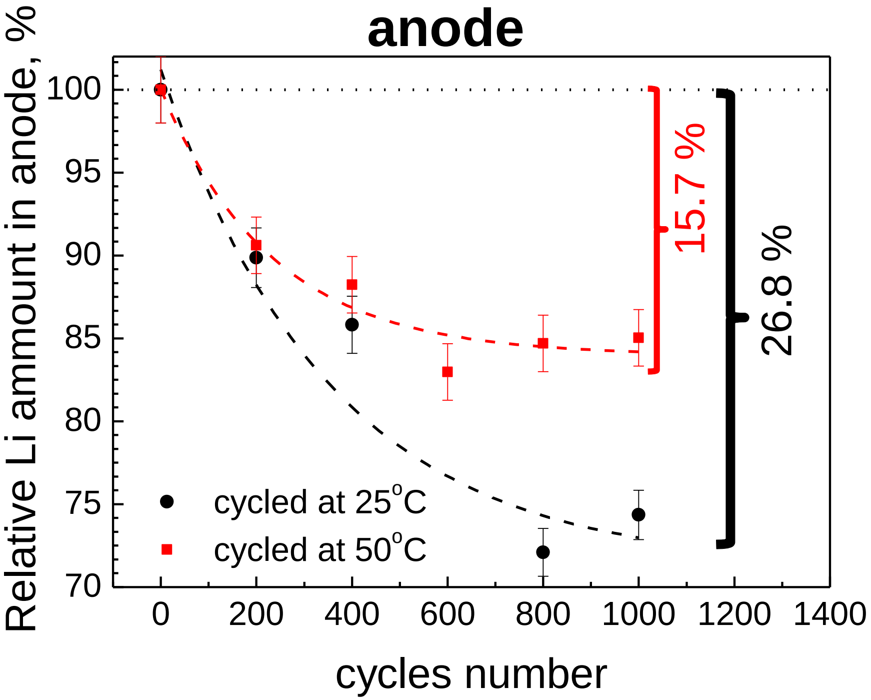
O. Dolotko et al., J. Electrochem. Soc. 2159(12) (2012) A2082-A2088

Fatigue of battery: crystal structure

Possible reasons: Li-plating (dendrite growth), microcracks formation in electrodes; oxidation processes and phase transformations; SEI growth; electrolyte decomposition

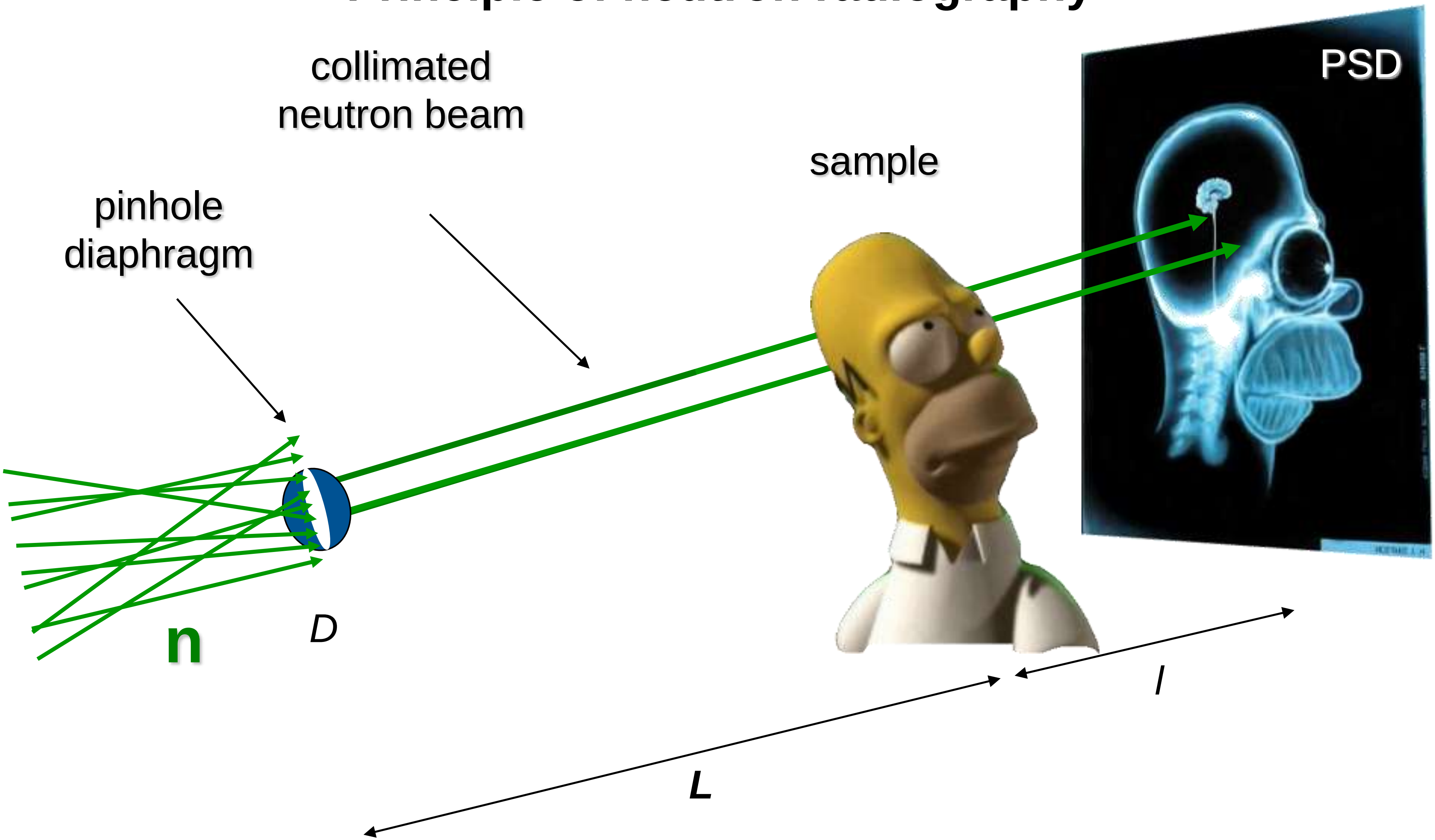
Effect on Li-concentration





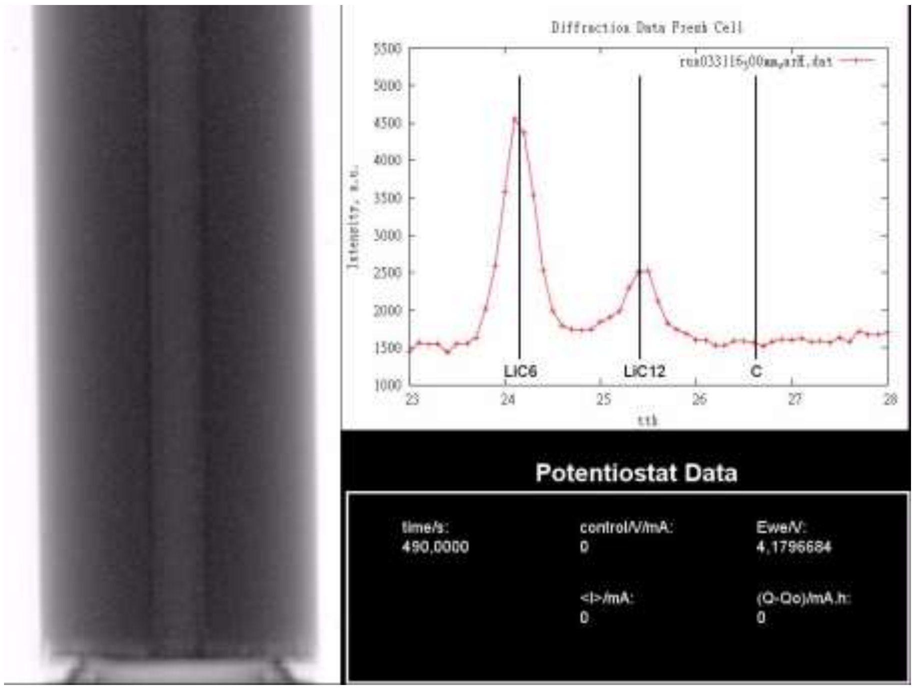
By the fatigue introduced the system looses free (transport) lithium;
Lithium loss correlate to the reduction of discharge capacity;

Principle of neutron radiography

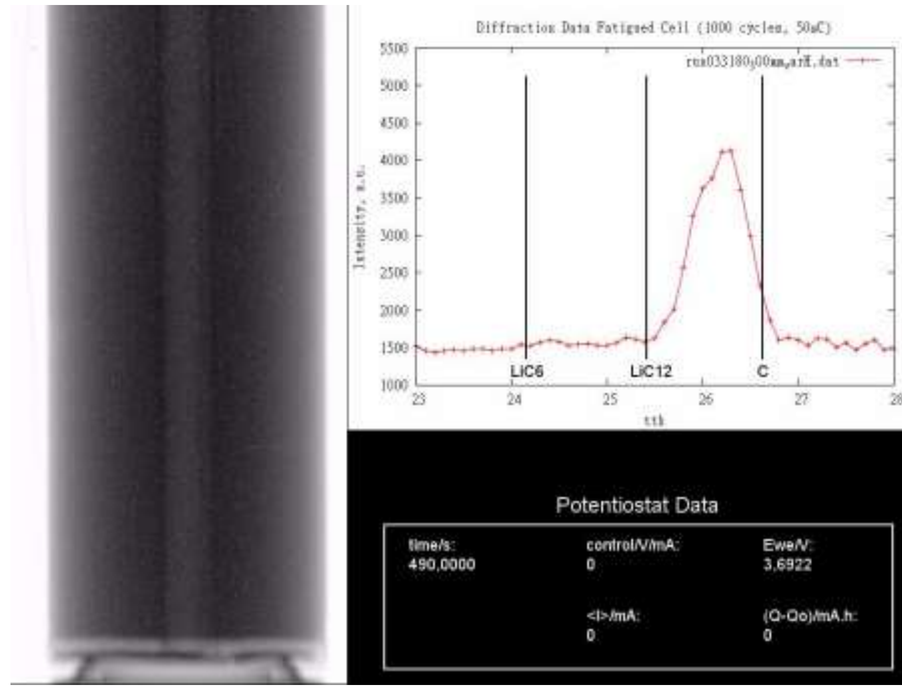


Simultaneous neutron radiography and diffraction data collection on 18650-type cell cycled up-side-down

Fresh cell



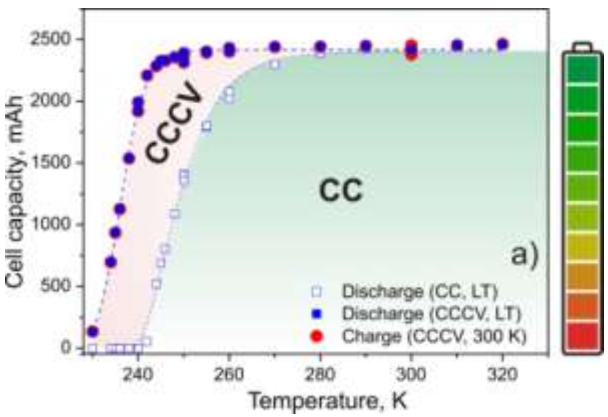
Fatigued cell



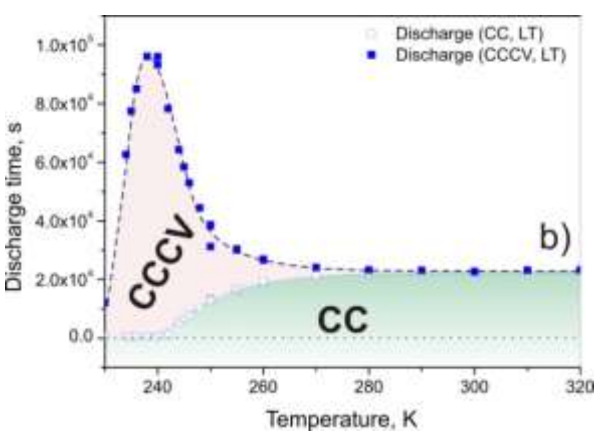
https://www.youtube.com/watch?v=ICPzHO_1nQ8

In situ structural studies on 18650-type cell at low temperatures

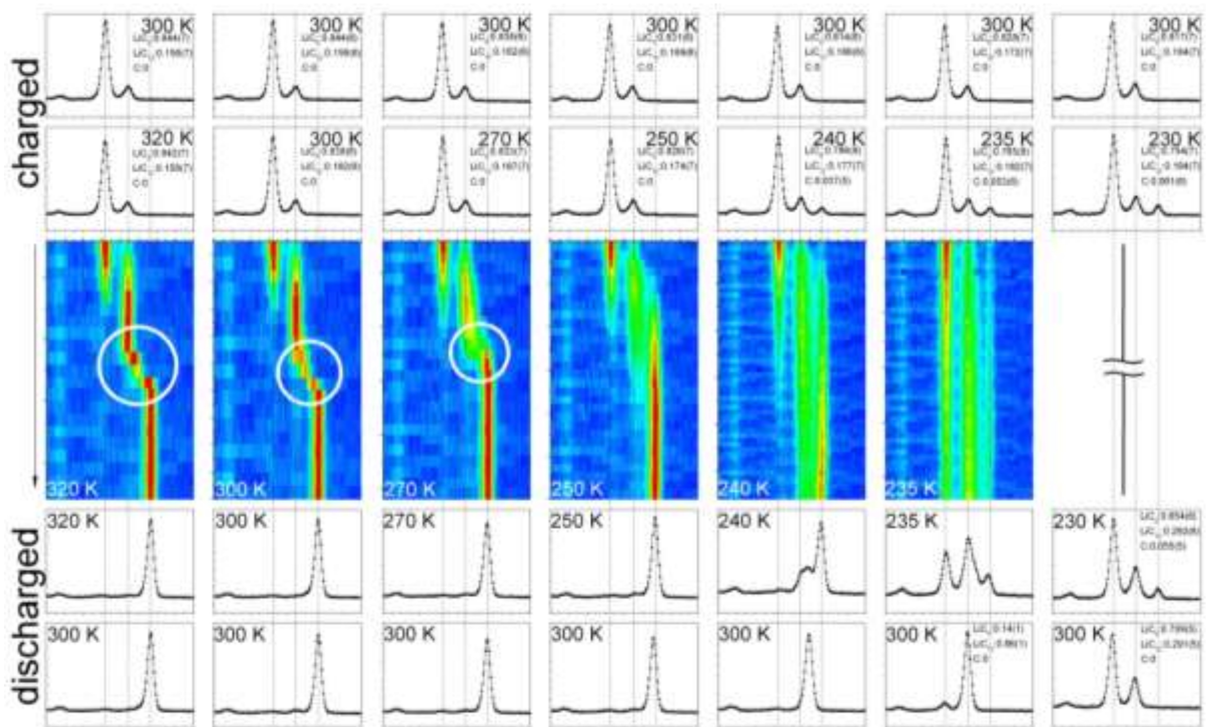
Cell capacity vs. T



Discharge time vs. T



Enlarged section of powder diffraction patterns highlighting lithium intercalation into graphite, LiC_6 (001), LiC_{12} (002) and C (002).



Towards higher capacity Li-ion batteries

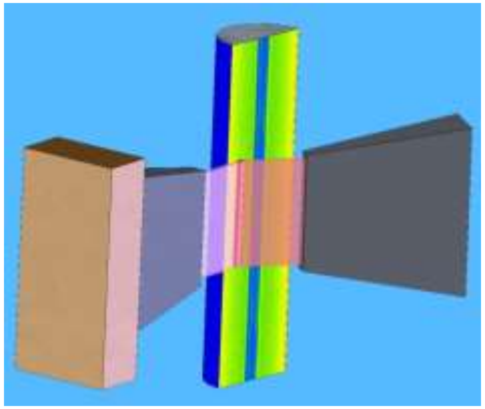
TESLA

NISSAN

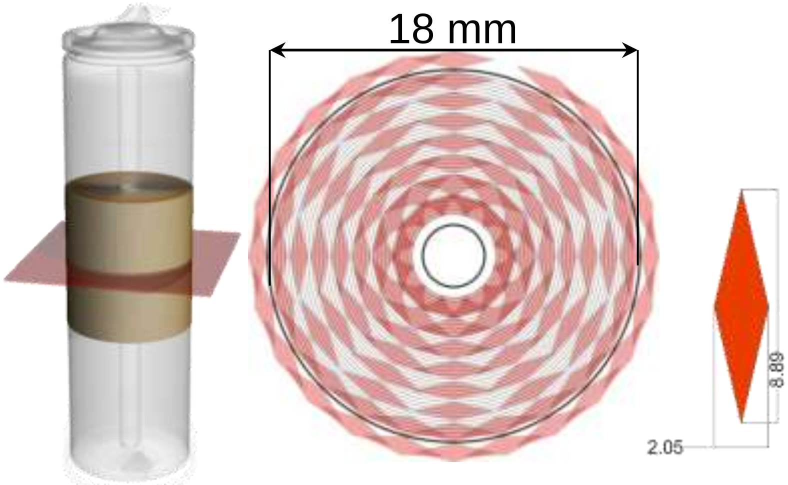
BMW

Spatially-resolved neutron powder diffraction

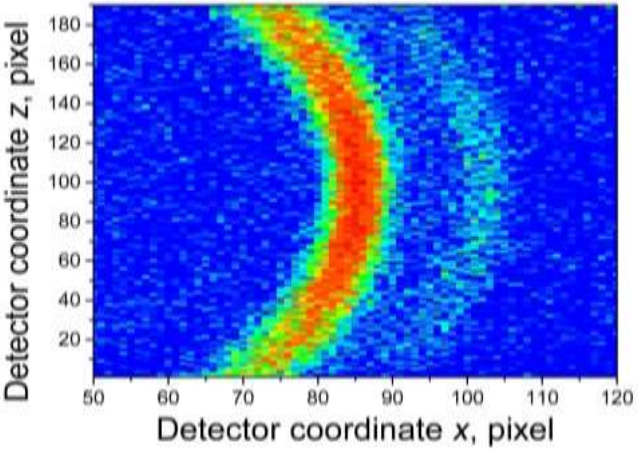
Experimental setup



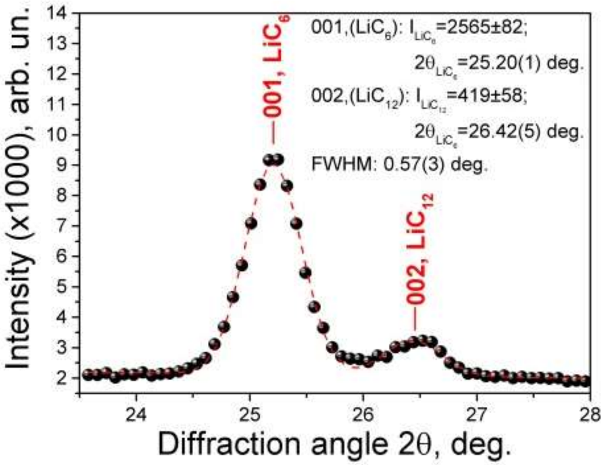
Distribution of gauge volumes



2D diffraction data

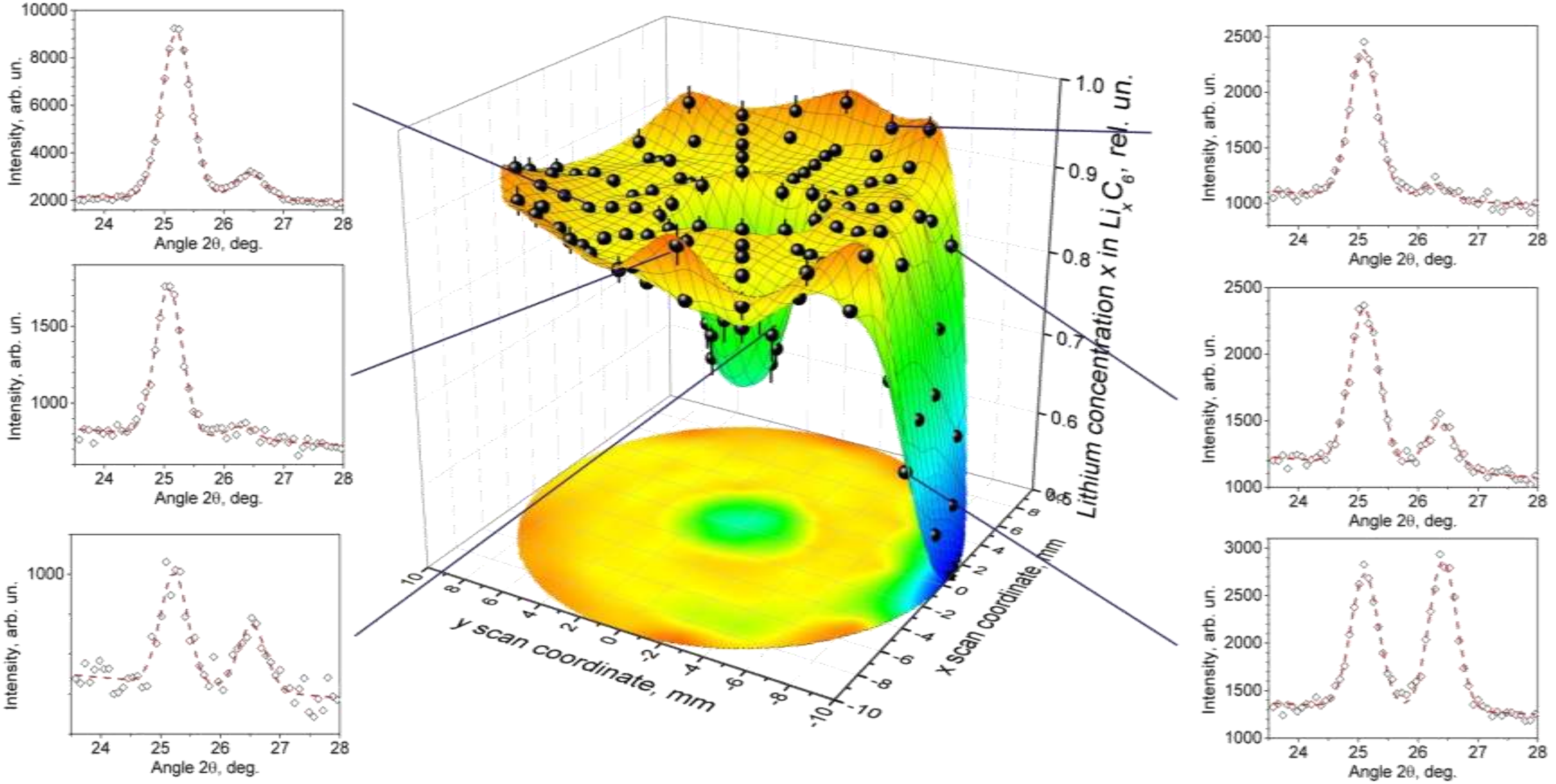


Diffraction pattern

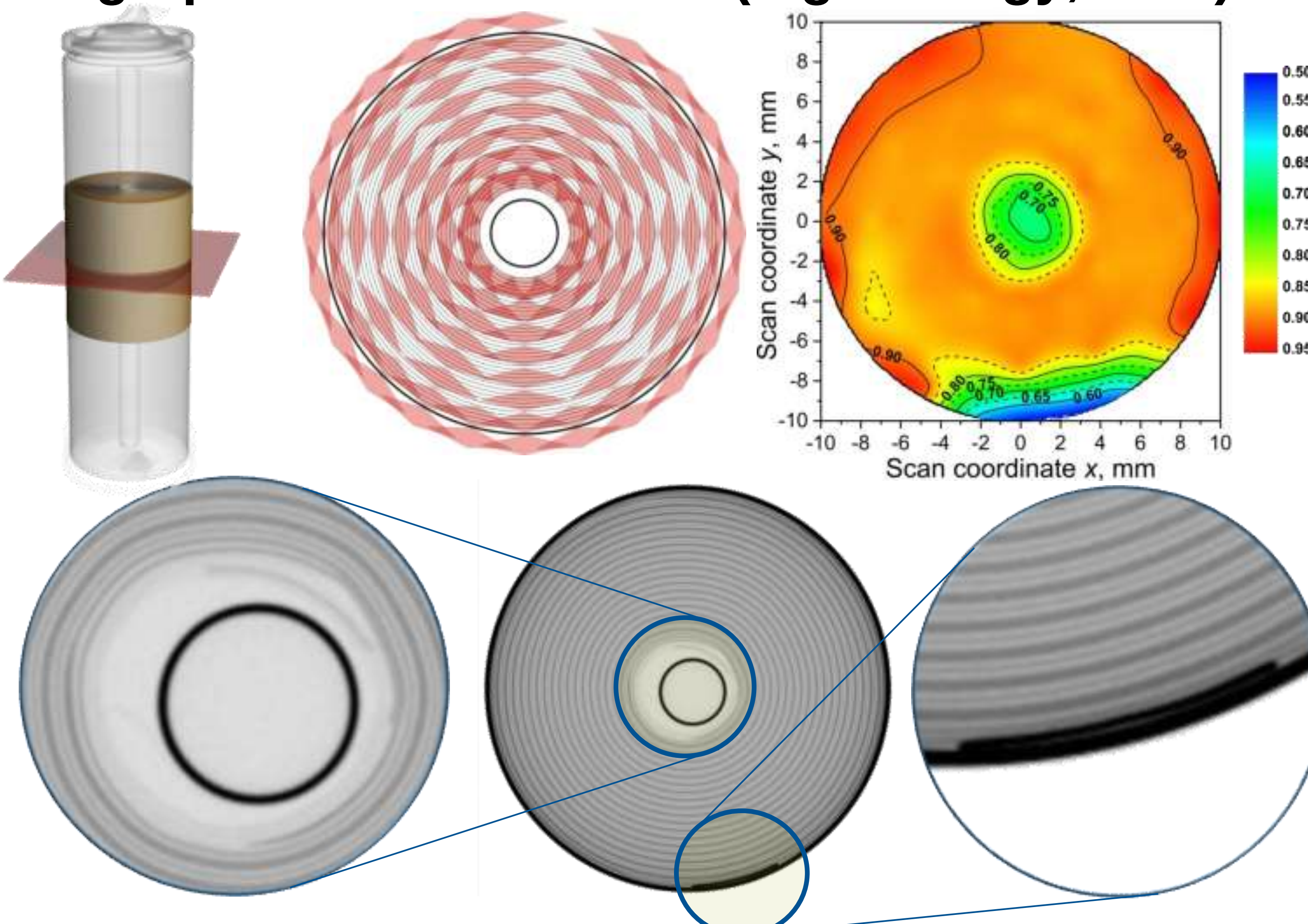


Spatial distribution of lithium concentration x (Li_xC_6) in the graphite anode of cell 1 (high energy, LCO)

Experimental data are shown by black points and surfaces in false color representation Insets illustrate obtained diffraction data at selected coordinates.

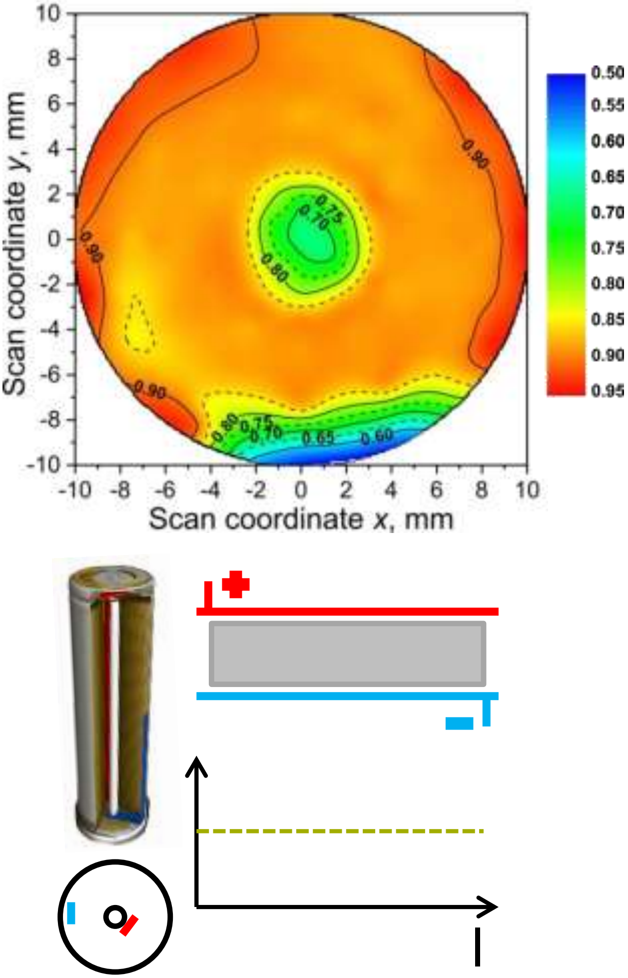


Spatial distribution of lithium concentration x (Li_xC_6) in the graphite anode of cell 1 (high energy, LCO)

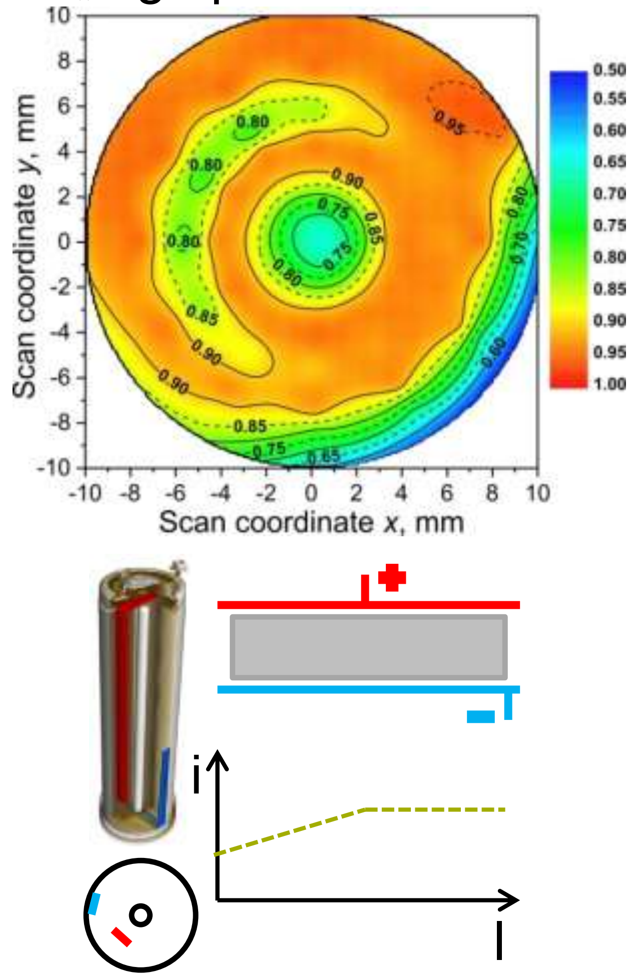


Spatial distribution of lithium concentration x (Li_xC_6) in the graphite anode of three cell

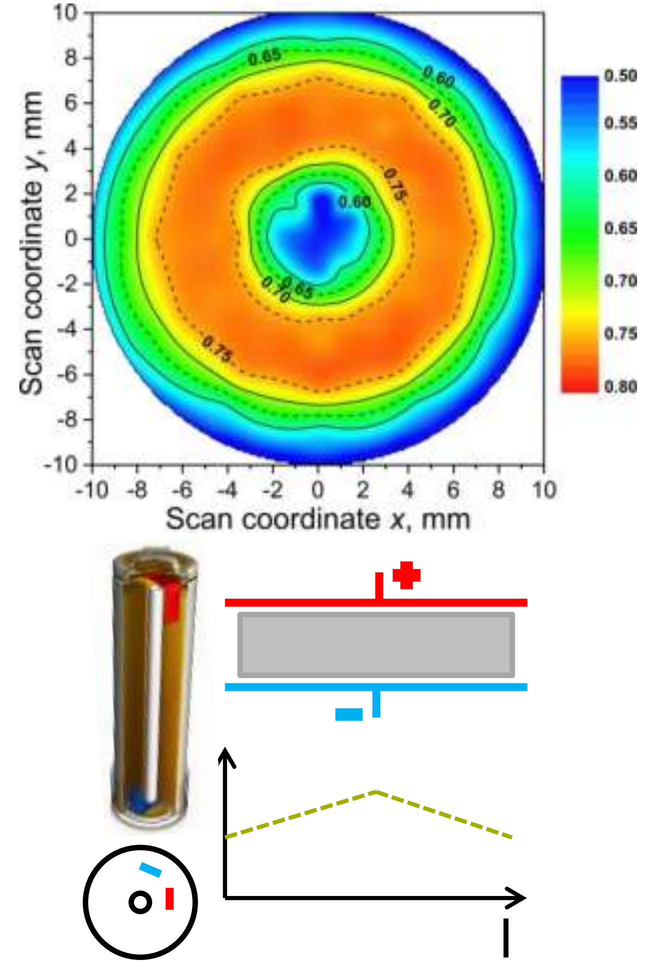
„high energy“



„high performance“



„high power“



Does cell fatigue affects the current distribution?

(cell 1, high energy, LCO)

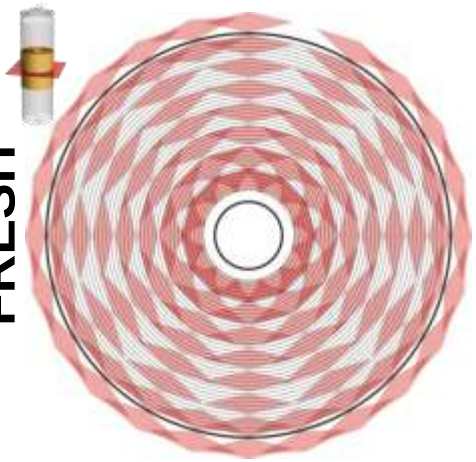
Gauge volume configuration

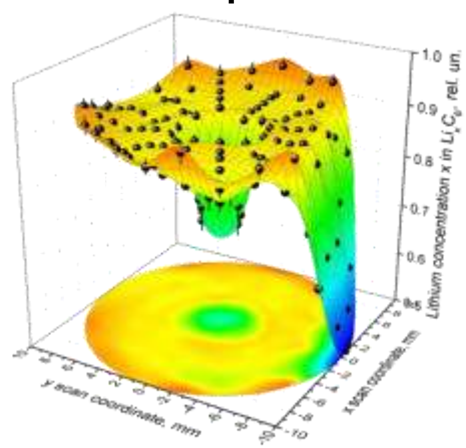
Lithium concentration x in Li_xC_6, rel. un.

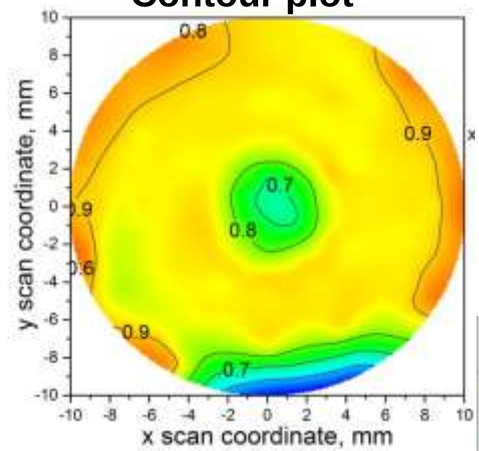
Surface plot **Contour plot**

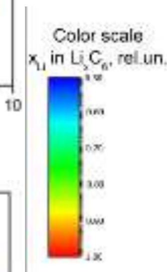
RT,
3 cycles
3.0-4.2 V
0.154C=
=400 mA
Charged, RT
0.154C=
=400 mA

FRESH



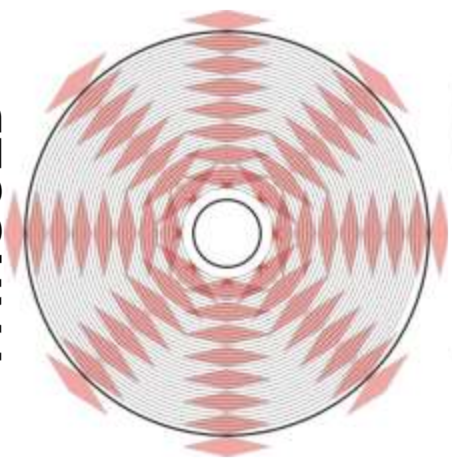


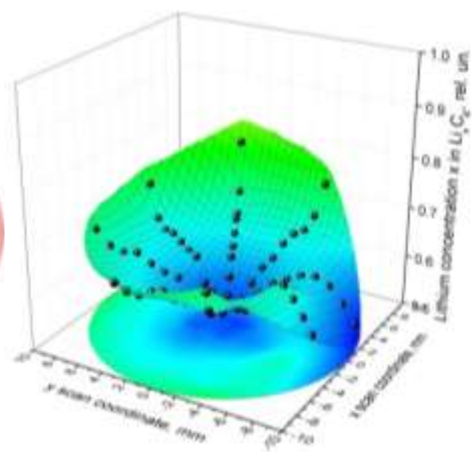


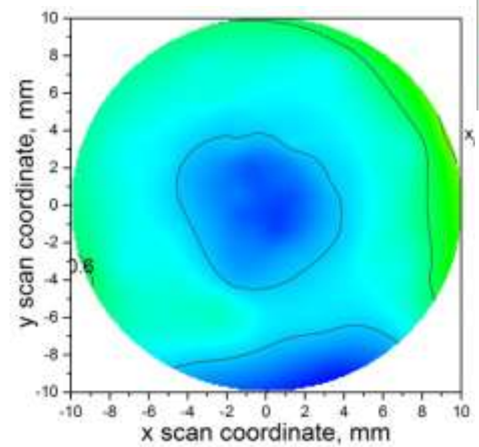


25° C,
1000 cycles
3.0-4.2 V
1C=2600 mA
Charged, RT
0.154C=
=400 mA

FATIGUED

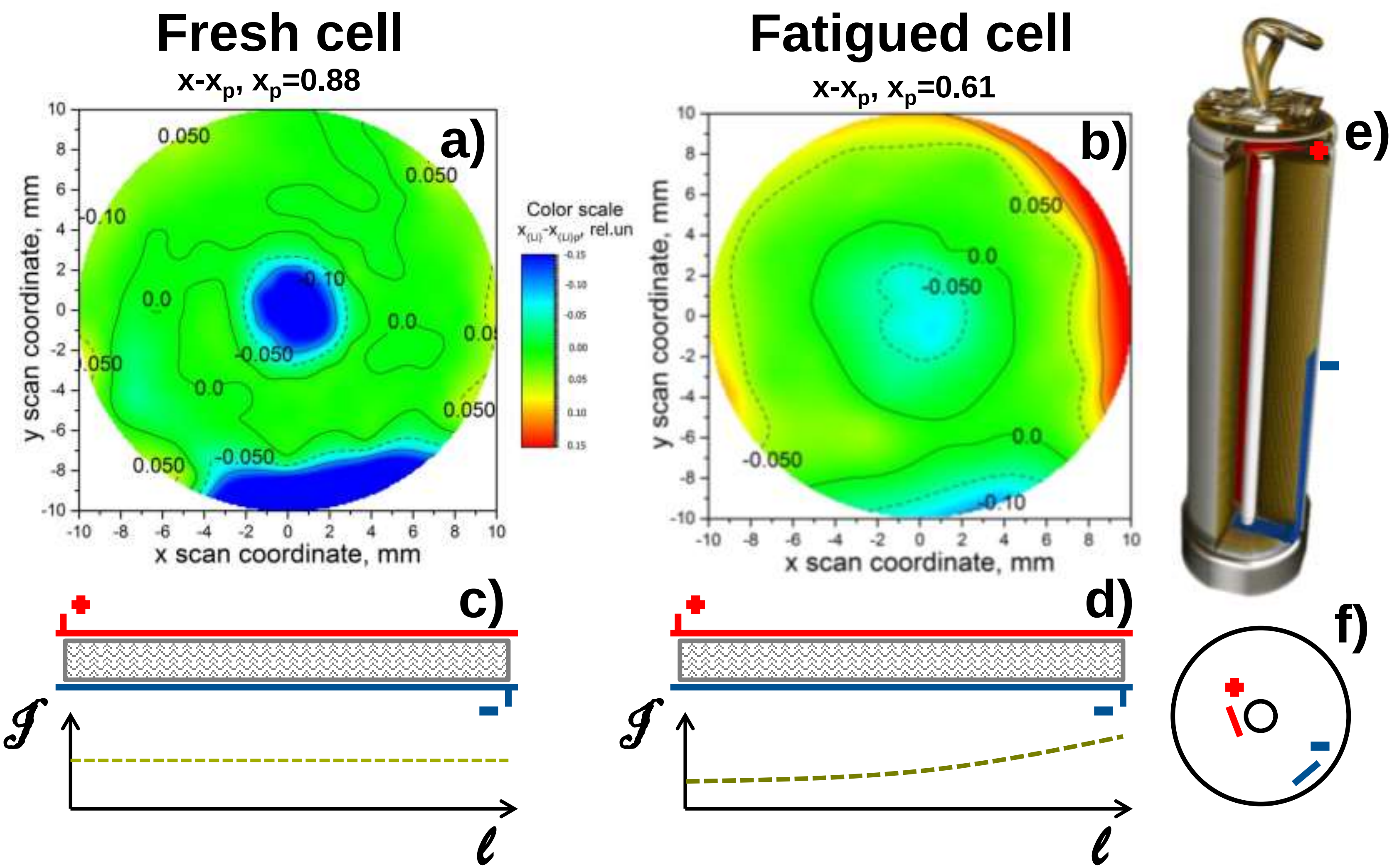






Does cell fatigue affects current distribution?

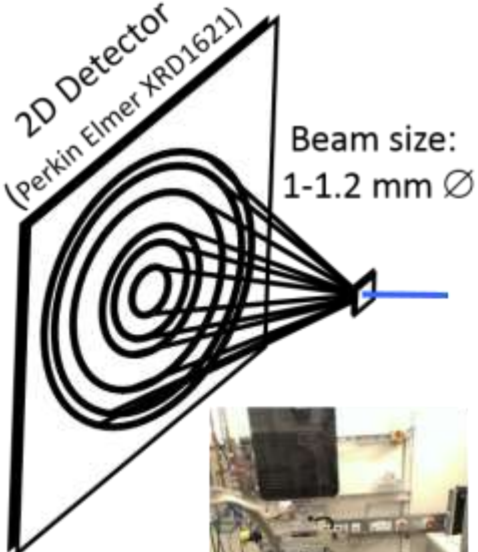
(cell 1, high energy, LCO)



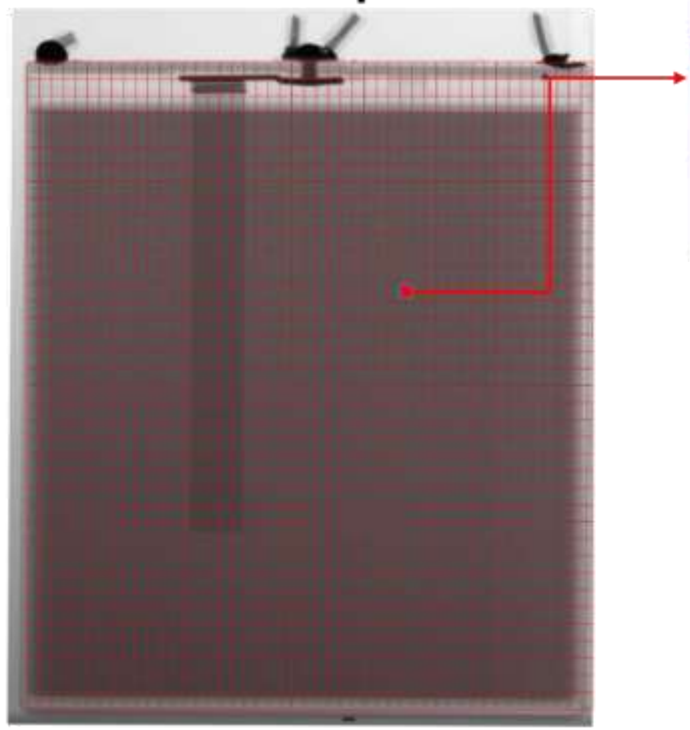
X-ray diffraction radiography

Beamline: P02.1, PETRA III synchrotron, 60 keV photon energy

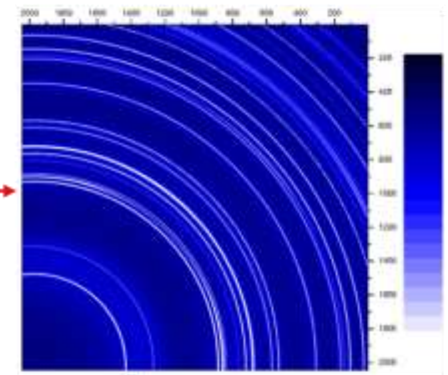
Experimental setup: sketch and photo



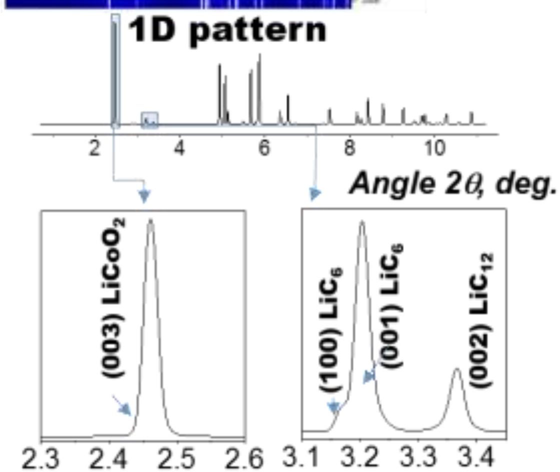
X-ray computed radiography and scanning mesh in diffraction experiment



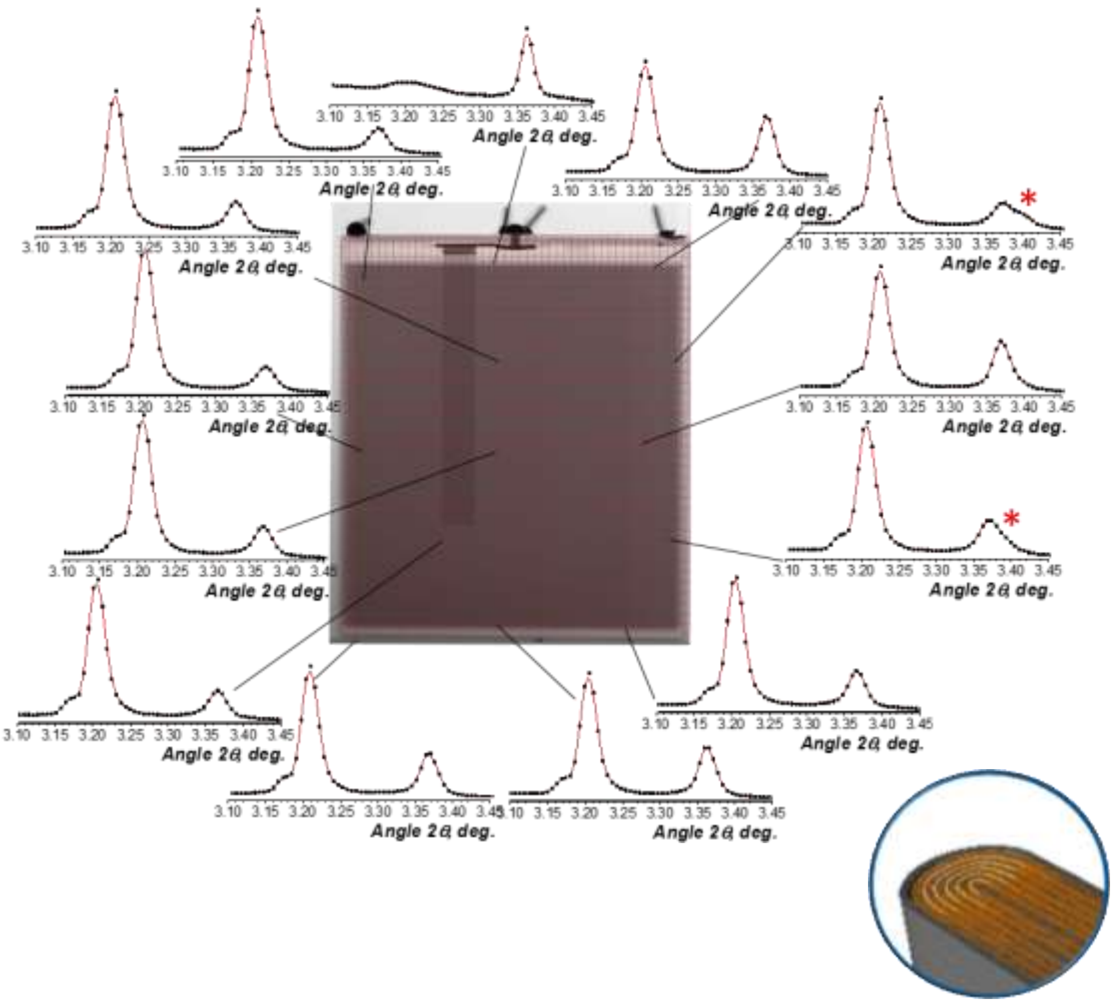
2D diffraction pattern

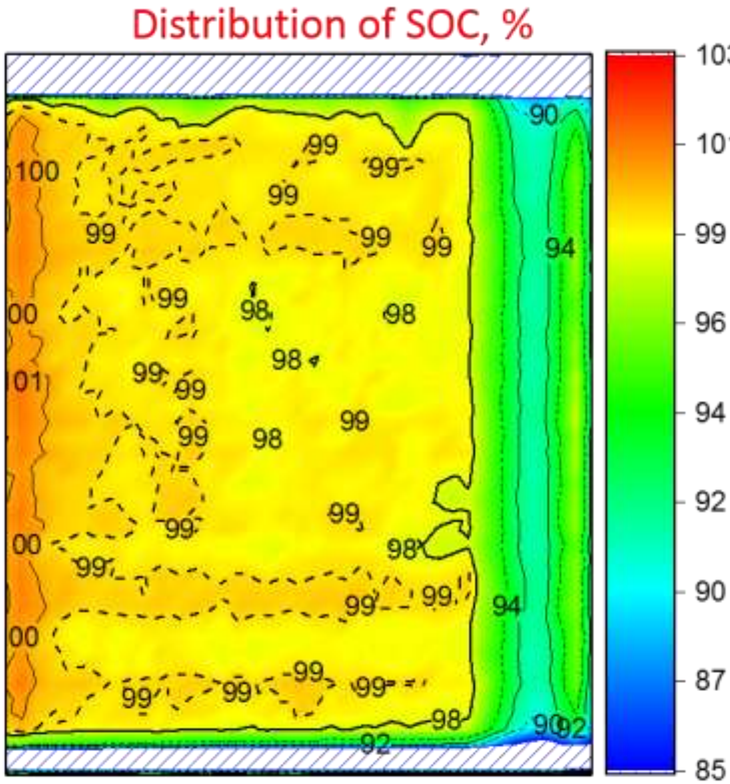


1D pattern



X-ray diffraction radiography - results





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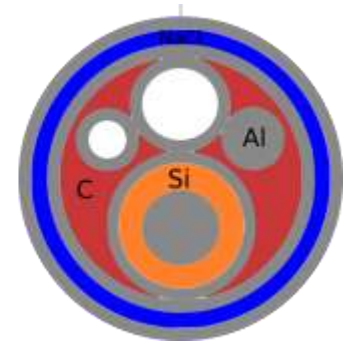
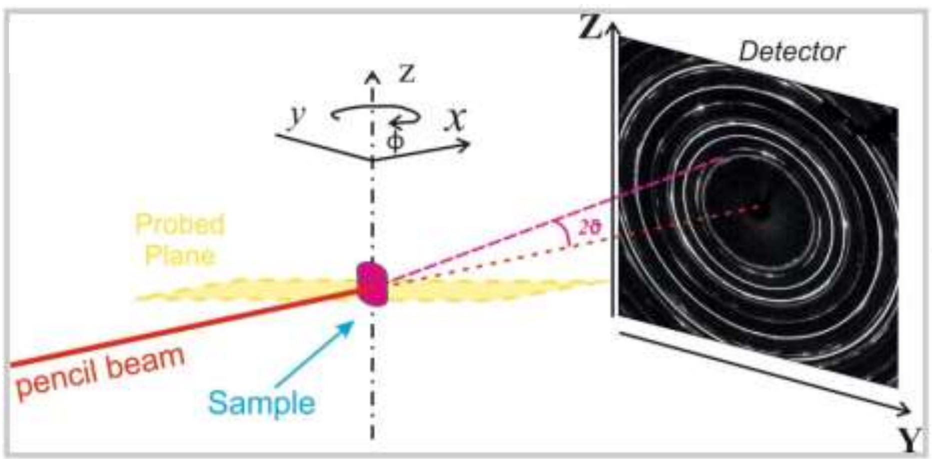
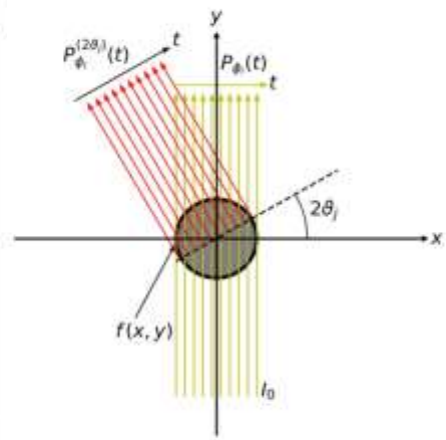
X-ray diffraction tomography

“Phantom” sample – object with the contrast sufficient for the method validation. The 3D printed aluminum cylinder (20 mm in diameter) with the following layout was filled with different powders:

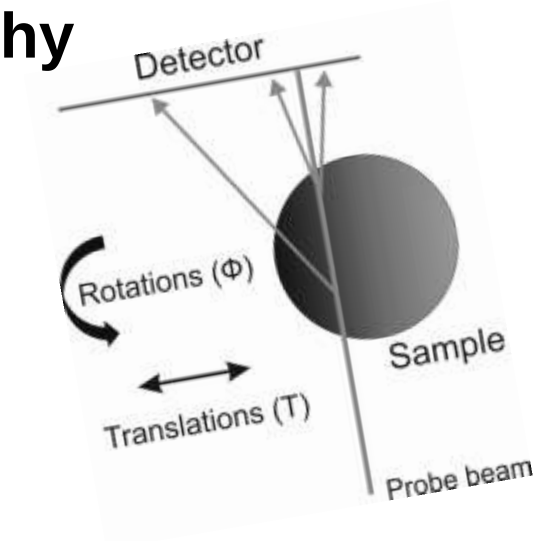






The XRD tomography experiment was performed on P07 beamline at PETRA III using 0.5x0.5 mm^2 sized beam of ca. 60 keV energy, 0.2 mm rastering step (111 translation points) and 61 projections collected upon 6° rotation. Altogether 6771 diffraction patterns were collected.

Absorption-based computed tomography

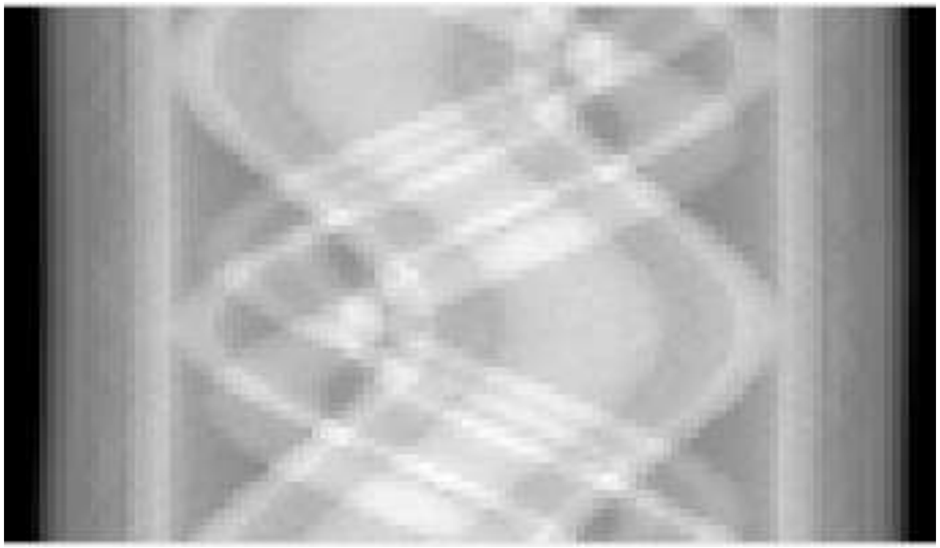


Along with the acquisition of diffraction signal, direct transmission was also registered and reconstructed.

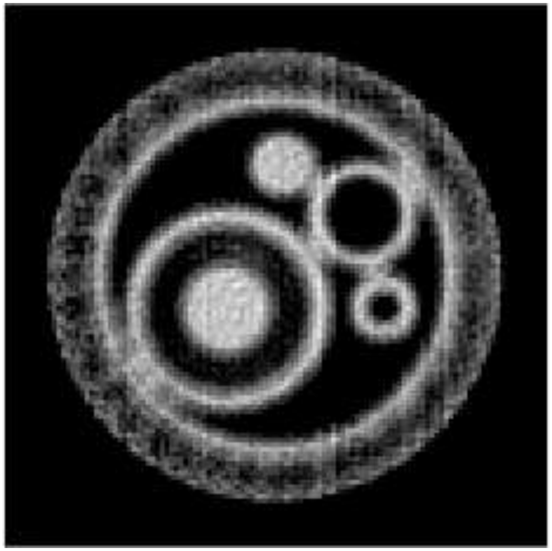
Sinogram

T

Φ

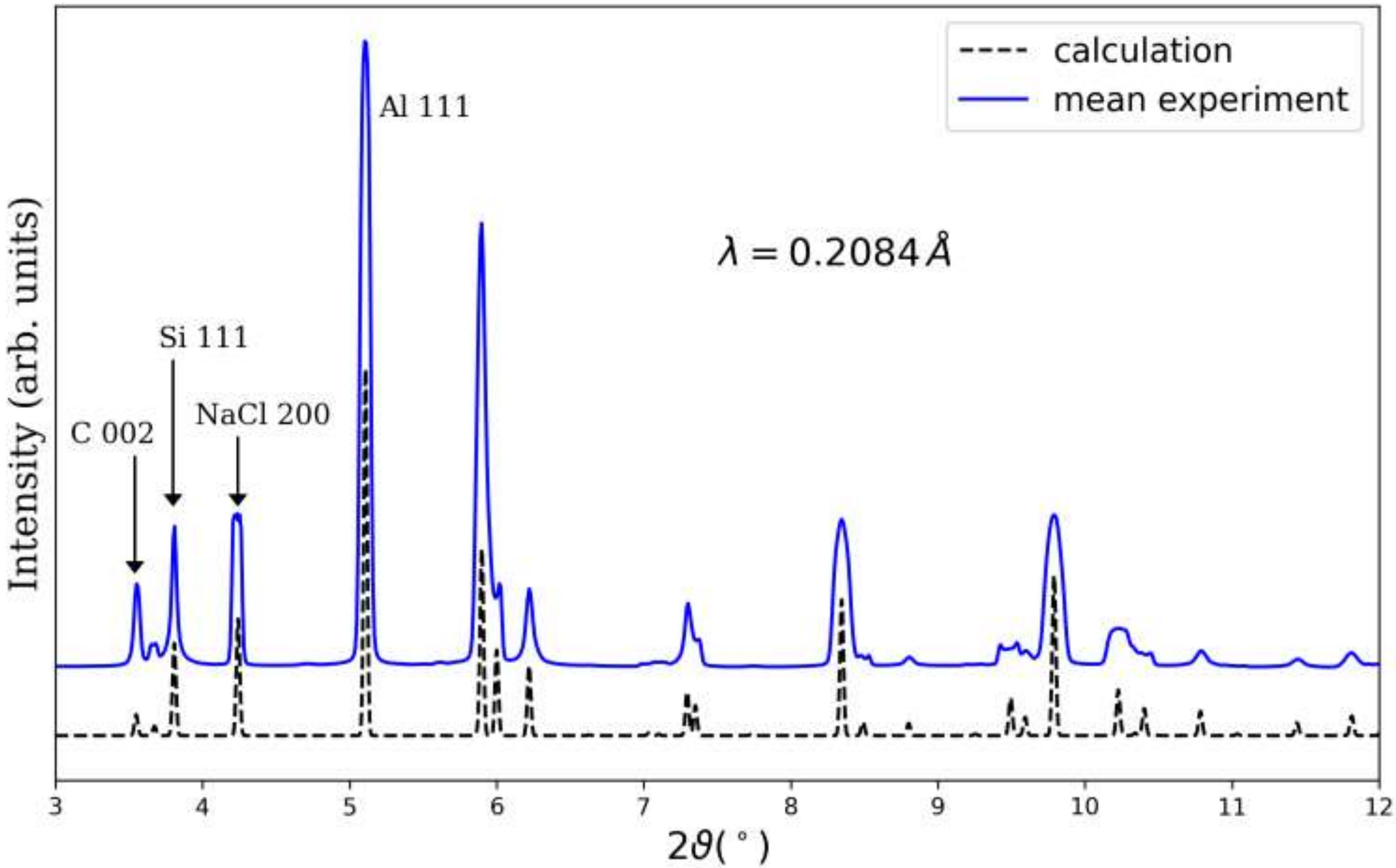


Reconstruction

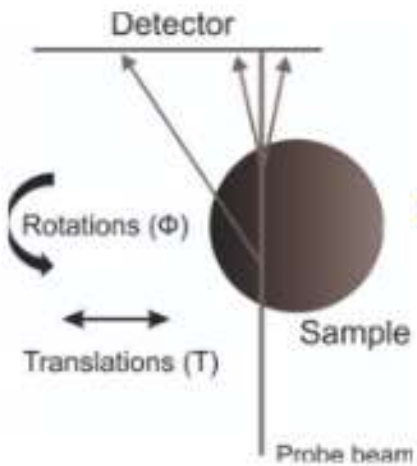


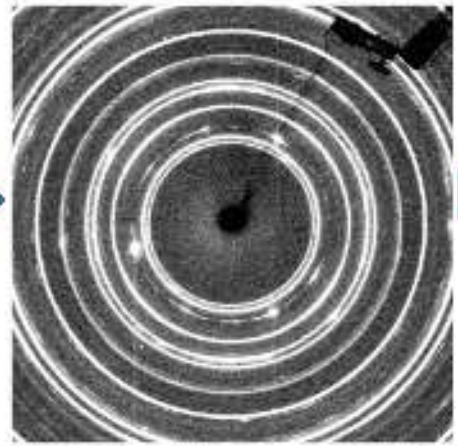
X-ray diffraction computed tomography

Theoretically generated diffraction pattern has been found in good agreement with the “mean” experimental diffractogram.



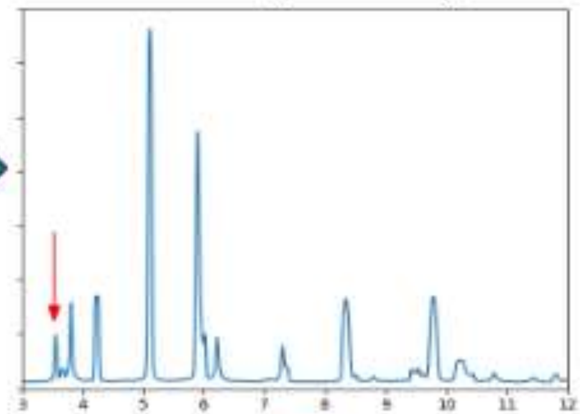
X-ray diffraction computed tomography - algorithm

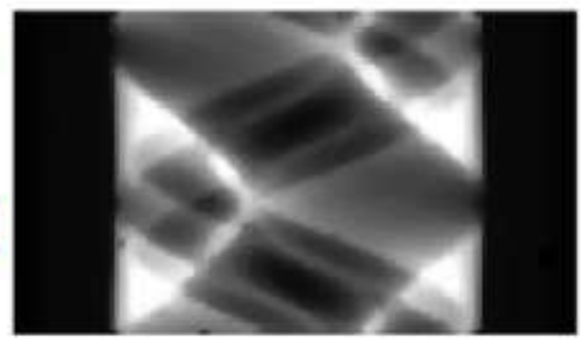




6771 diffractograms collected

6771 diffractograms integrated



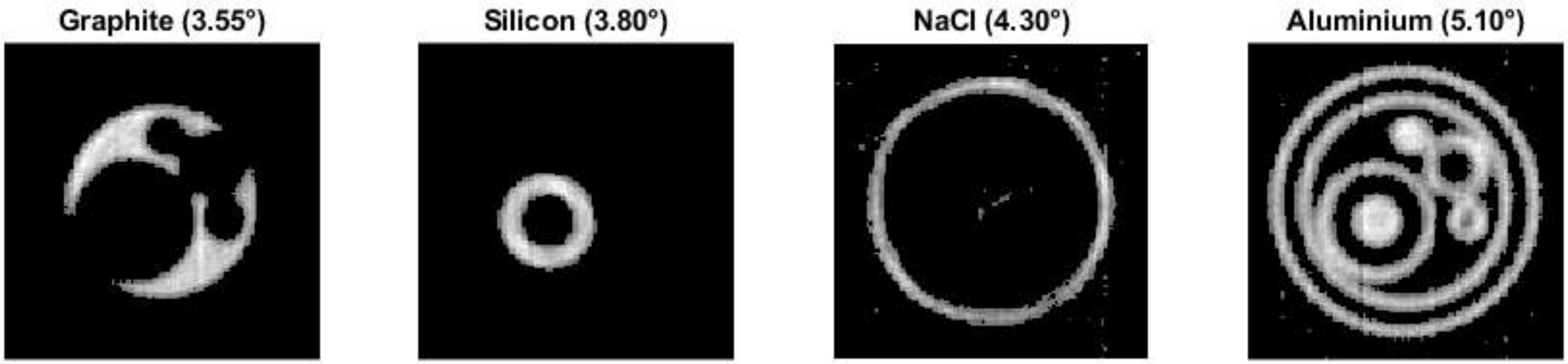


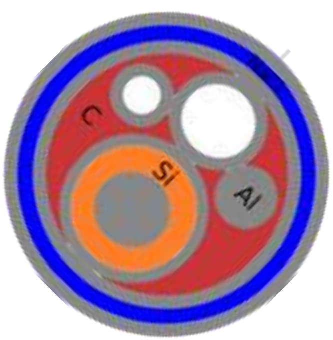
For the chosen characteristic angle the sinogram of size 111x61 is formed

Filtered back project

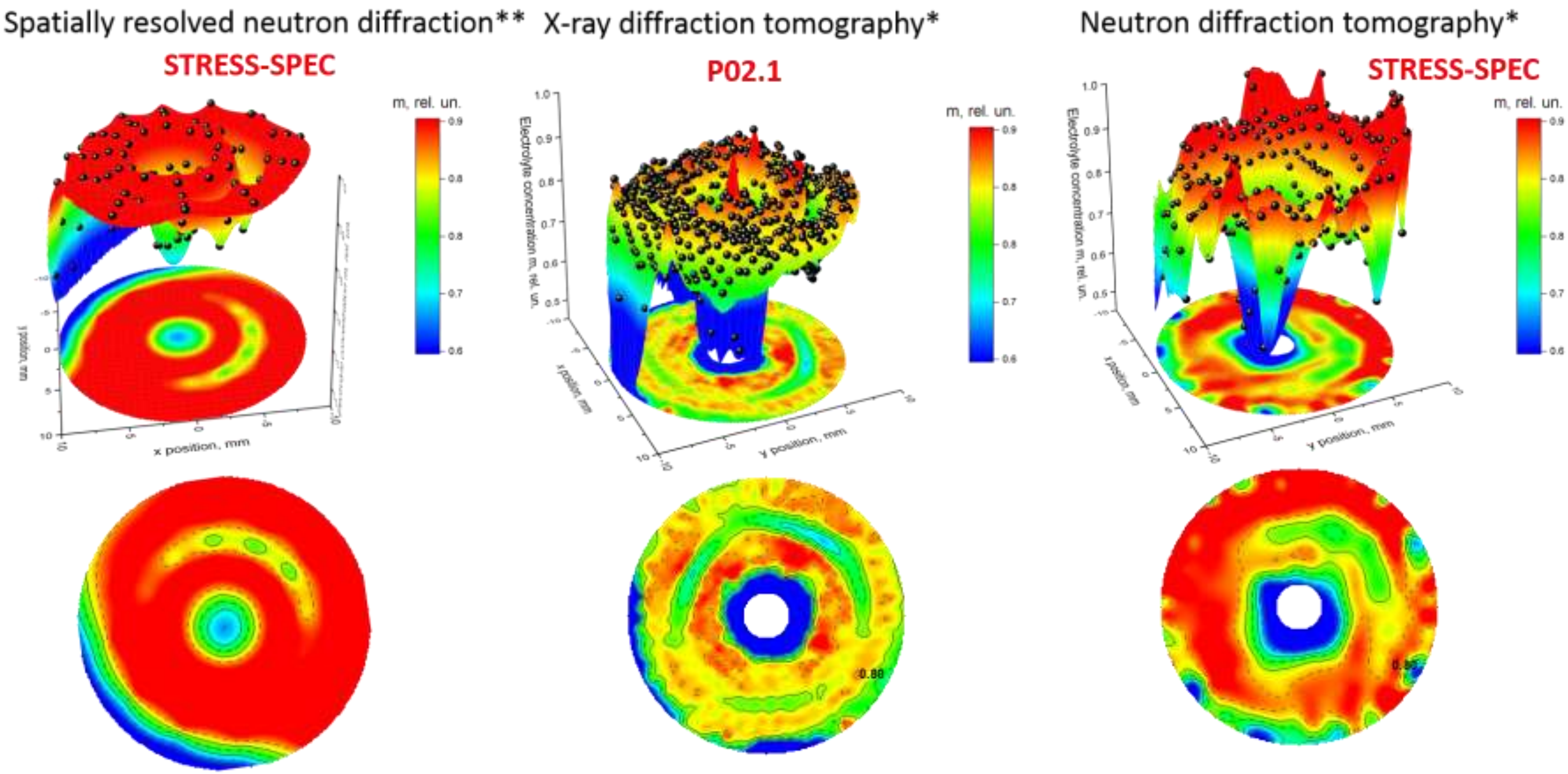
Reconstructed image corresponding to scattered X-rays at 3.55° (Bragg peak of graphite)

X-ray diffraction computed tomography - results





Lithium distribution in the graphite anode of 18650-type lithium ion battery



Summary

- Present toolbox of experimental methods requires an opening of the cell usually supplemented by a possible evaporation of electrolyte, contamination of surfaces, unwanted modification of cell materials etc.
- Diffraction and imaging methods deliver unique information, which can be hardly obtained by any other means
- *In operando*, *in situ*, non destructive, extended contrast techniques …
- Spatially-resolved neutron diffraction provides a unique experimental input in a non-destructive way on lithium distribution in the graphite electrode materials
- Crystallography is a theoretical tool helping to get most out of our data
- The capability limit of these techniques is not reached by far and still need to be explored …
- Diffraction-based techniques have a lot of potential in probing the current and electrolyte distribution in the Li-ion cells of industrial standards: PGAA, diffraction, energy-resolved neutron radiography etc.

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MLZ Group „Structure Research“

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