FRM II
Forschungs-Neutronenquelle
Heinz Maier-Leibnitz

MLZ
Heinz Maier-Leibnitz Zentrum

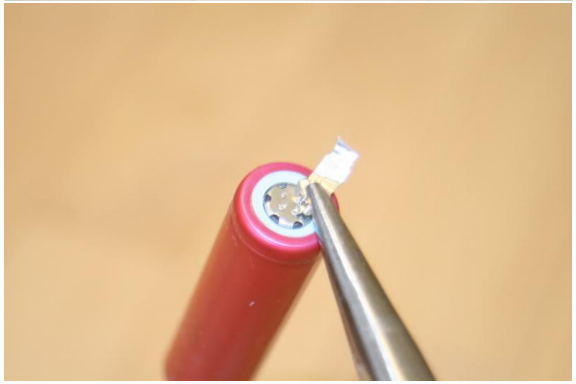
KIT Karlsruher Institut für Technologie
TECHNISCHE UNIVERSITÄT DARMSTADT
MLZ Heinz Maier-Leibnitz Zentrum
SFB 595 Deutsche Forschungsgemeinschaft DFG

Neutron scattering studies of Li-ion batteries

A. Senyshyn, M.J. Mühlbauer, O. Dolotko, H. Ehrenberg

РНСИ-КС 2014

Совещание по использованию рассеяния нейтронов и синхротронного излучения в конденсированных средах 27-31 октября 2014, Санкт-Петербург, Старый Петергоф



Studied objects

Commercial Li-ion cell
(18650-type, cylinder)

∅ 18 mm, H_{tot}=65 mm

Protected

Q_{max} ~ 2600 mAh

Operating voltages:

3.0-4.2 V window

Accessible C-rate:

0.5C at 25^{o}C (standard)

1.0C at 25^{o}C (rapid)

Electrodes:

$LiCoO_2$ (negative)

Graphite (positive)

Electrolyte:

EC/DMC

Separator:

Cellgard^{TM}

Weight:

46 g

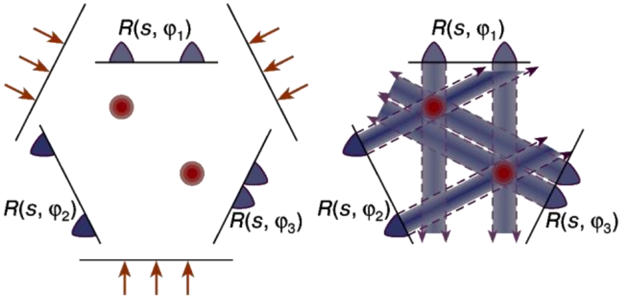
Operating temperature:

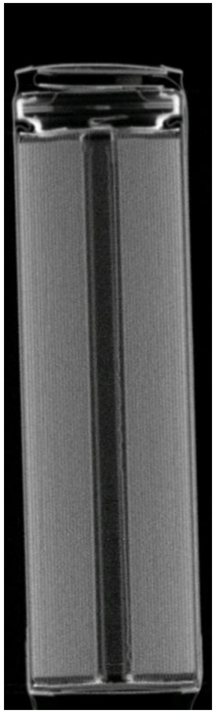
0-45^{o}C (charge)

-10^{o}C-60^{o}C (discharge)

Computed neutron tomography

ANTARES - Neutron radiography and tomography
Collimation ratio L/D=800,
Field of view 100x100 mm^2 ~ 60 μm pixel resolution



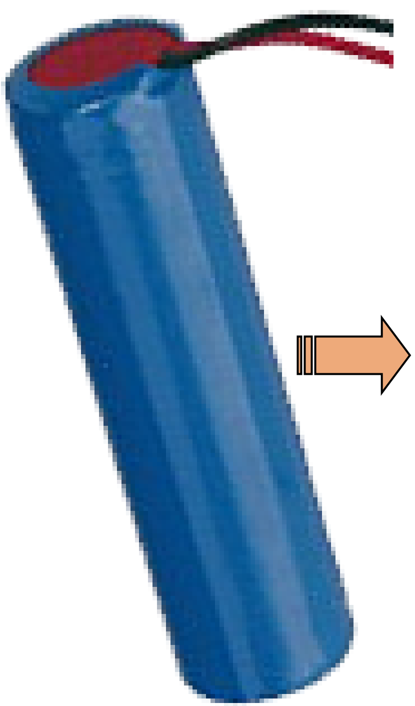


Inverse Radon transformation;
filtered back projection algorithm;
number of projections 600;

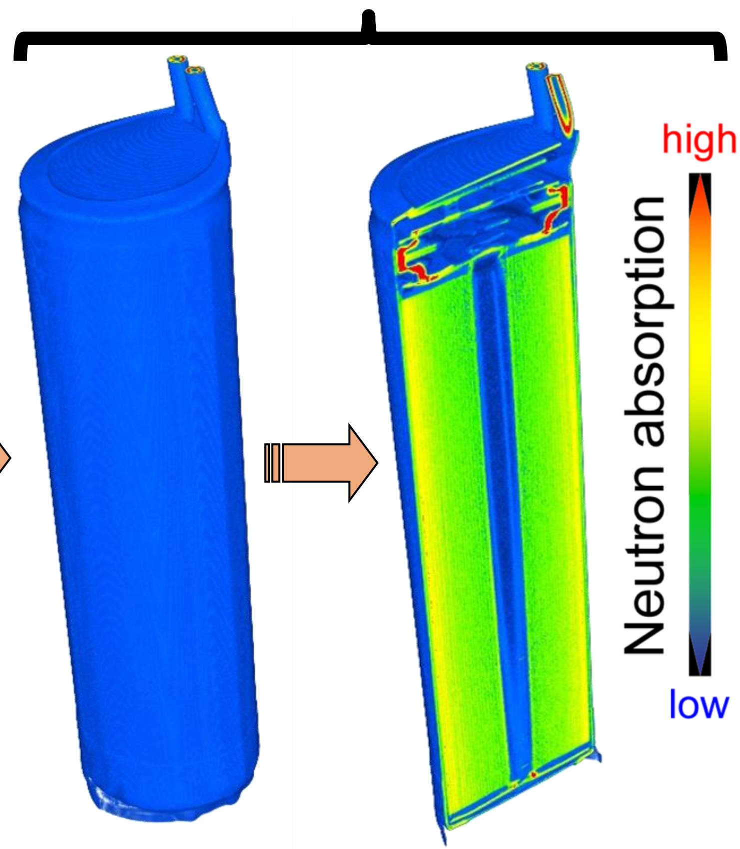
Assignment of Absorption Levels
to a chosen color scheme

Tomography reconstruction on 18650-type battery

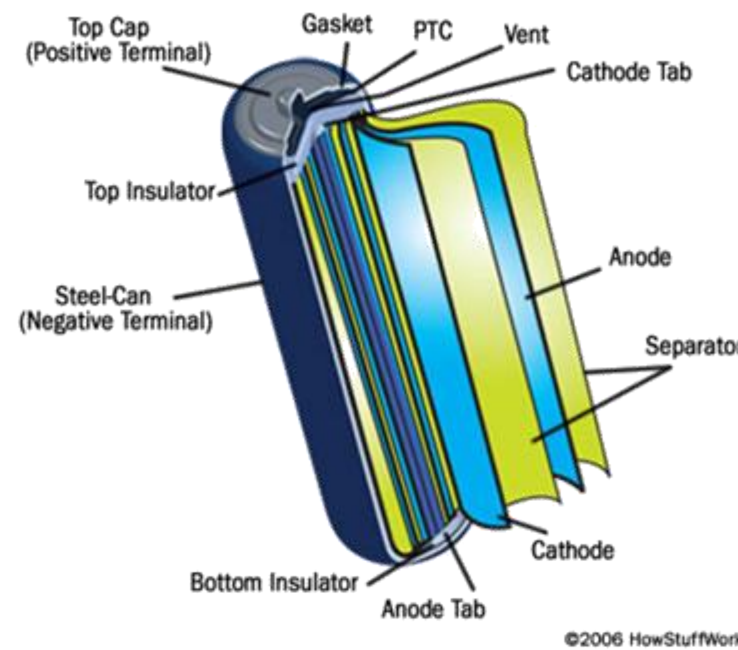
Photo



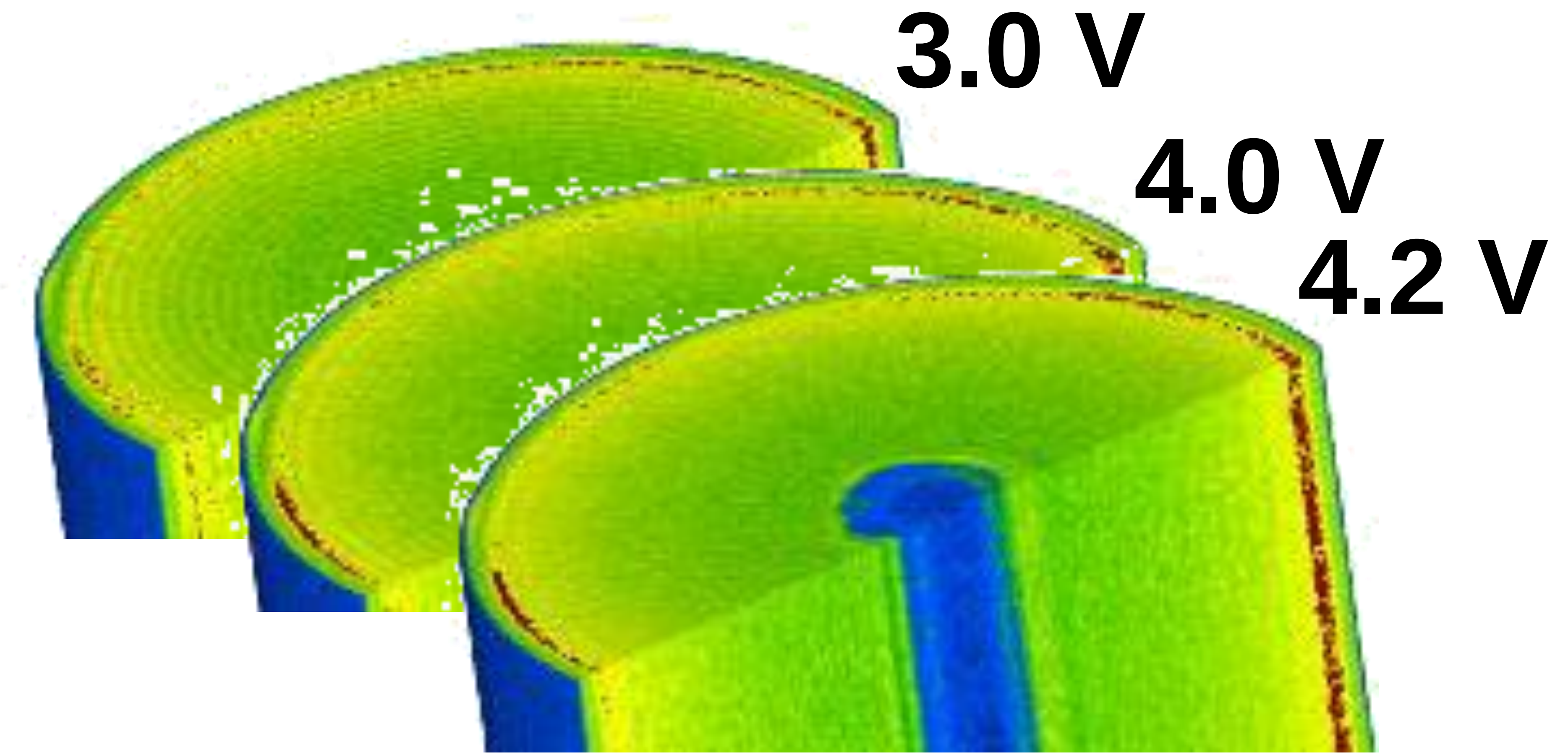
3D model



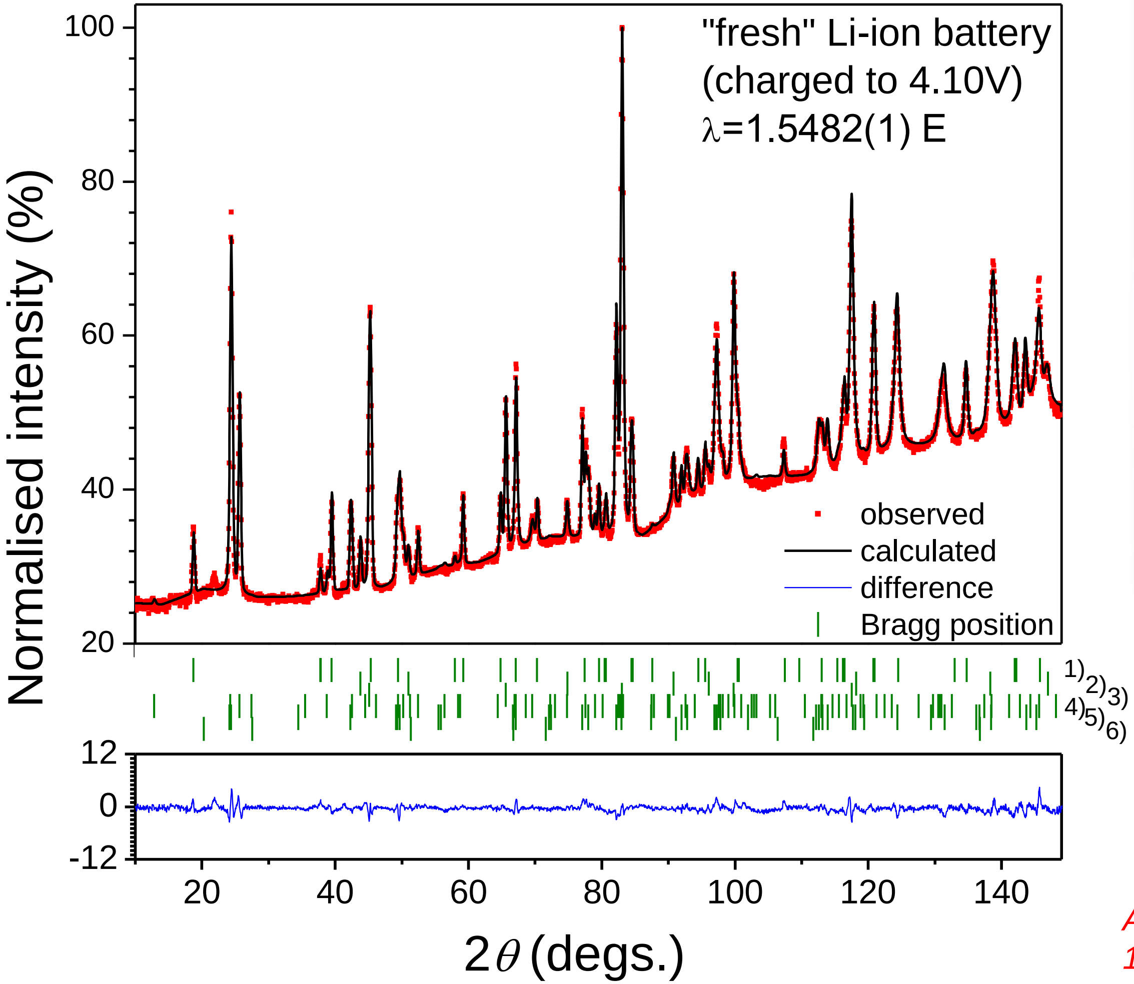
Sketch

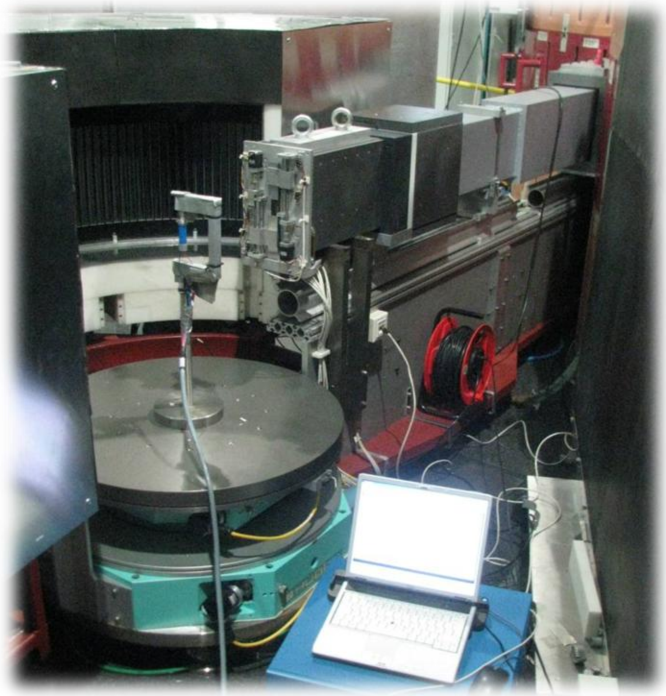


Tomography reconstruction on 18650-type battery



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)

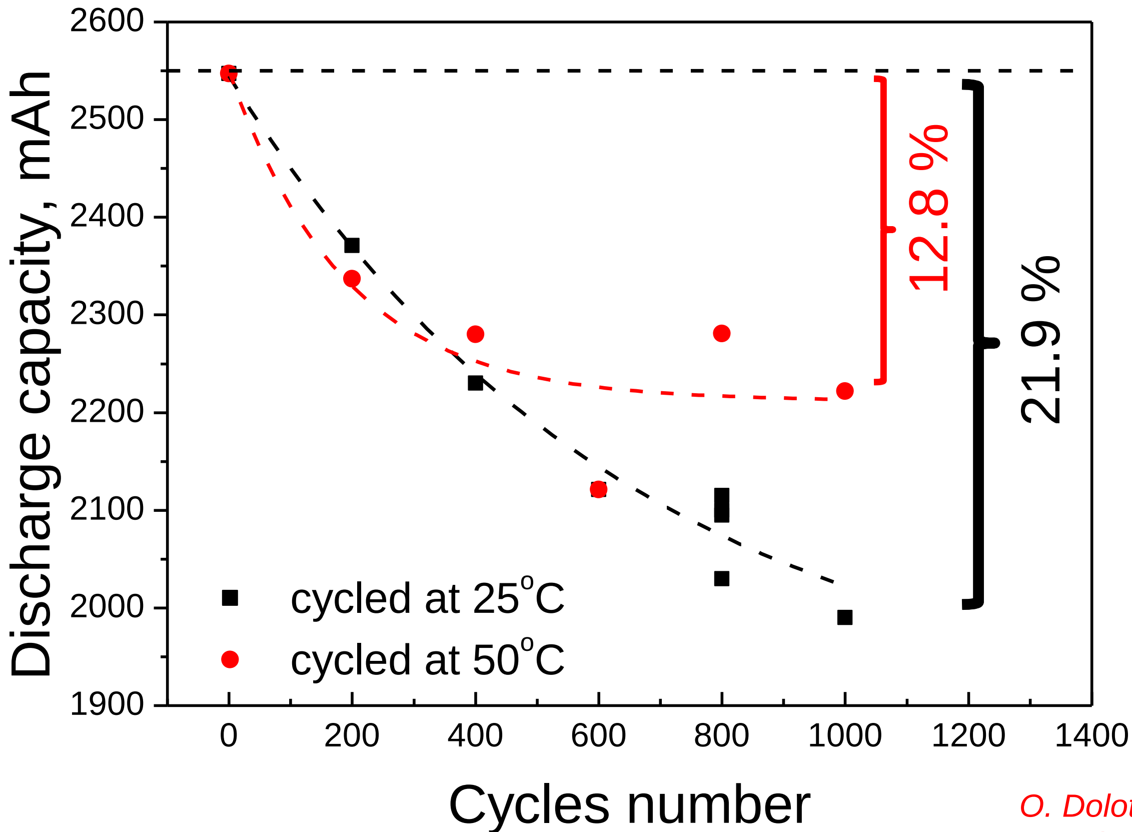
Beam size: 40×25 mm^2
2θ range: 0-160^o

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

Fatigue of battery: 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

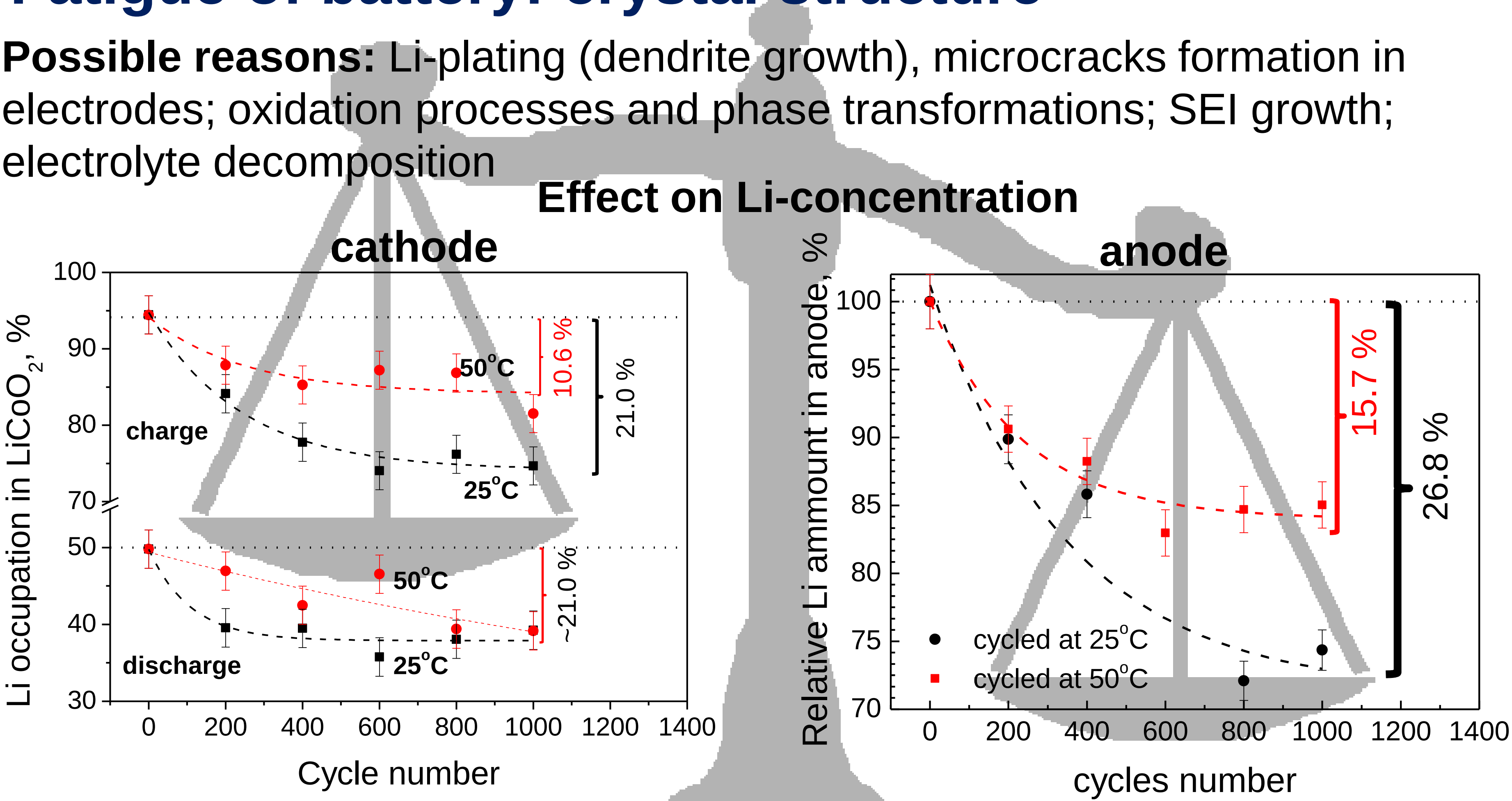


O. Dolotko et al., J. Electrochem. Soc. 2159(12) (2012) A2082-A2088

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

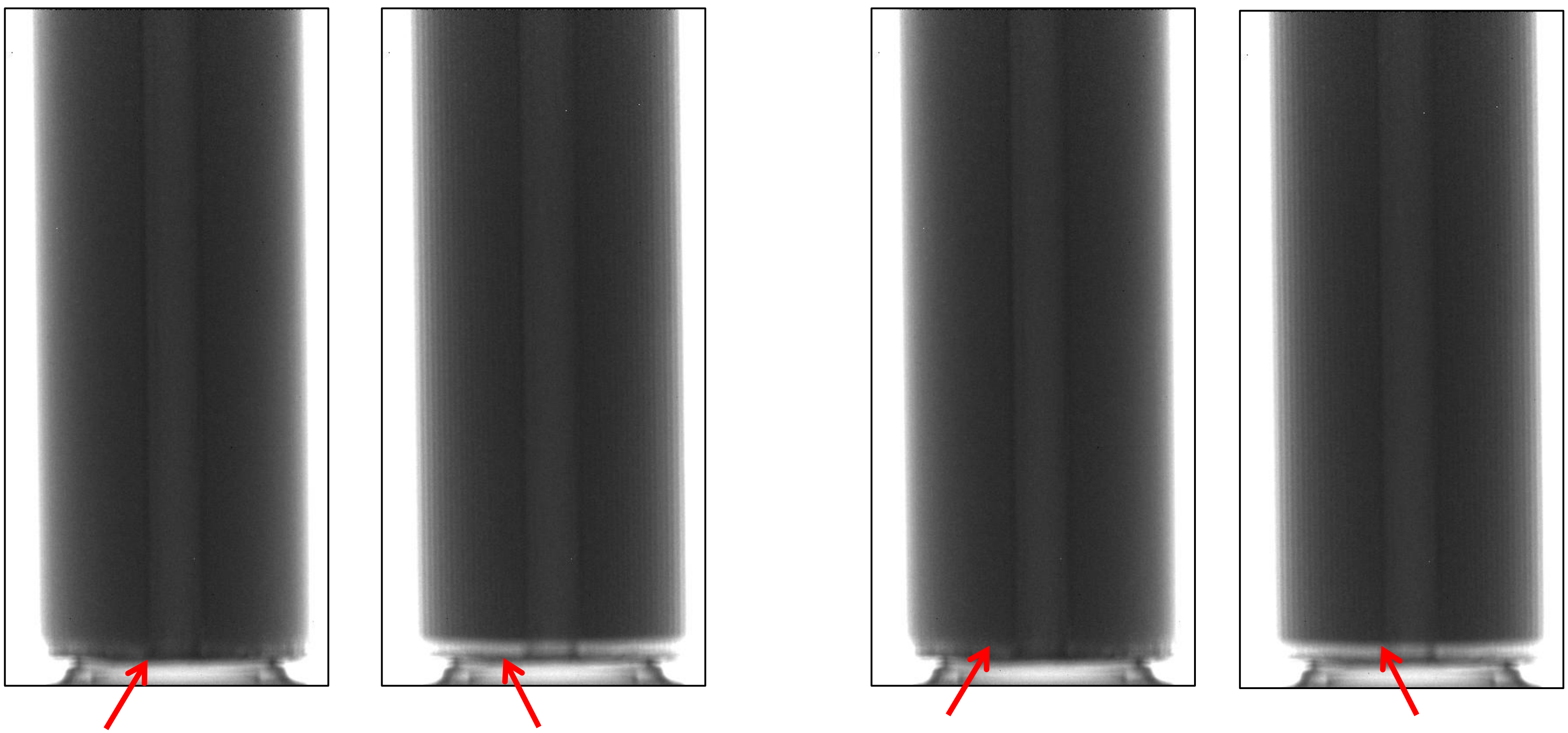


By the fatigue introduced the system looses free (transport) lithium;
Lithium loss correlate to the reduction of discharge capacity;

Fatigue of battery: neutron radiography

fresh — charged | discharged

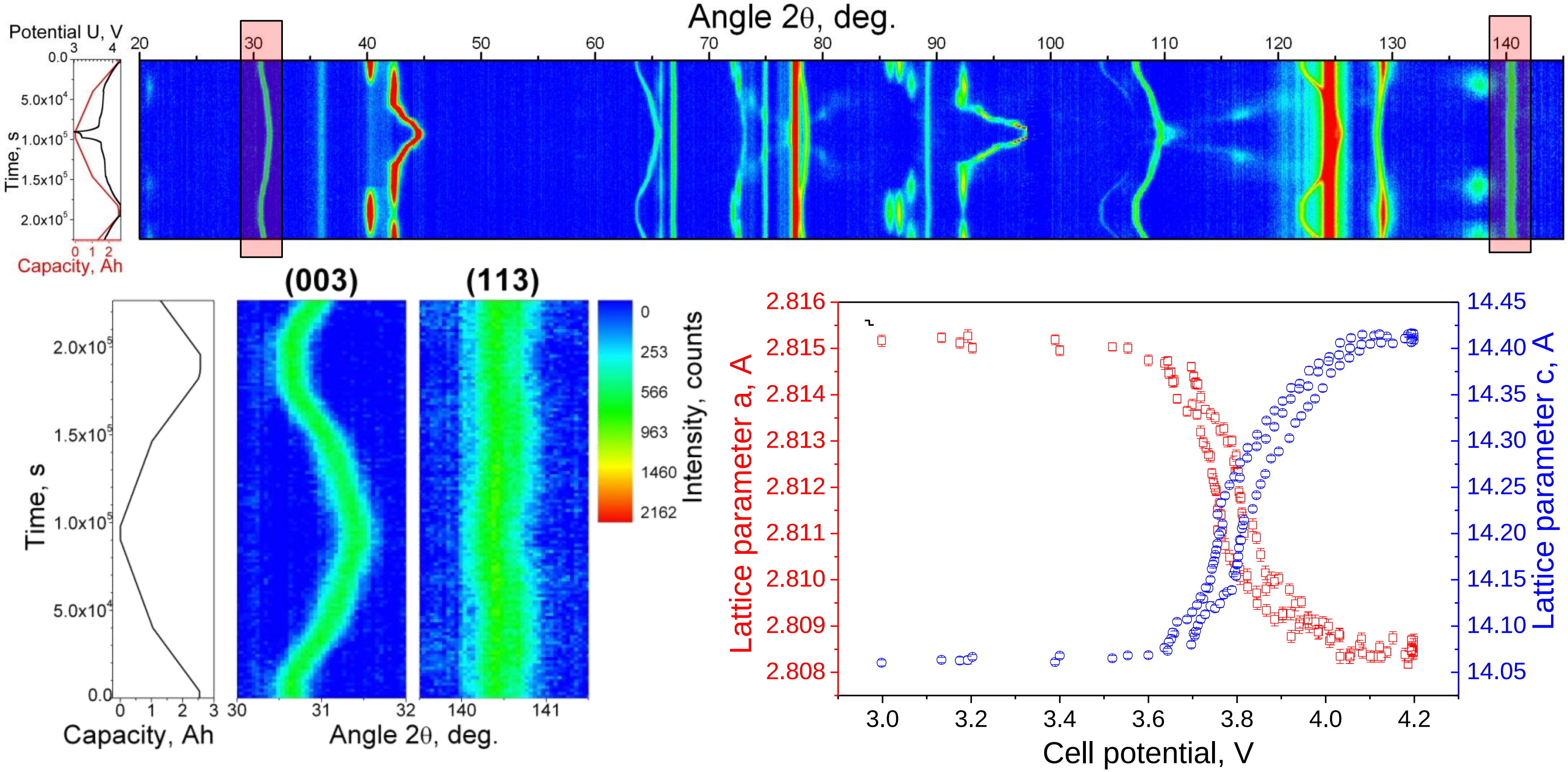
fatigued — charged | discharged



filled — “empty” — partially empty — “empty”

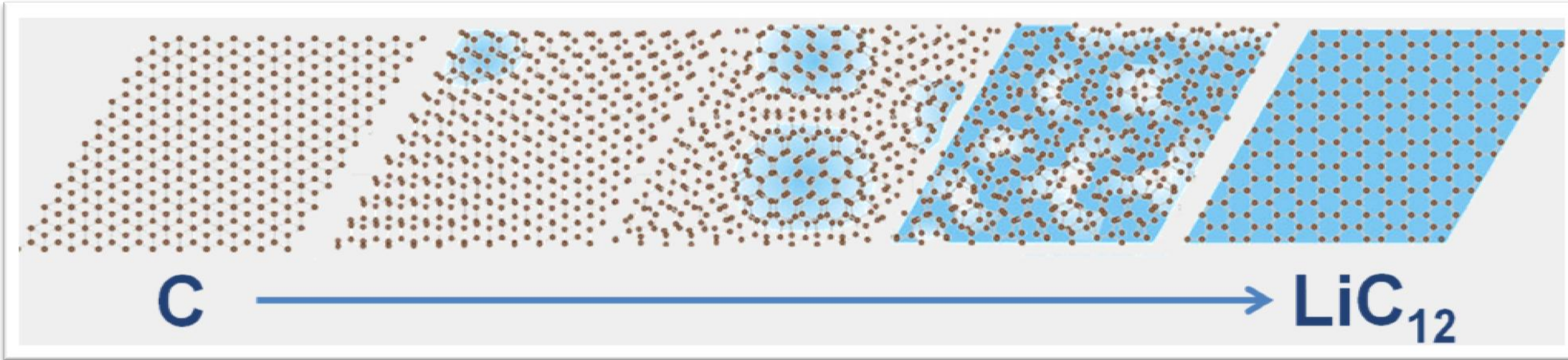
Evolution of diffraction data vs. Electrochemical treatment

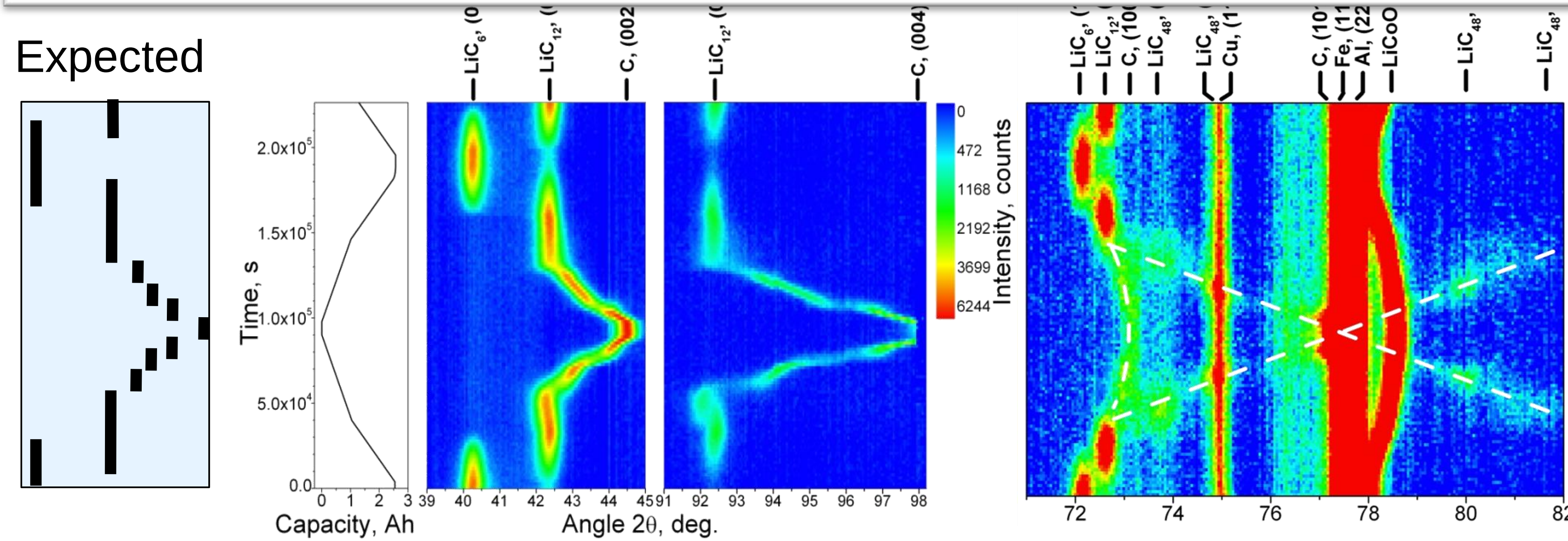
(Cathode $LiCoO_2$, λ=2.536 Å)



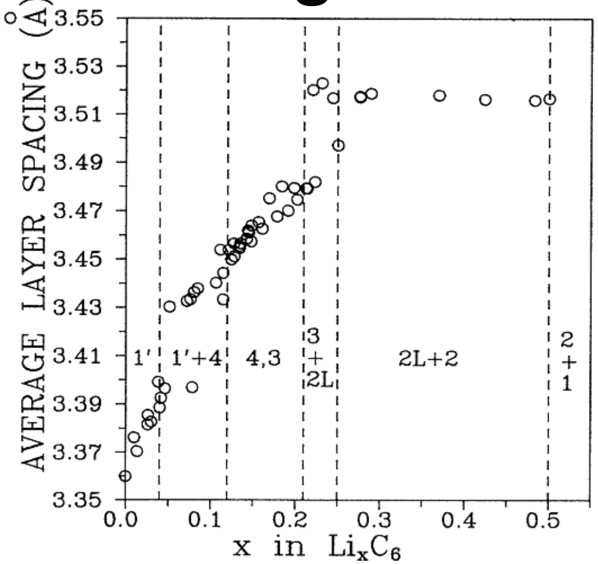
A. Senyshyn et al., J. Electrochem. Soc. 160(5) (2013) A3198-A3205

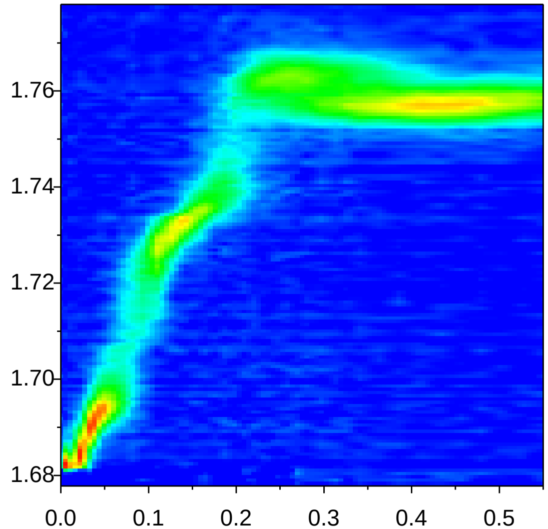
Evolution of diffraction data vs.

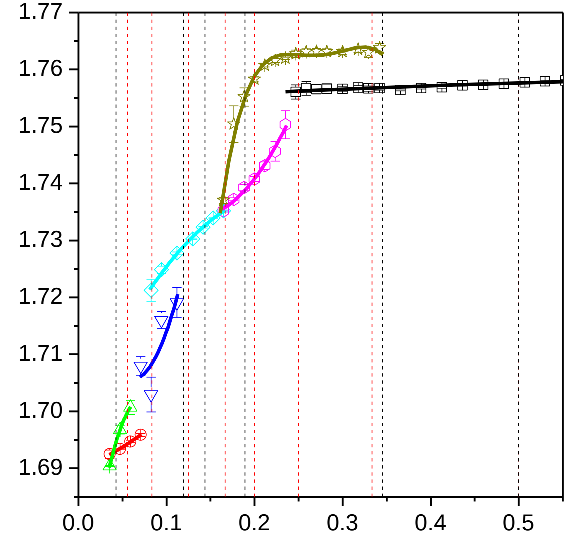




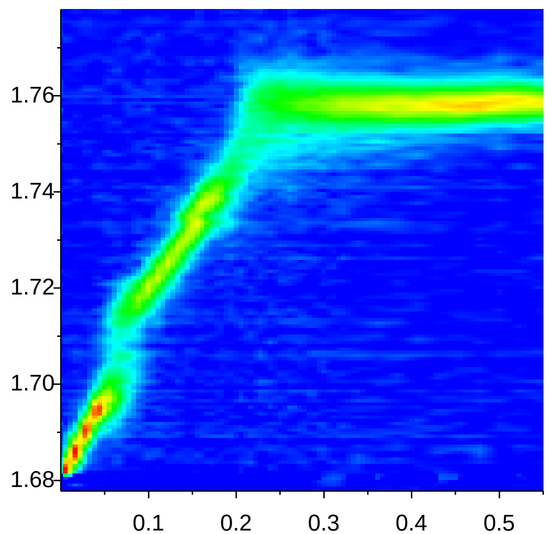
Phase diagram of Li-intercalated carbons

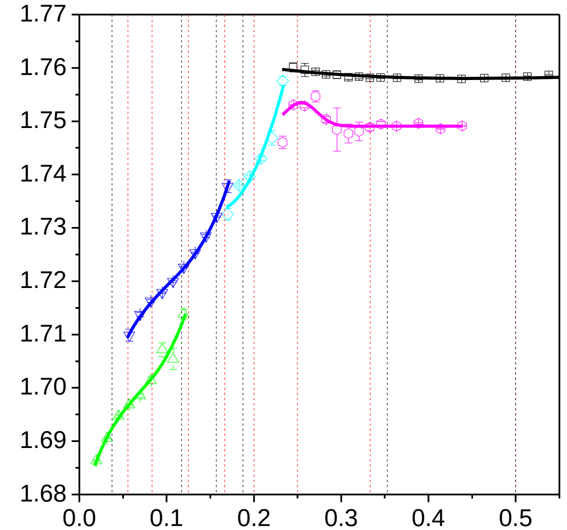






J.R. Dahn, Phase diagram of Li_xC_6, Phys. Rev. B 44(17) 9170-9177 (1991).
T. Ohzuku, Y. Iwakoshi, K. Sawai, Formation of Lithium-Graphite Intercalation Compounds in Nonaqueous Electrolytes and Their Application as a Negative Electrode for a Lithium Ion (Shuttlecock) Cell , J. Electrochem. Soc., 140(9) 2490-2498 (1993).



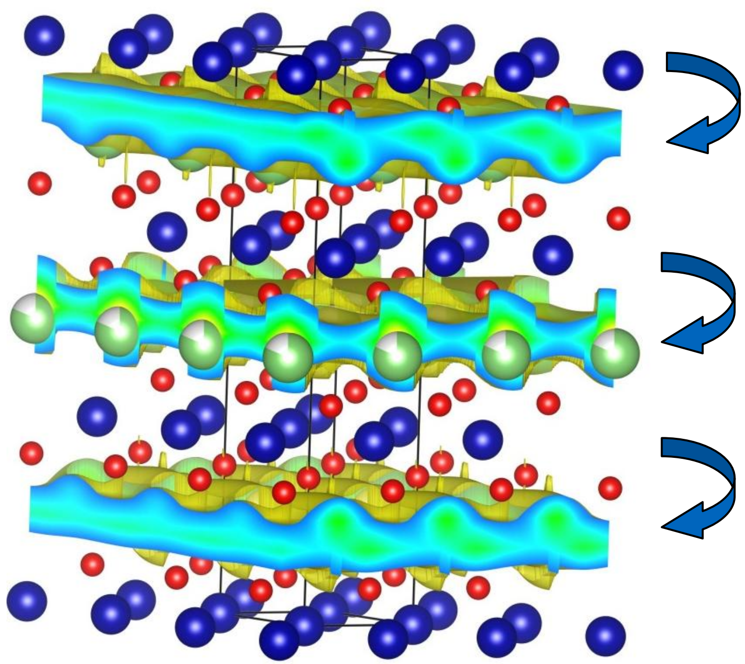


Cation mixing in NMC-type cathode

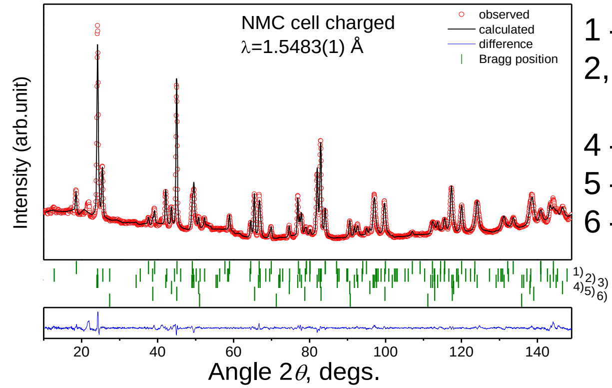
The $LiCoO_2$ has a high energy density, but cobalt is expensive and reactive …

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



Diff. pattern of NMC-based cell



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.

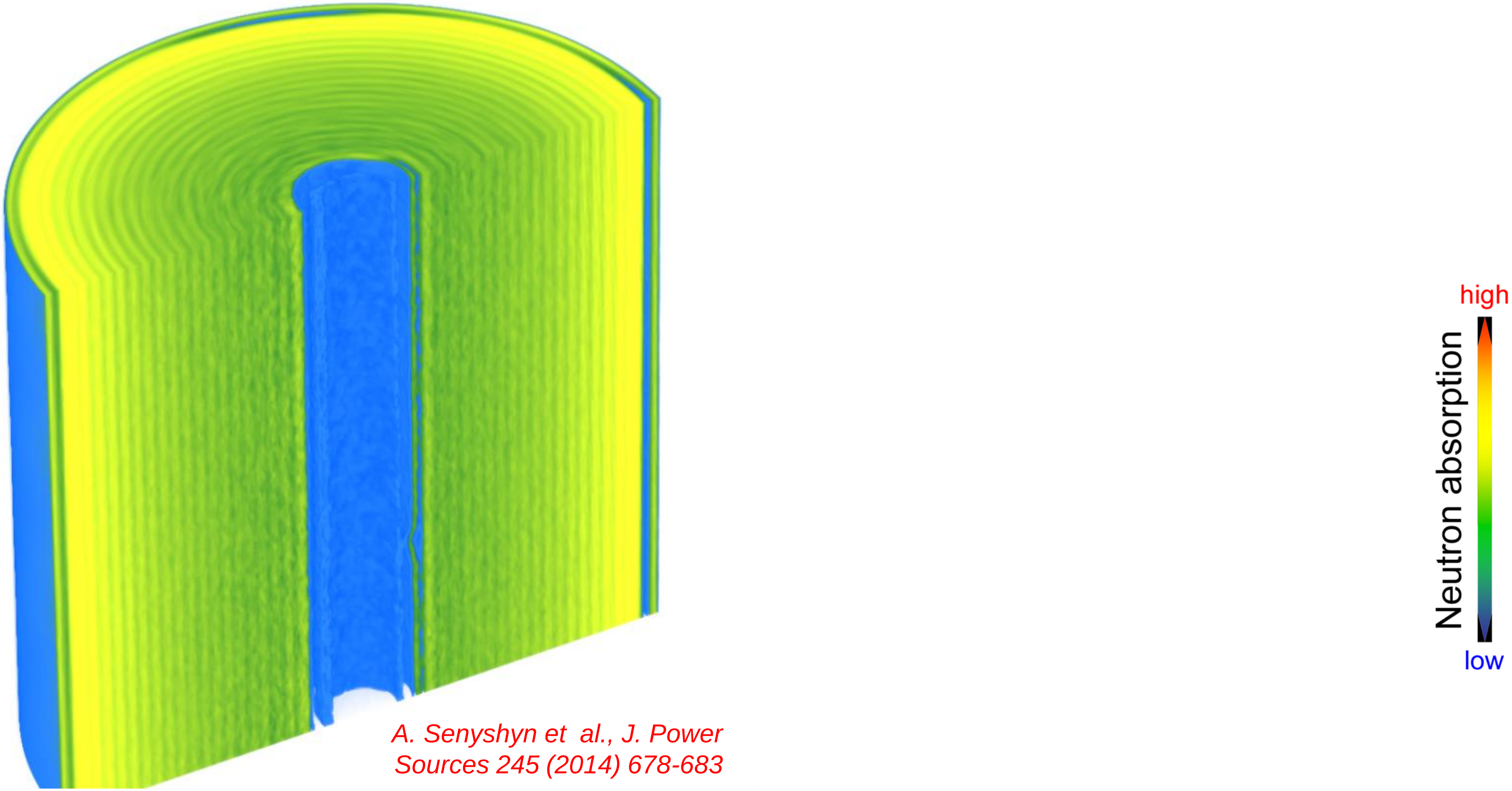
O. Dolotko et al., J. Power Sources 255 (2014) 197-203

Obtained structural parameters

Cell capacity, mAh	Li site occupancy x_{Li}, frac. un. Li1 (3a)	Li site occupancy x_{Li}, frac. un. Li2 (3b)	R_p, R_{wp}, χ^2
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

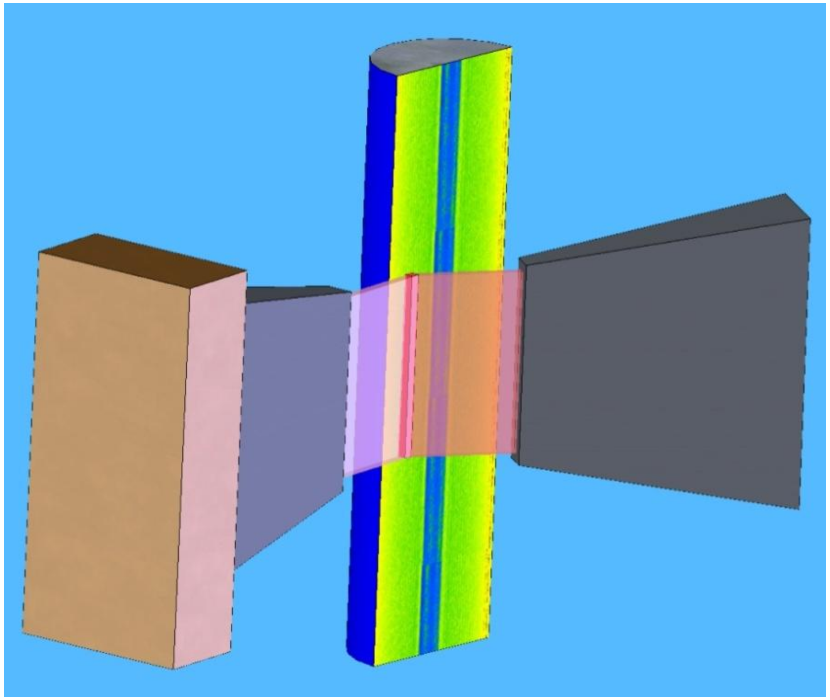
Tomography reconstruction on 18650-type battery

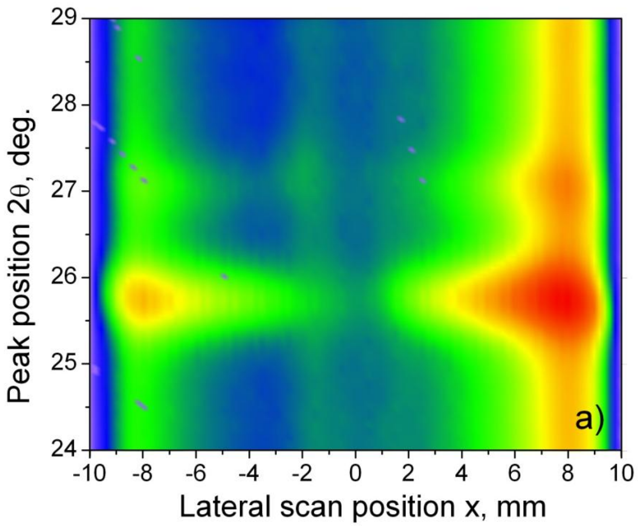
Polychromatic beam

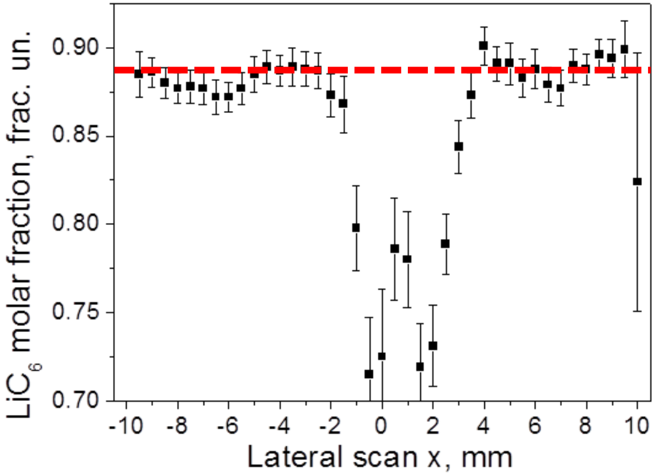


A. Senyshyn et al., J. Power Sources 245 (2014) 678-683

Spatially-resolved neutron powder diffraction







- strain scanner SALSA (ILL, France) with the use of hexapod sample stage (Gough-Stewart platform); gauge volume 1x1x20 mm^2
- engineering diffractometer STRESSPEC (FRM II); gauge volume 2x2x20 mm^2

A brief summary

Still long way to go …

- Effect of temperature, charge rate, depth of discharge, overcharge, materials morphology, various chemistries, cell shape need to be studied;
- Adaption of Li-ion cells to capabilities of existing instrumentation;
- Instrumentation with better resolution (both diffraction and spatial), higher neutron flux, improved signal-to-noise ratio;
- Use of other neutron scattering techniques: spatially-resolved activation analysis, small angle neutron scattering, positron spectroscopy, neutron reflectometry, inelastic neutron scattering;
- Complementarity with other techniques (electrochemistry, NMR, theory);
- Synchrotron-based techniques have significant potential for studies of Li-ion batteries.

Thank you for attention.