Quantification of operation-driven active material losses in Li-ion batteries using neutron diffraction

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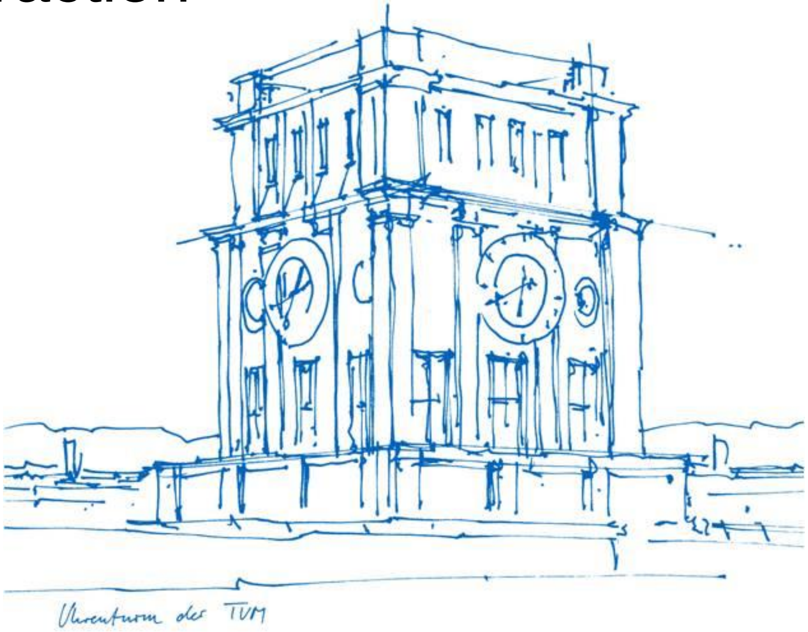
Forschungsneutronenquelle Heinz Maier-Leibnitz (FRM II)

Heinz Maier-Leibnitz Zentrum (MLZ)

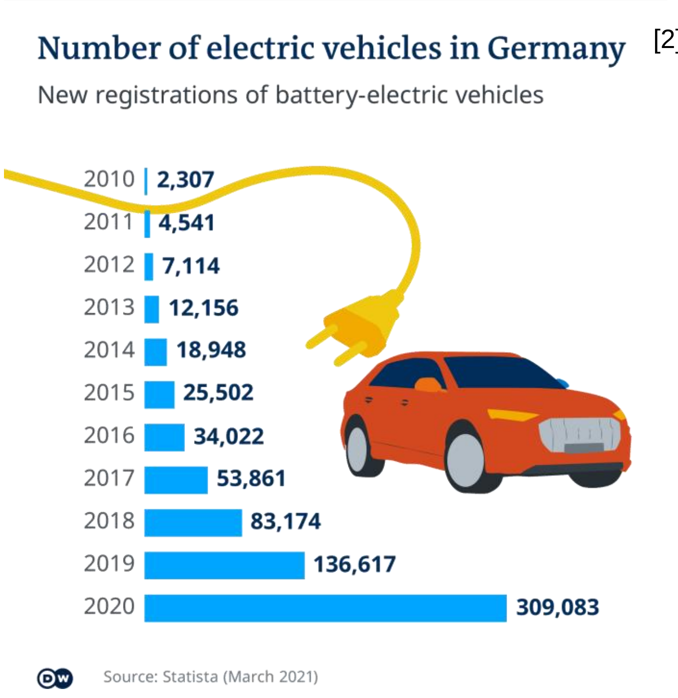
Technische Universität München

ILL-ESS User Meeting, Lund, October, 07, 2022



Li-ion batteries

[3]

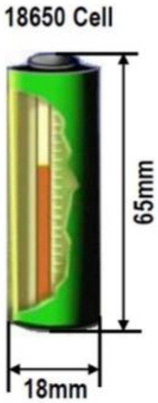


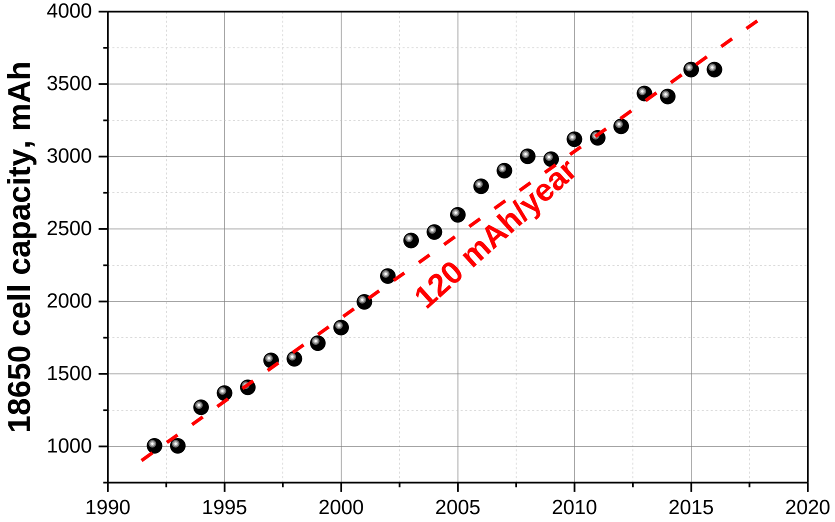
[2]

Y. Liang, et al., InfoMat, 2019, (1), 6-32

Evolution of LIB characteristics

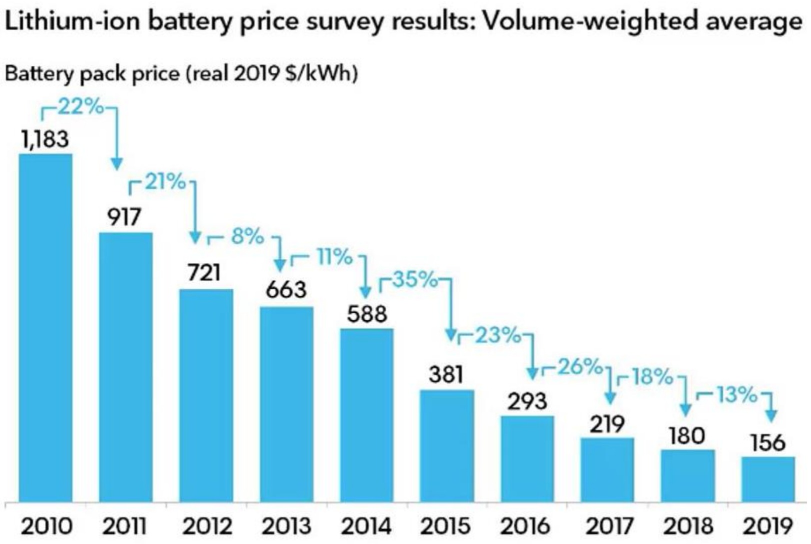
Evolution of cell capacity





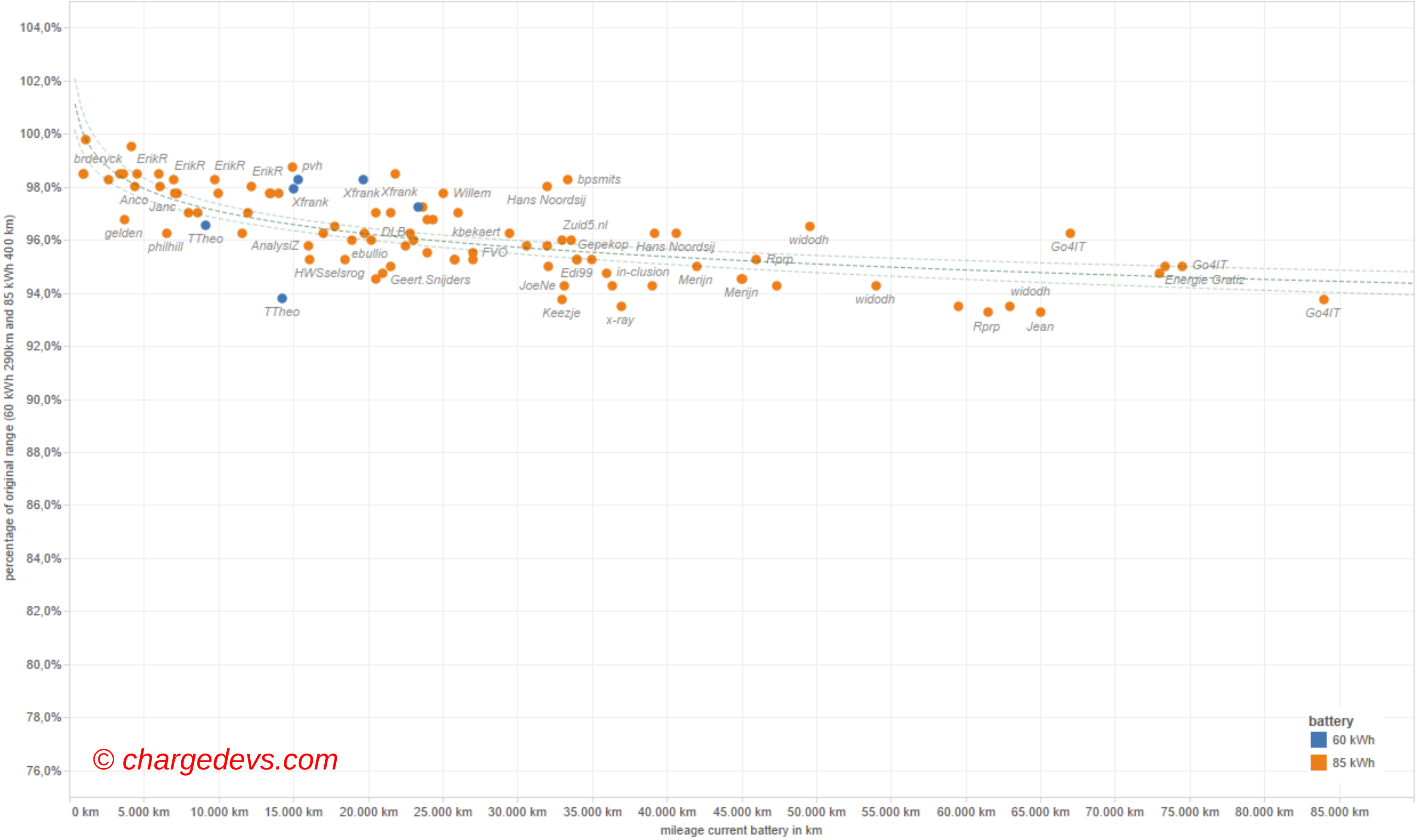
© Panasonic

Battery cost ($/kWh)



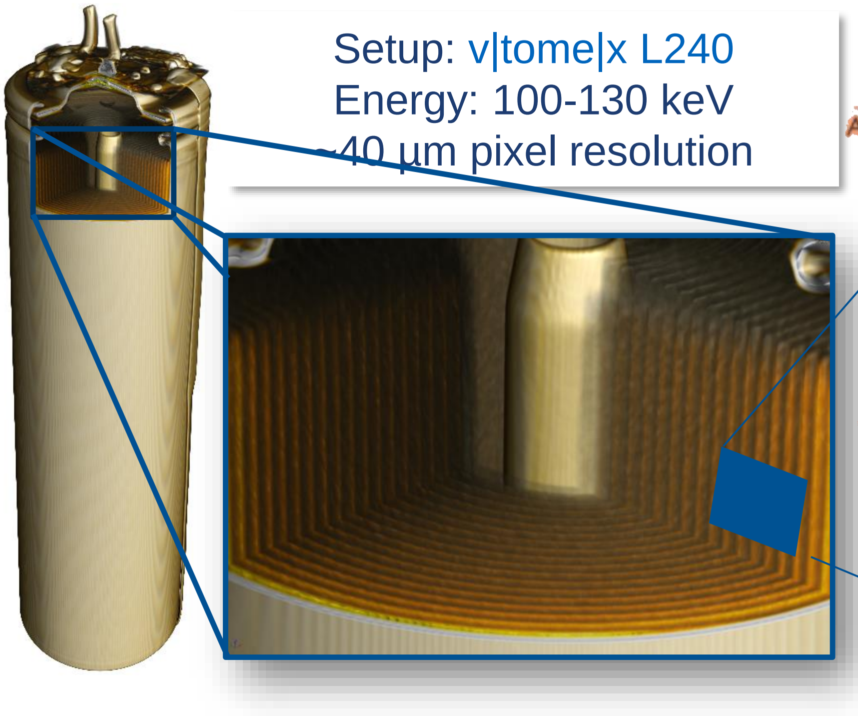
© Bloomberg

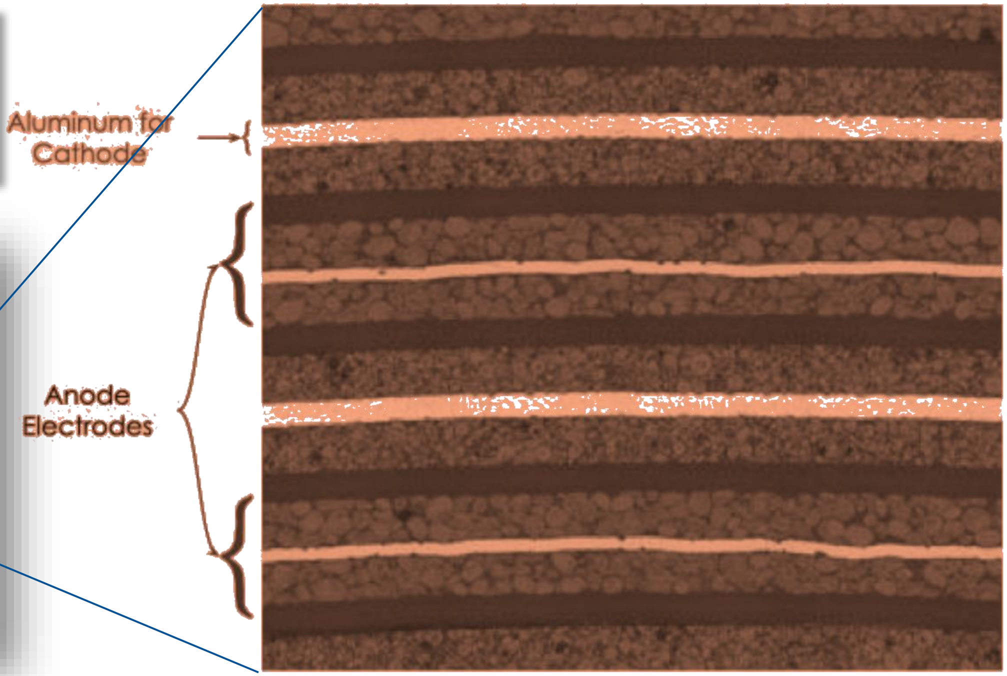
Percentage of range loss vs. distances driven



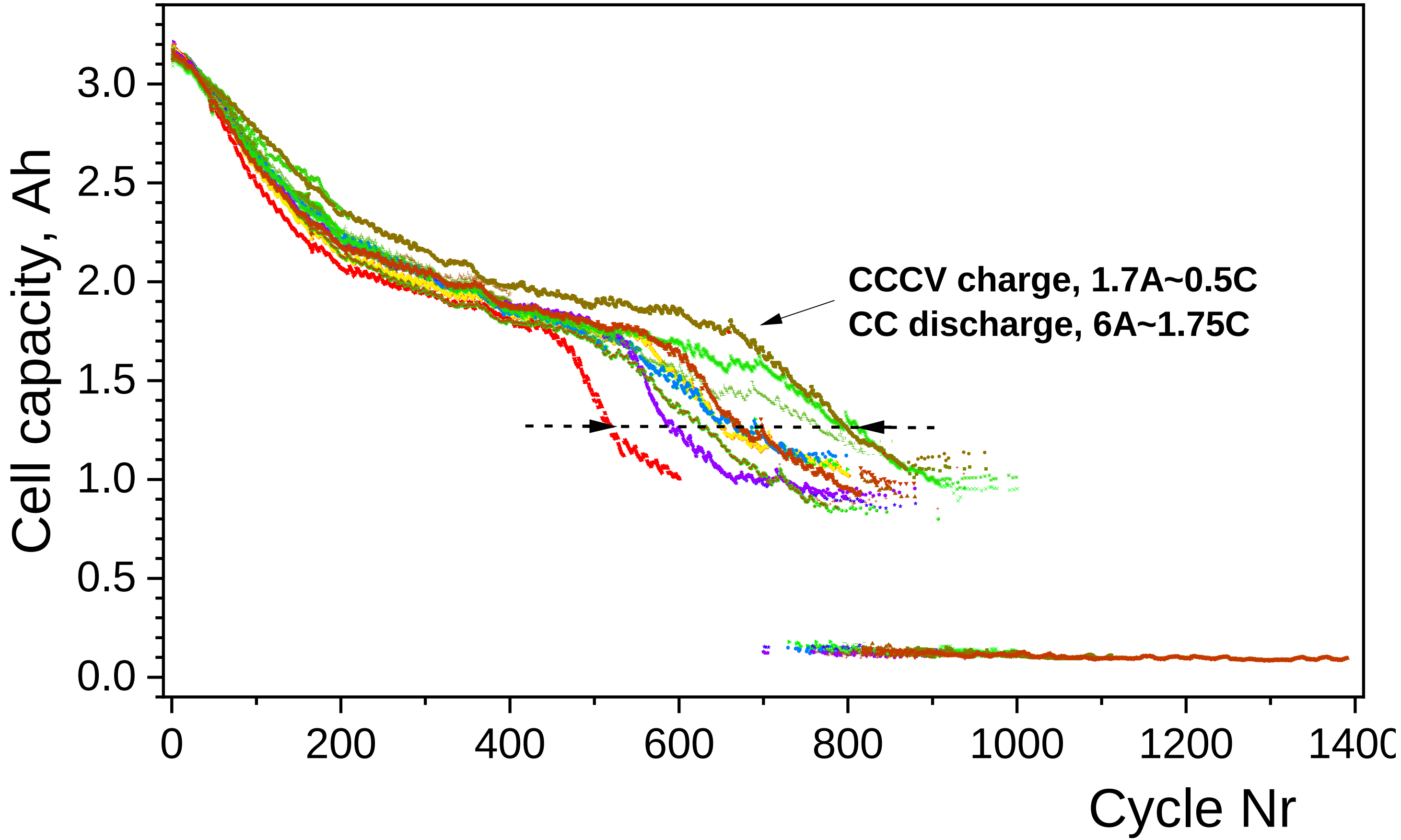
Design of typical cylinder-type (18650) cell

Setup: v|tome|x L240
Energy: 100-130 keV
~40 µm pixel resolution

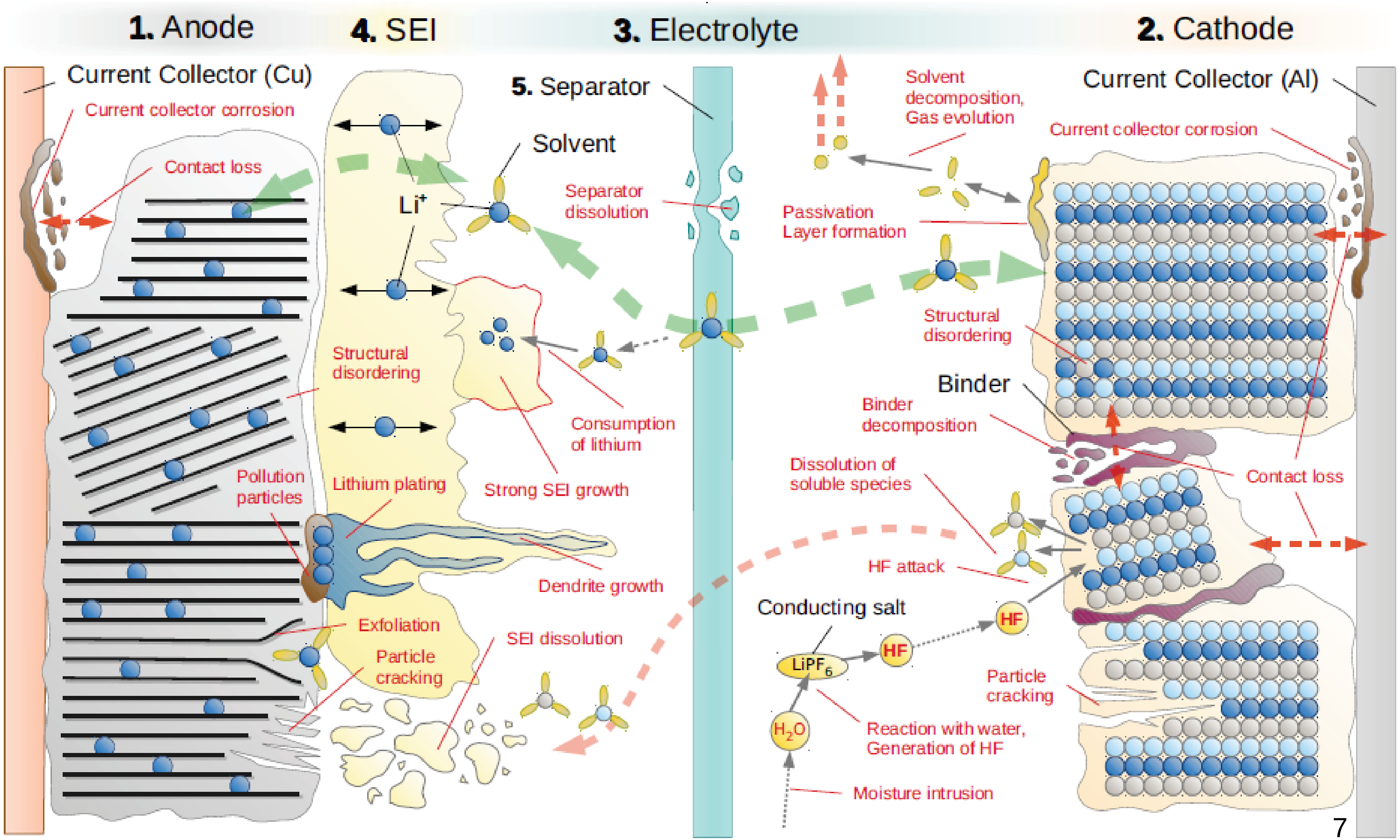




Capacity losses in Li-ion batteries

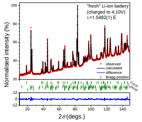


Main aging mechanisms within a Li-ion cell

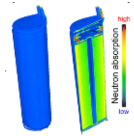


C. Schlasza et al. IEEE Transportation Electrification Conference and Expo (ITEC) (2014): 1-6.

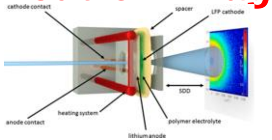
Neutron-based experimental techniques with proven relevance in battery research



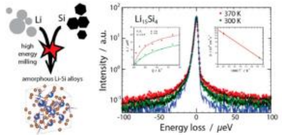
Neutron diffraction: detail of crystal structure, localisation and quantification of lithium; microstructural studies; phase analysis



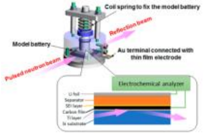
Neutron imaging: lithium distribution, gas formation, electrolyte dynamics



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



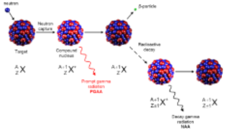
Quasielastic neutron scattering: in-situ structure and mobility of electrolytes in Li-ion batteries



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

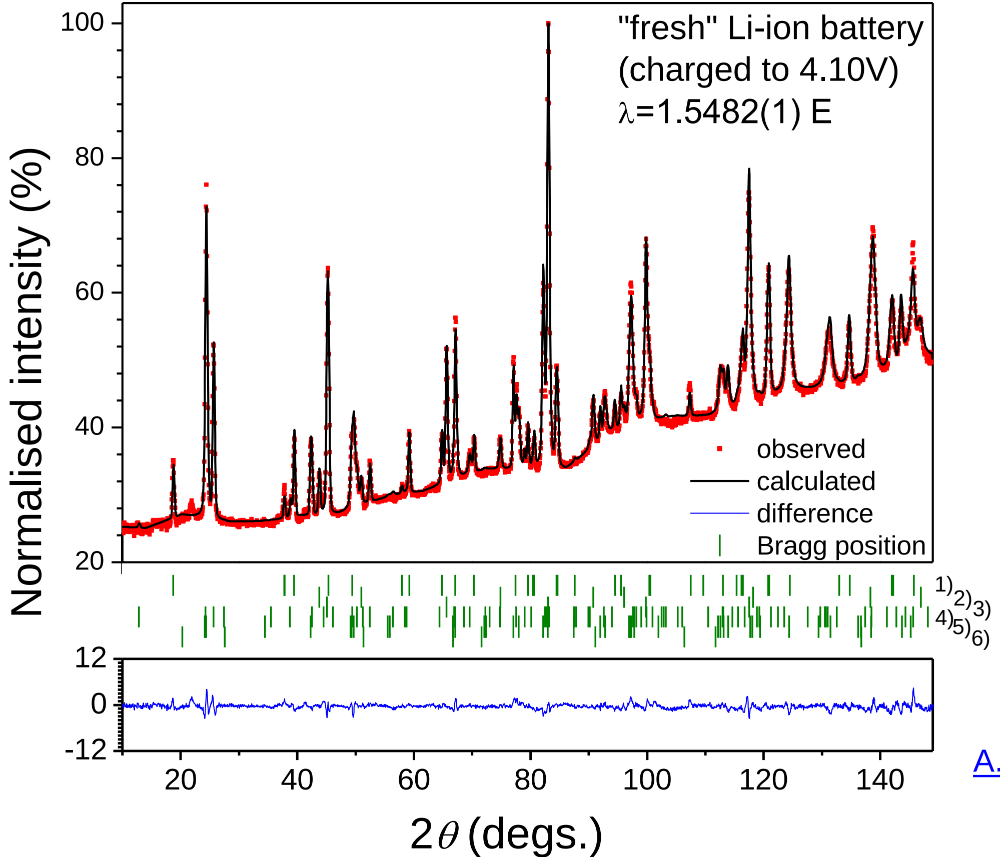
Neutron depth profiling: nanometer sensitive probe of lithium concentration in electrode materials

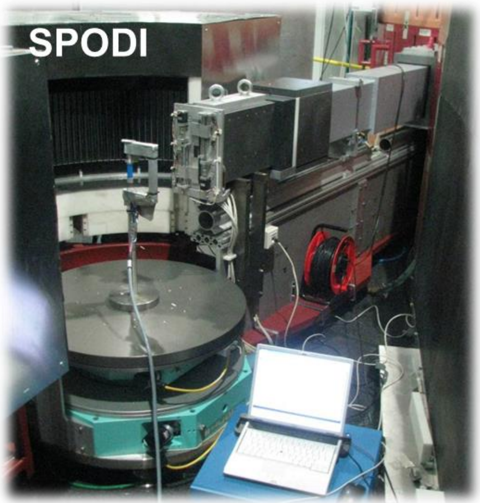
Positron spectroscopy: charge- and fatigue-induced defect formation



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

Rietveld refinement of typical diffraction pattern from high-energy 18650 Li-ion battery (SOC ~90%)



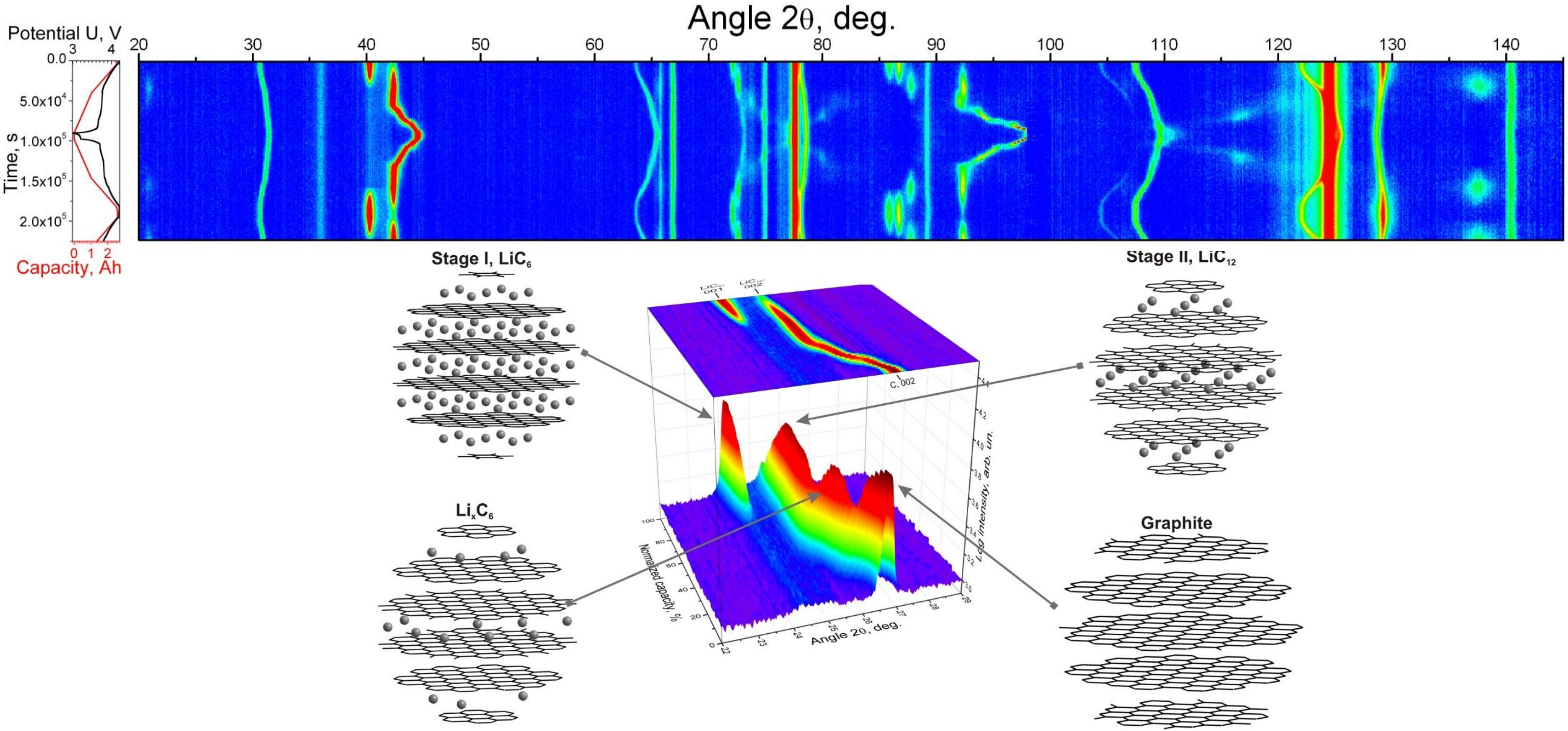


$LiCoO_2$ (1)
Cu (2)
Fe (3)
LiC_{12} (4)
LiC_6 (5)
Al (6)

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

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

Structural signature of Li-intercalation in the graphite

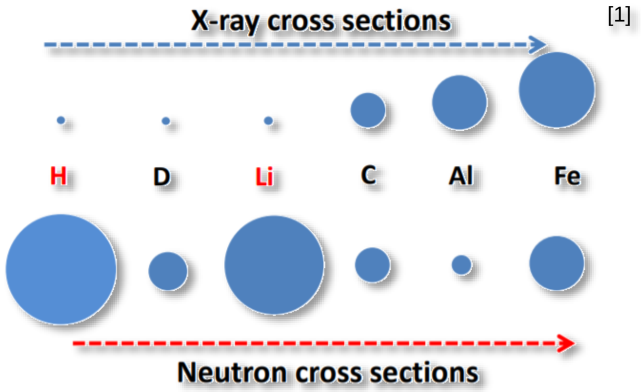


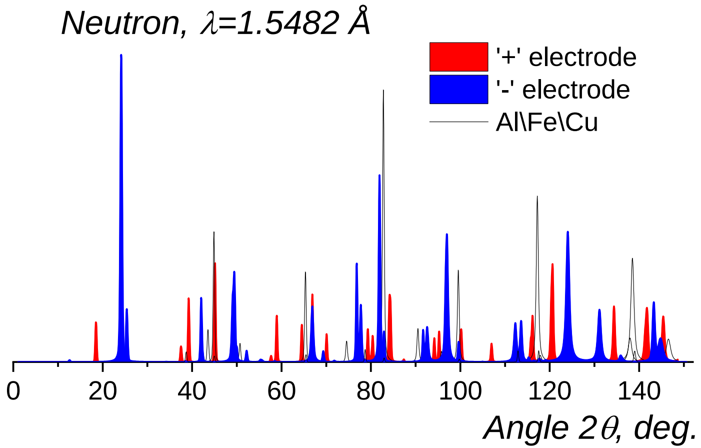
A. Senyshyn *et al.*, *J. Electrochem. Soc.* **160 (**2013) A3198

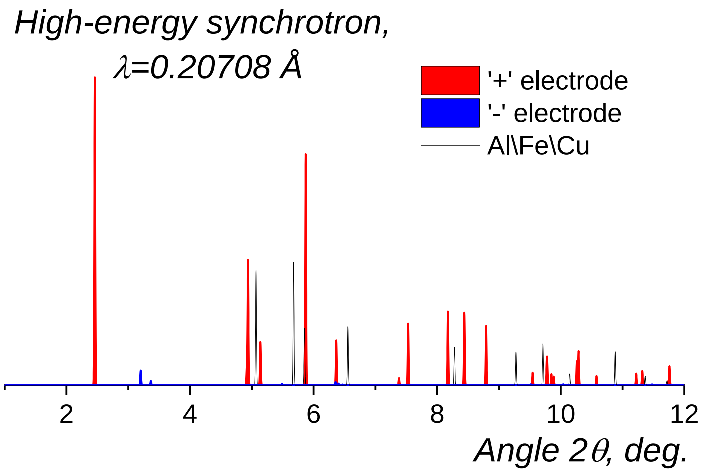
Comparison between X-Rays and neutrons

- X-Rays scatter at the electron cloud of the atoms
  → Stronger scattering power for heavier atoms

- Neutrons scatter at the nucleus of the atoms
  → Unsystematic scattering power
  → Sensitive to light elements





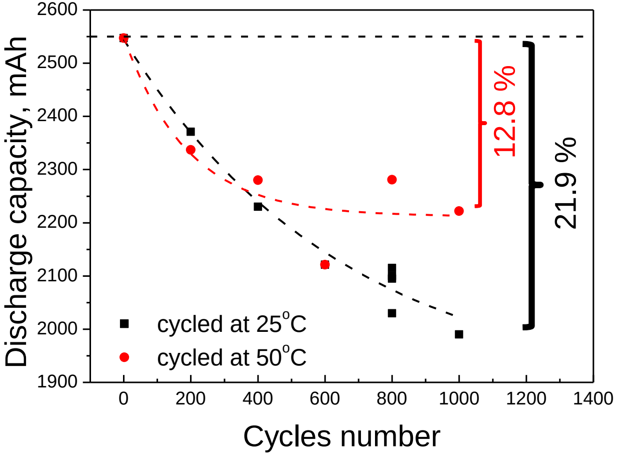


Active lithium losses

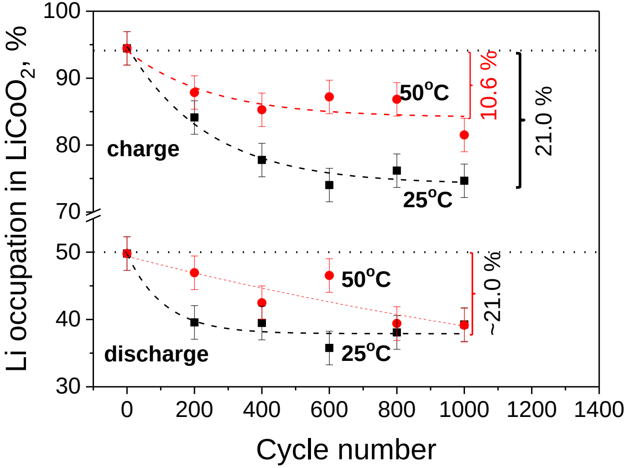
Non-destructive quantification of lithium in the anode and cathode

Effect on Li-concentration

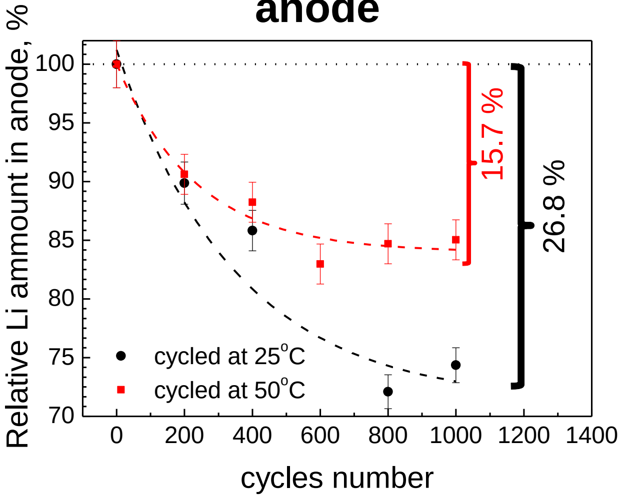
Cell capacity



cathode



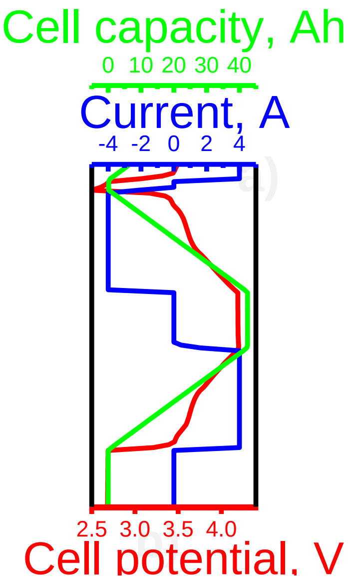
anode

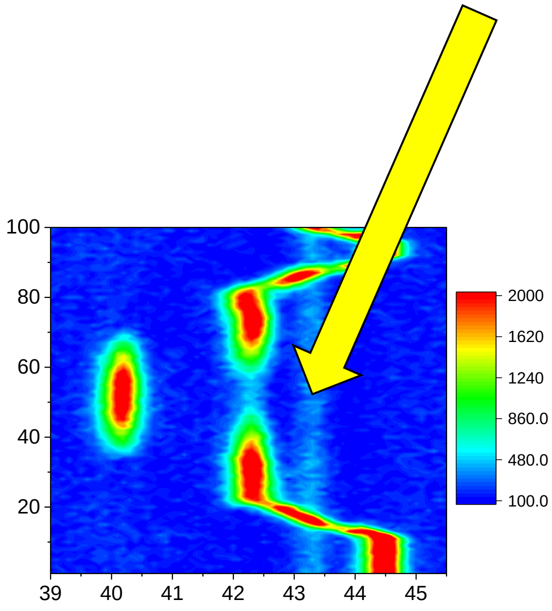


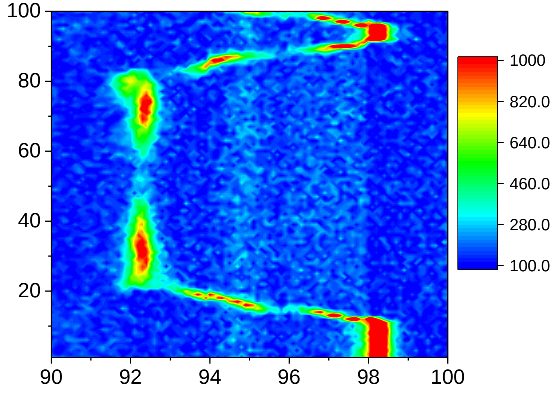
O. Dolotko et al., J. Electrochem. Soc. 2159(12) (2012) A2082-A2088

Loss of active anode

ca. 10% w/w of the graphite does not take part in the lithiation

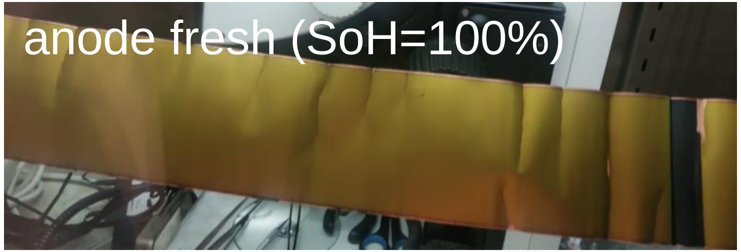


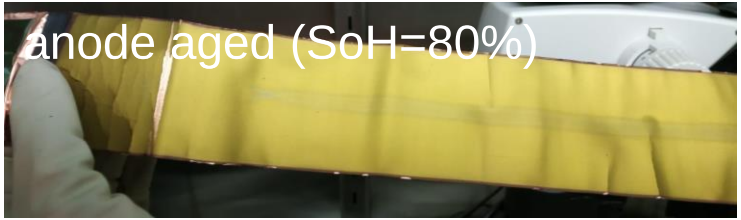


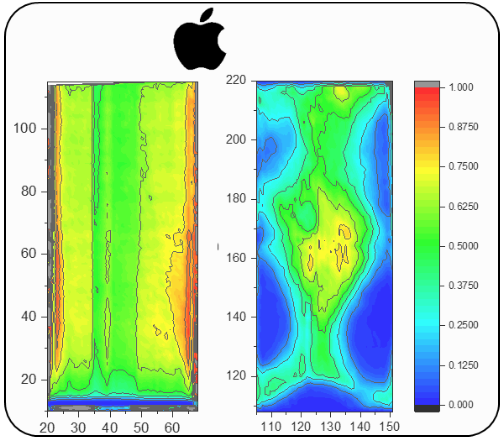


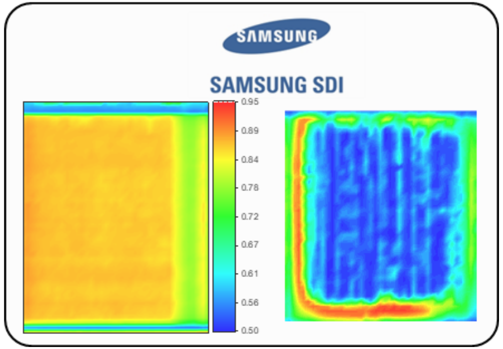
(unpublished)

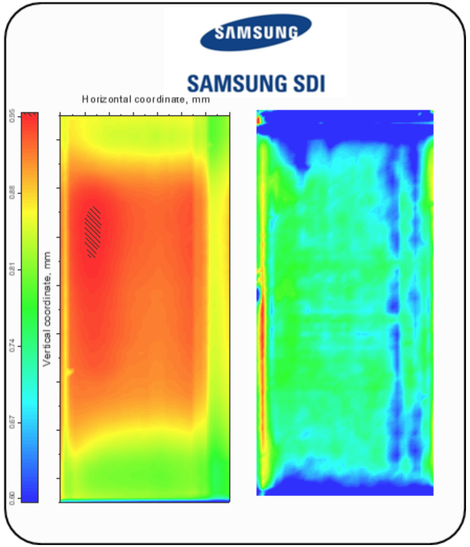
Lithium distribution uniformity – a challenge





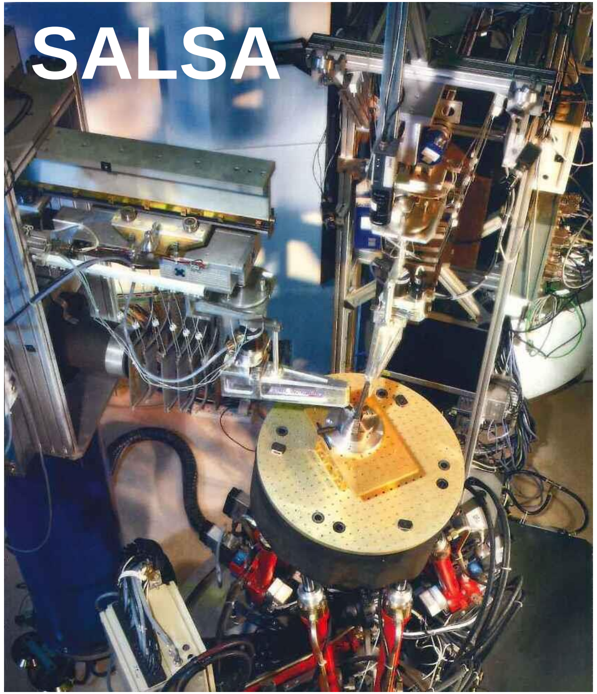






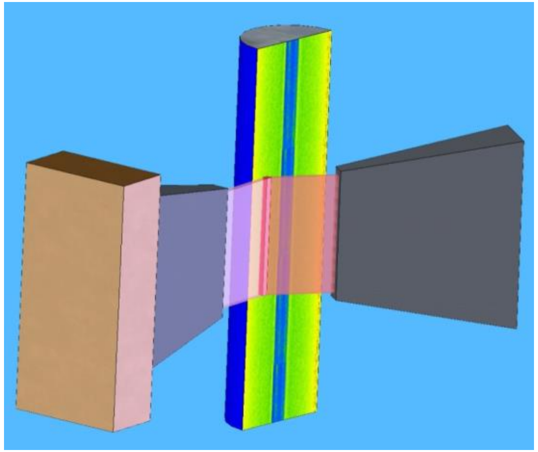
(unpublished)

Spatially-resolved neutron diffraction – setup (constant λ)



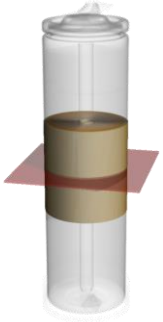
Spatially-resolved neutron diffraction – setup (constant λ)

Sketch of scattering setup

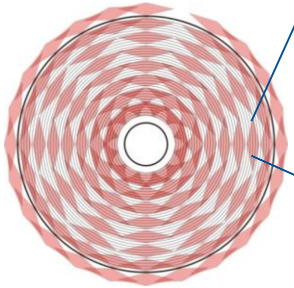


SALSA(ILL), STRESS-SPEC(MLZ)

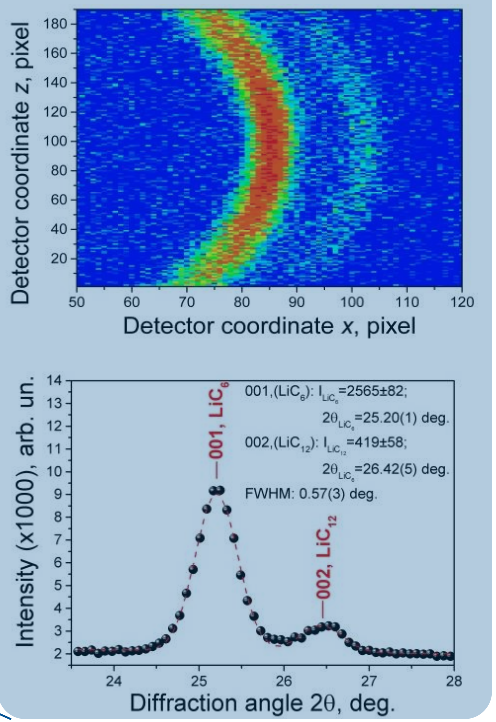
Cell irradiated volume



Gauge volume

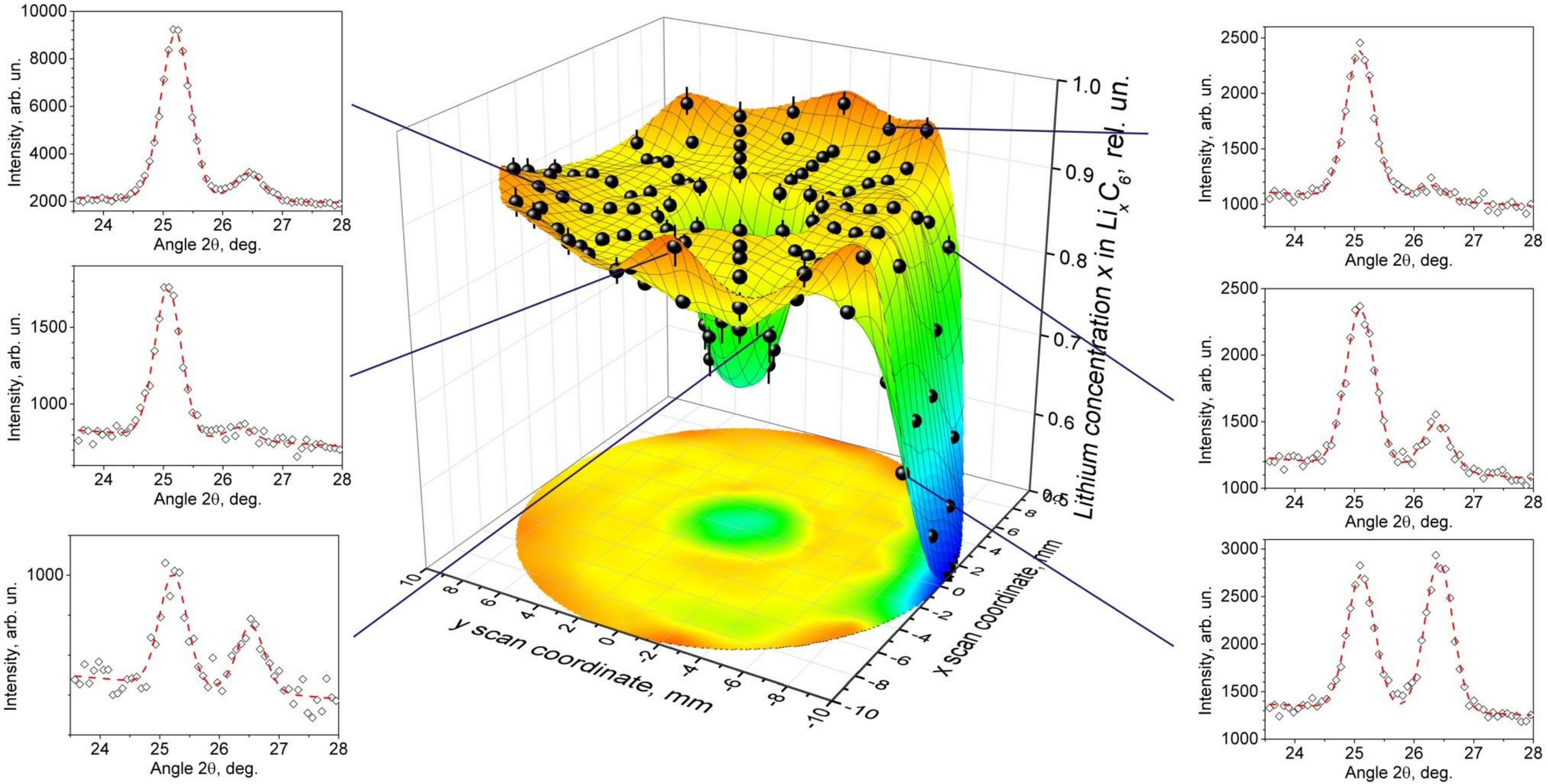


2D diffraction data



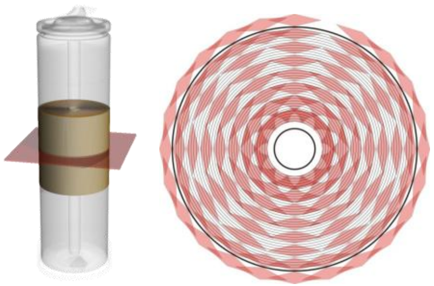
A.S. et al., Journal of Power Sources, 245 (2014) 678-683.

Spatially-resolved neutron diffraction on LIB: an example

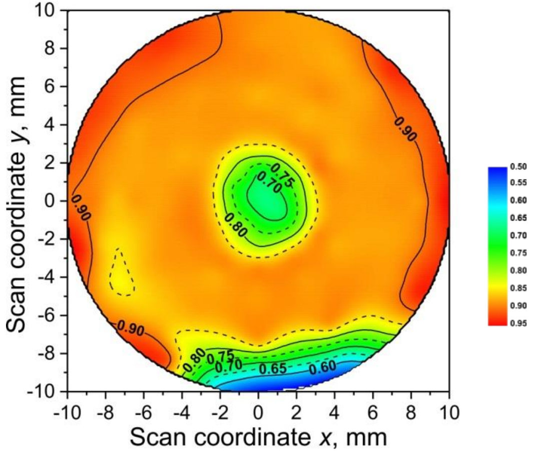


A.S. et al., Sci Rep, 5 (2015) 18380.

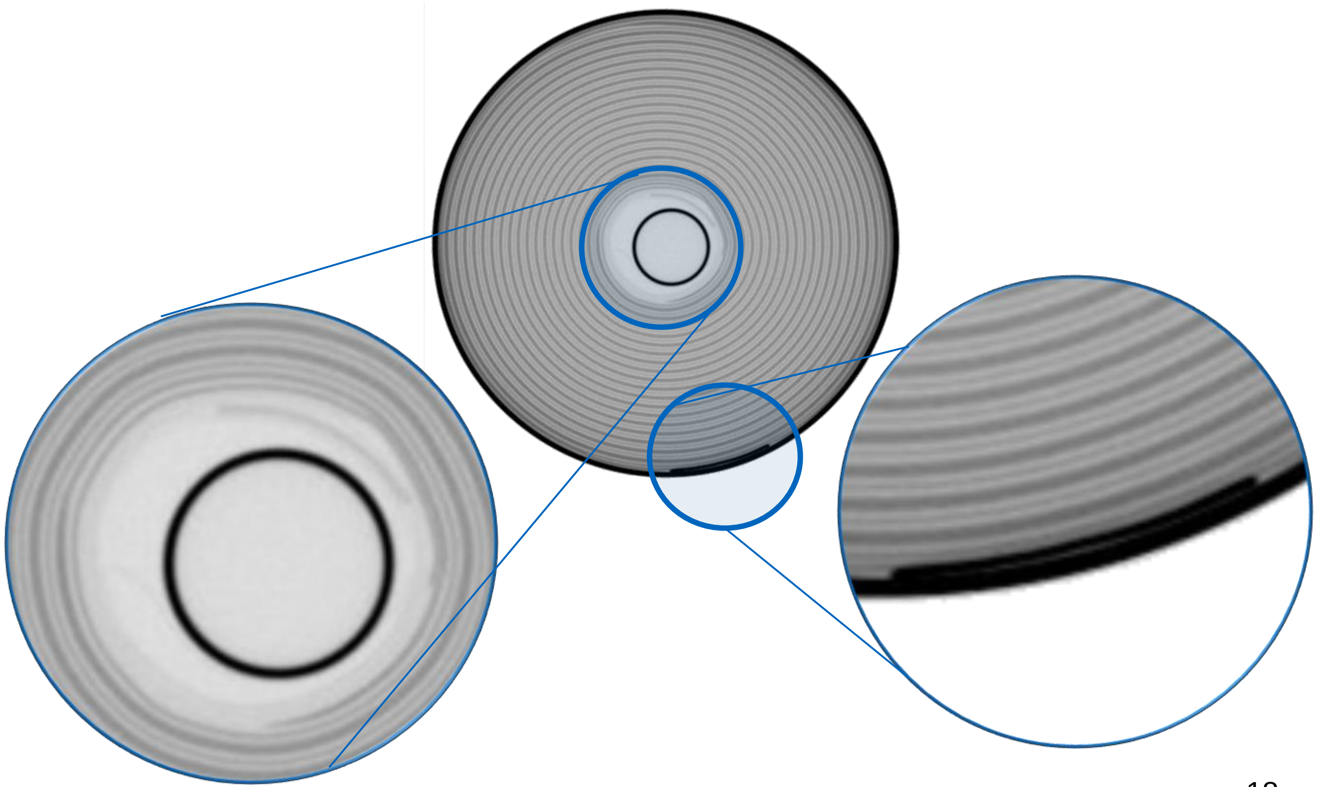
Spatially-resolved neutron diffraction on LIB: example



Neutron diffraction

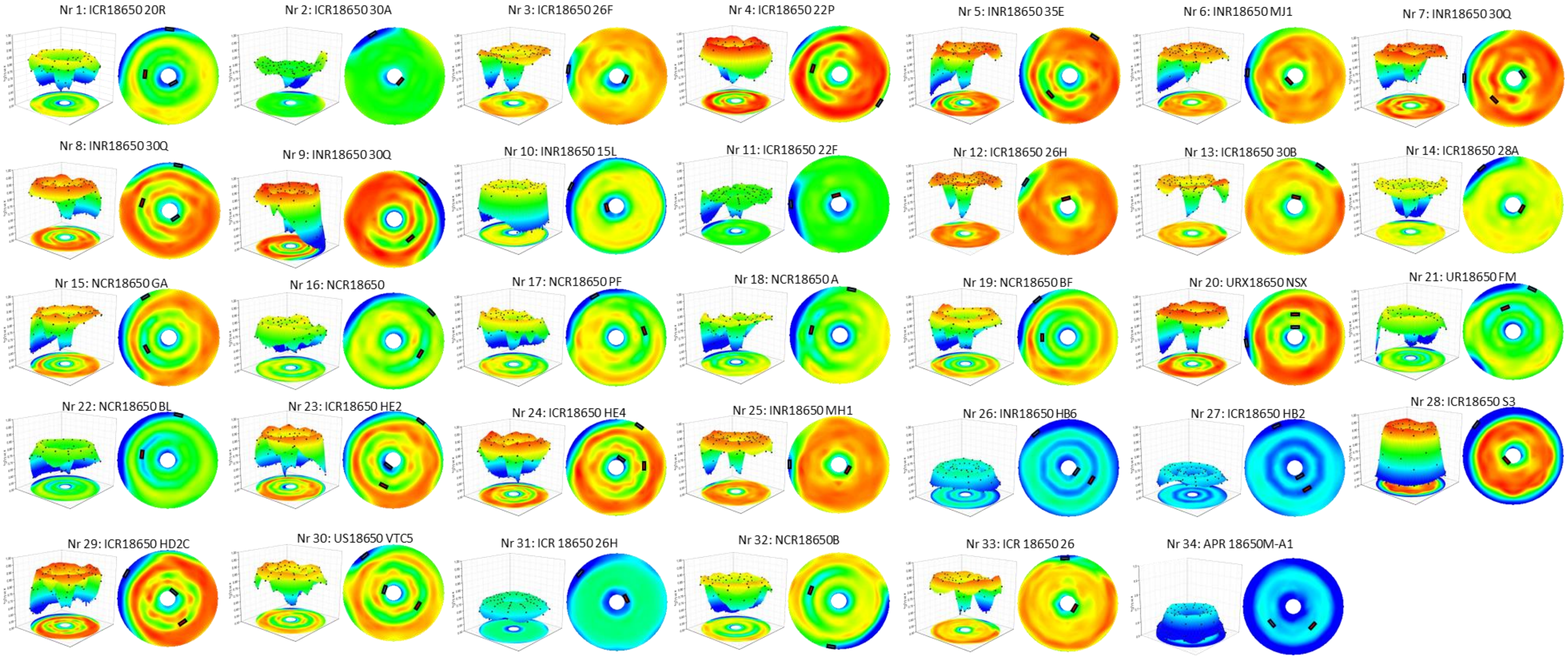


Lab X-ray CT



A.S. et al., Sci Rep, 5 (2015) 18380.

Lithium heterogeneities in state-of-the-art cylinder LIBs



Different kinds of lithium distribution were observed for a batch consisting of 34 LIBs

D. Petz, …, A.S., Batteries & Supercaps, 4 (2021) 251-251.

Lithium uniformity of high-energy LIB – effect of aging

Gauge volume configuration

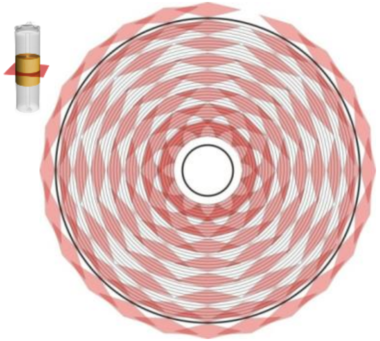
Lithium concentration x in Li_xC_6, rel. un.

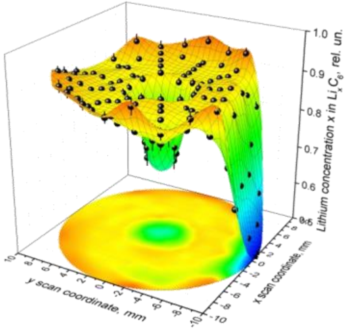
Surface plot

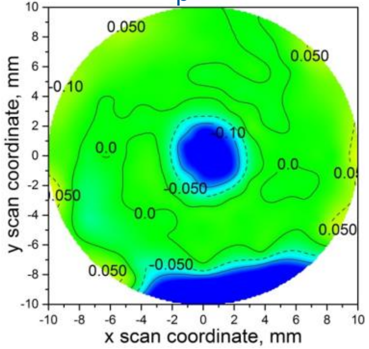
$x - x_p = 0.88$

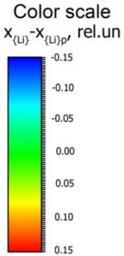
FRESH

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



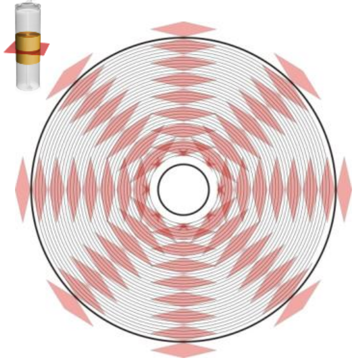


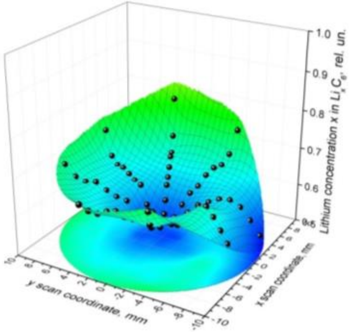


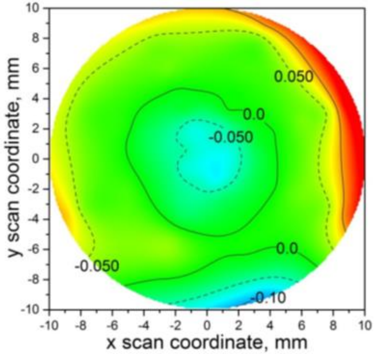


AGED

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



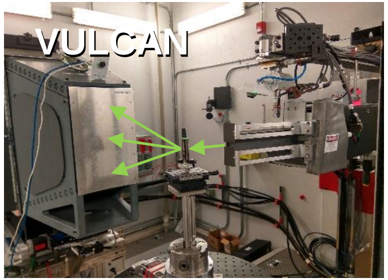


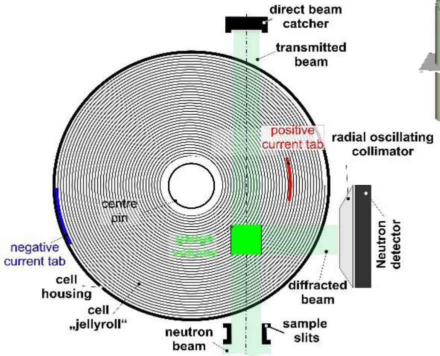


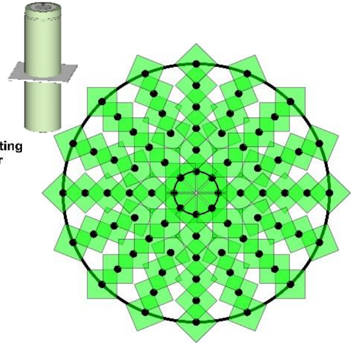
M.J. Muhlbauer … ,A.S., J. Power Sources, 348 (2017) 145-149.

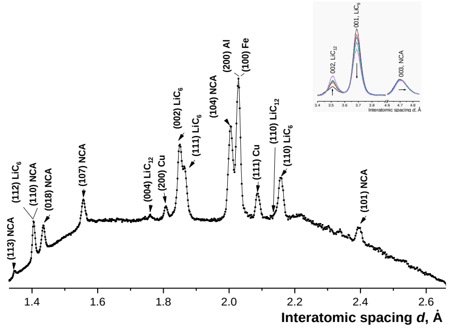
Cell (type 2) uniformity – effect of aging (time-of-flight)

OAK RIDGE National Laboratory

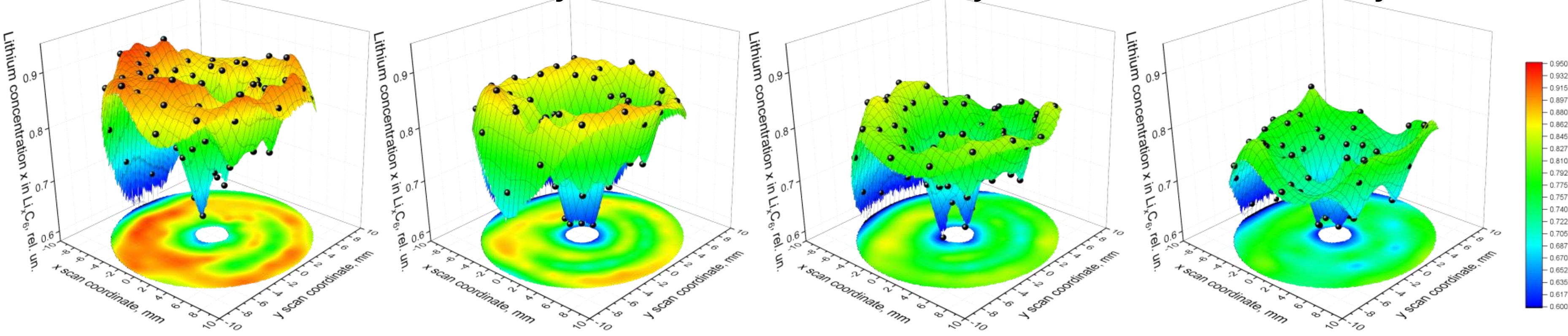








Fresh | 120 cycles | 200 cycles | 400 cycles

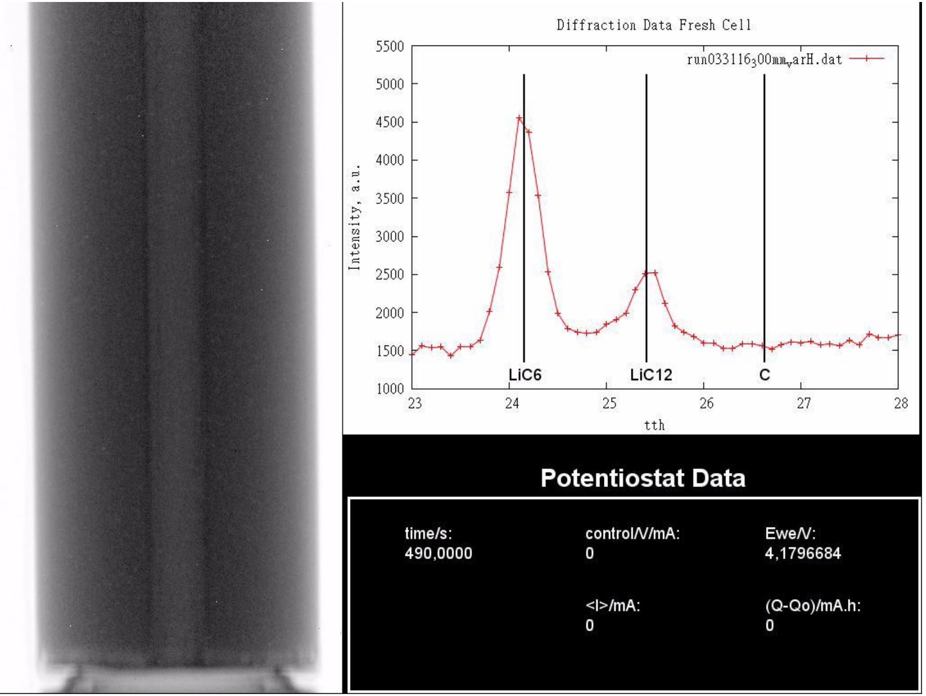


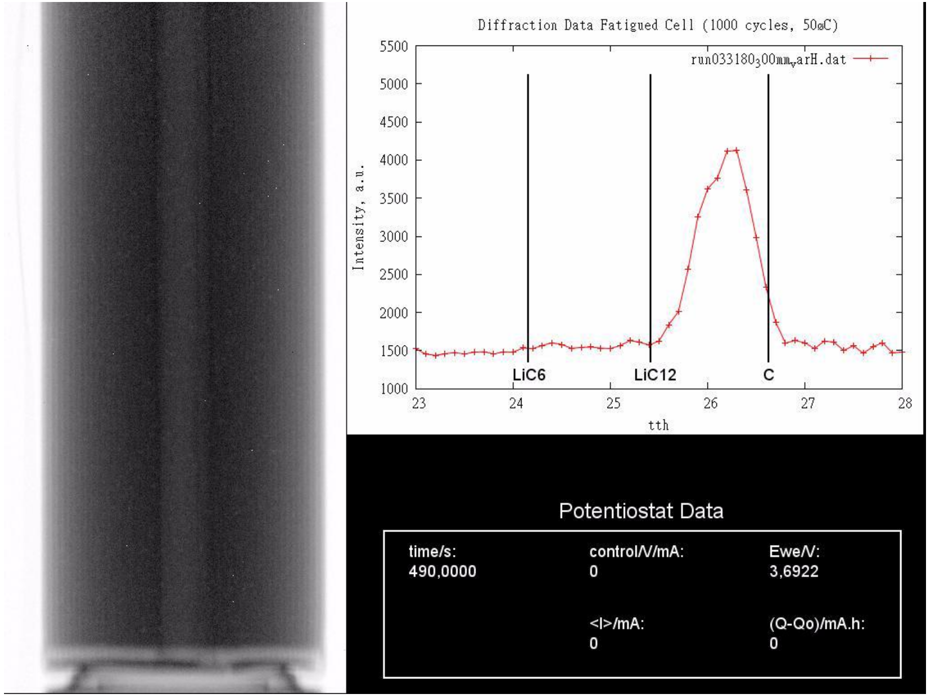
D. Petz et al., J. Power Sources 448 (2020) 227466

Loss of liquid electrolyte

fresh

aged



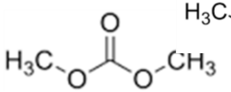


M.J. Mühlbauer, et al., J. Power Sources. (2017). **348**, 145-149

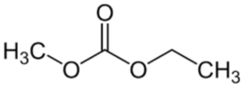
Quantification of electrolyte in cylinder-type LIB

LIB electrolyte: mixture of organic solvents with lithium salt

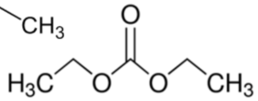
Dimethyl carbonate



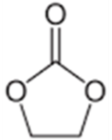
Ethyl methyl carbonate



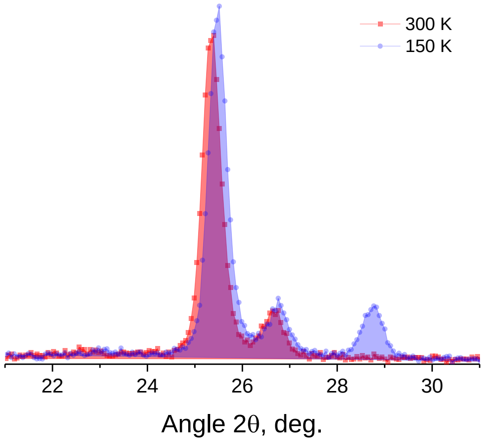
Diethyl arbonate

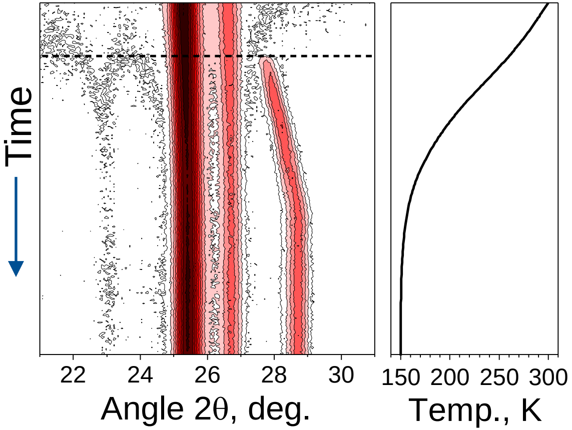


Ethylene carbonate

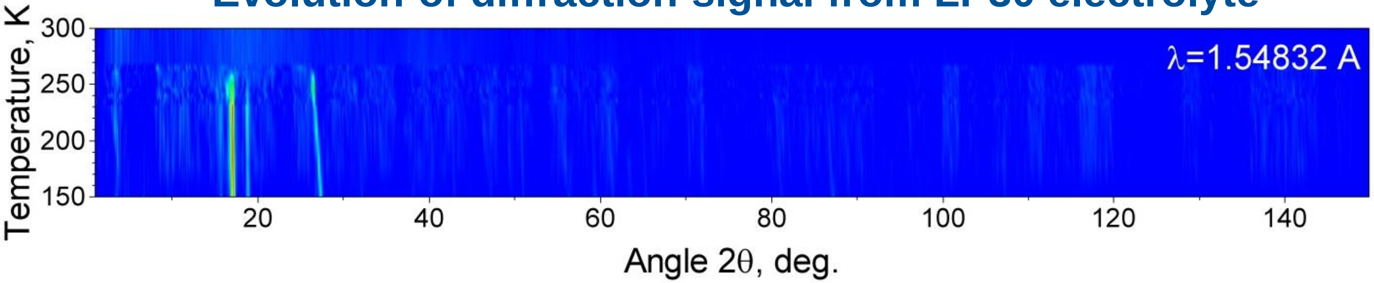


Diffraction pattern from 18650-type LIB at low temperature





Evolution of diffraction signal from LP30 electrolyte



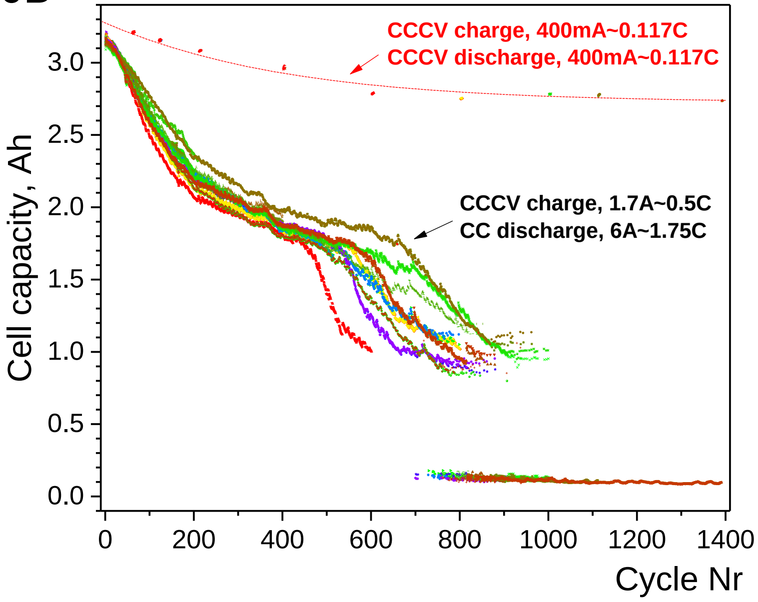
A.S. et al., J. Power Sources, 282 (2015) 235-240.

Capacity and diffraction on a „high-performance“ LIB

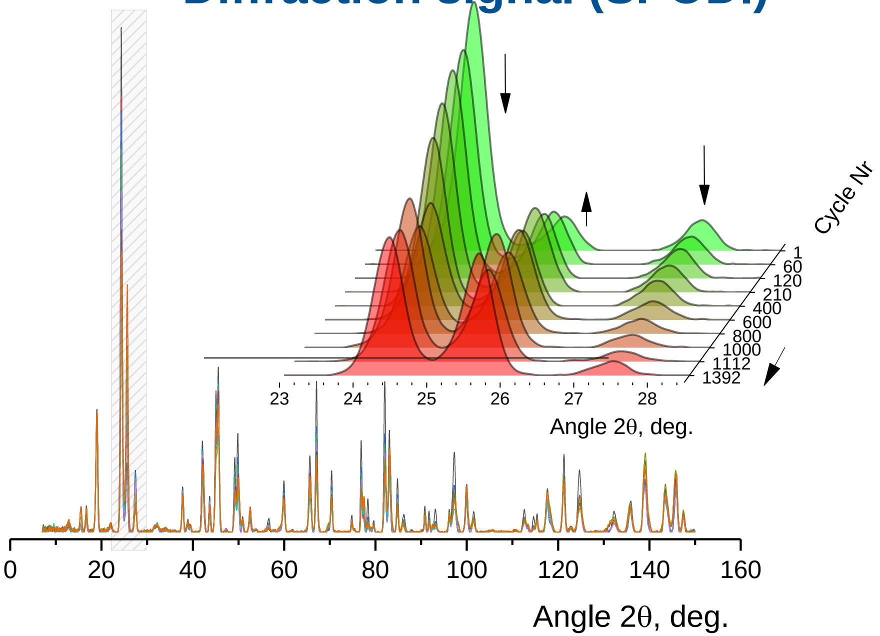
Panasonic
NCR18650B

NCA|C
3.4 Ah

Evolution of cell capacity

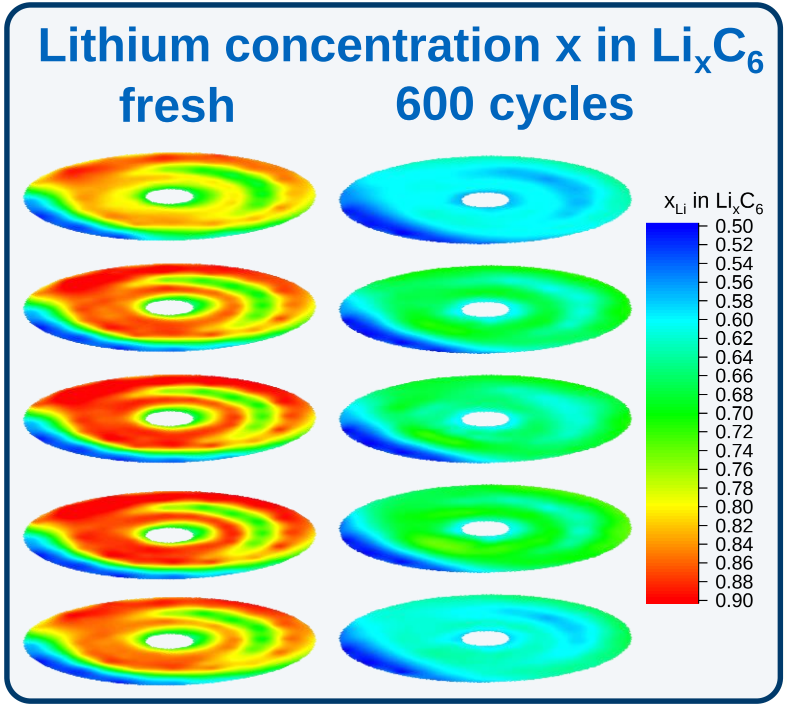


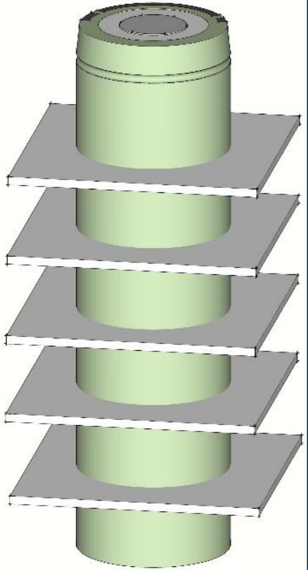
Diffraction signal (SPODI)

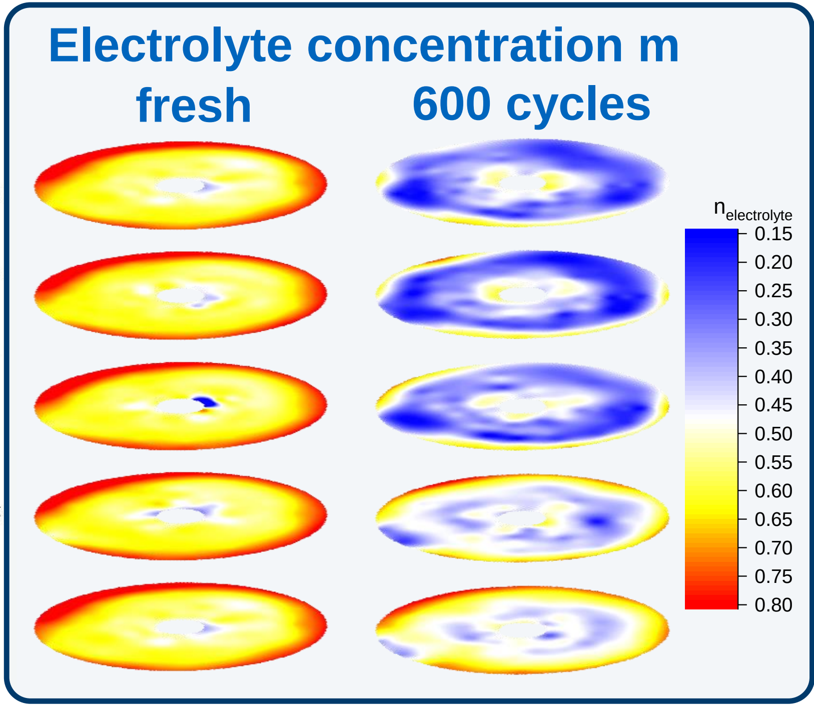


M. Mühlbauer, …, A.S., J. Power Sources, 475 (2020) 228690.

Lithium and electrolyte distribution in cylinder-type LIB

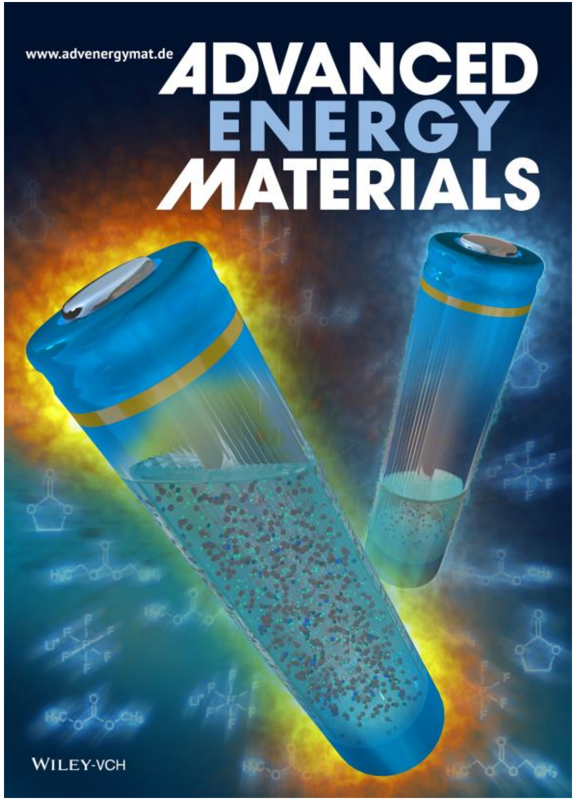


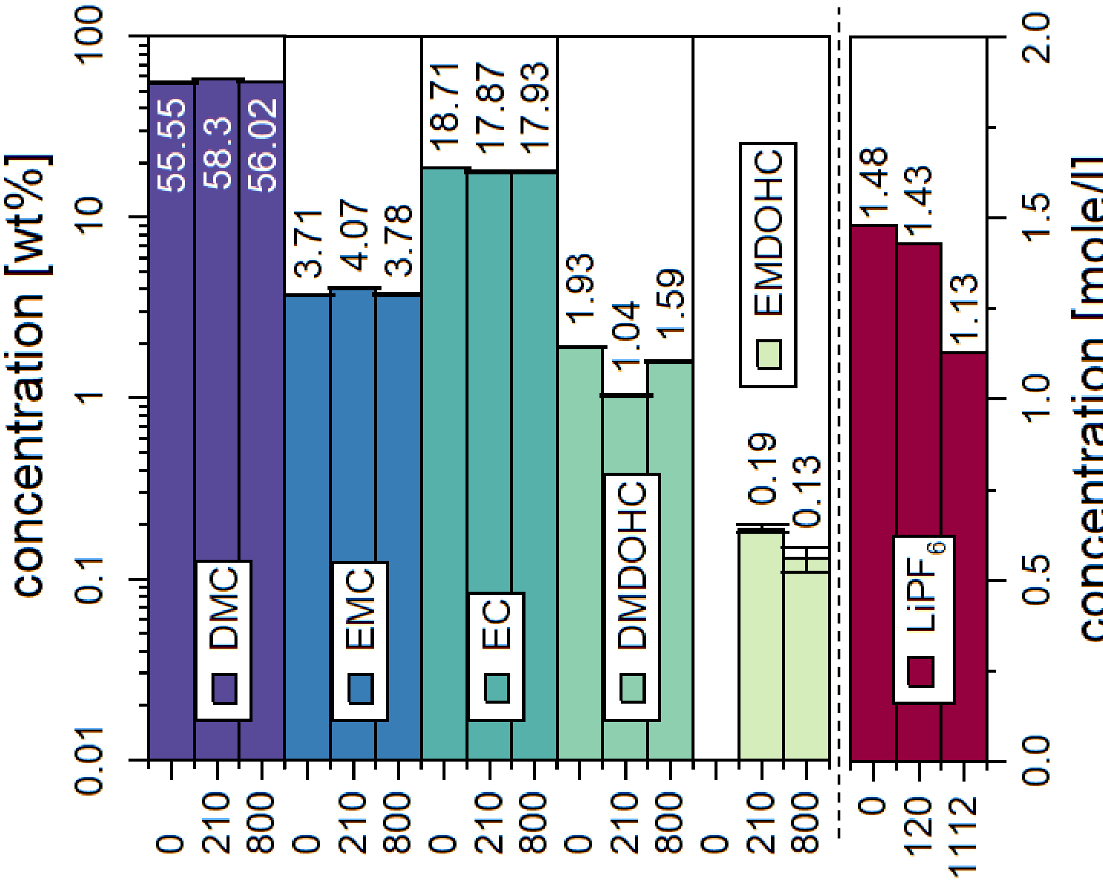




M. Mühlbauer, …, A.S., J. Power Sources, 475 (2020) 228690.

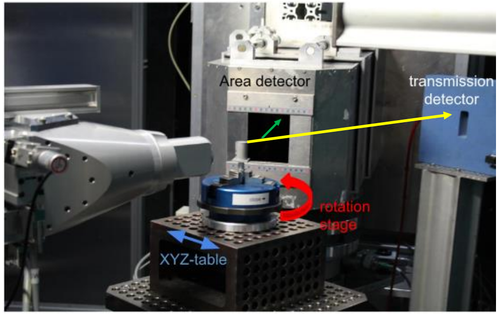
Losses of lithium salt





D. Petz et al., *Adv. Energy Mater.* 2022, 2201652.

Future prospects: Neutron-diffraction CT



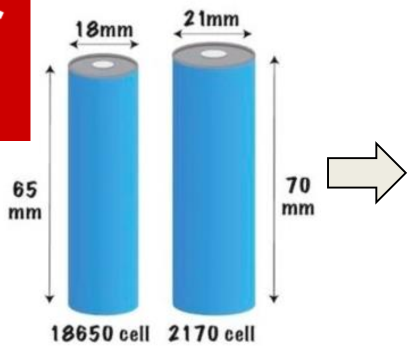
Note: Synchrotron-based XRD is poorly sensitive to electrolyte

ND-CT: : development and adaptation

Reported ND-CT for the first time at STRESS-SPEC (MLZ)

V. Kochetov, …, A.S. J. Phys. Cond. Matter, 33 (2021) 105291.

- LIBs for automotive applications are getting bigger



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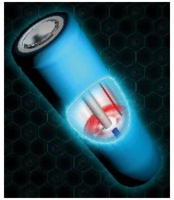
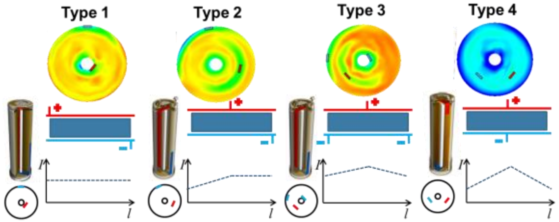
Summary

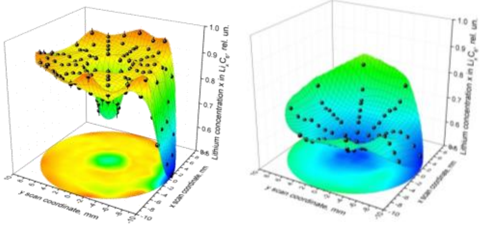
Understanding of structure can be a key for the development and optimisation of closed electrochemical systems

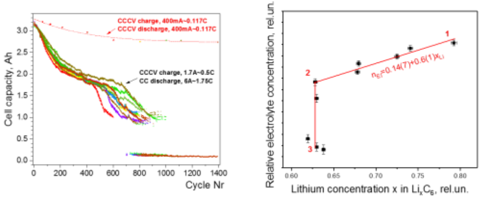




Lithium distribution in the graphite anode is non-uniform, degree of its uniformity depends on the cell type and properties and correlated to current densities

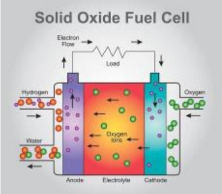
Aging-driven electrode degradation is non-uniform along and across the electrode stripe, creating a heterogeneous stress distribution





Two-regimes of the cell cycling were observed from the correlation of lithium and electrolyte losses in commercial Li-ion batteries

Developed methods can be used in other fields, e.g. „beyond-lithium“, solid-oxide fuel cells, catalysts under operation



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Thank you for listening