MLZ
Heinz Maier-Leibnitz Zentrum

Neutron diffraction and imaging on battery systems¶

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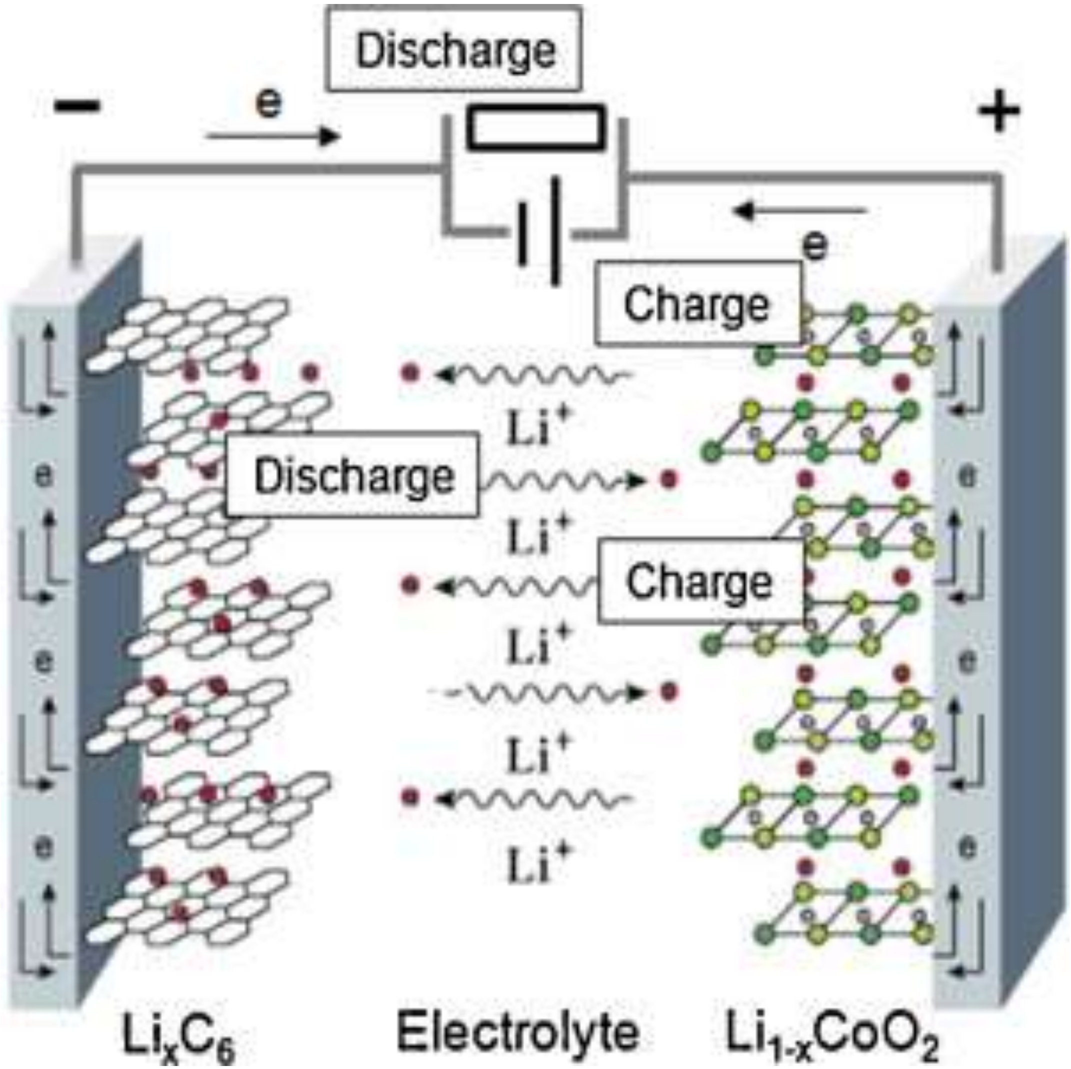
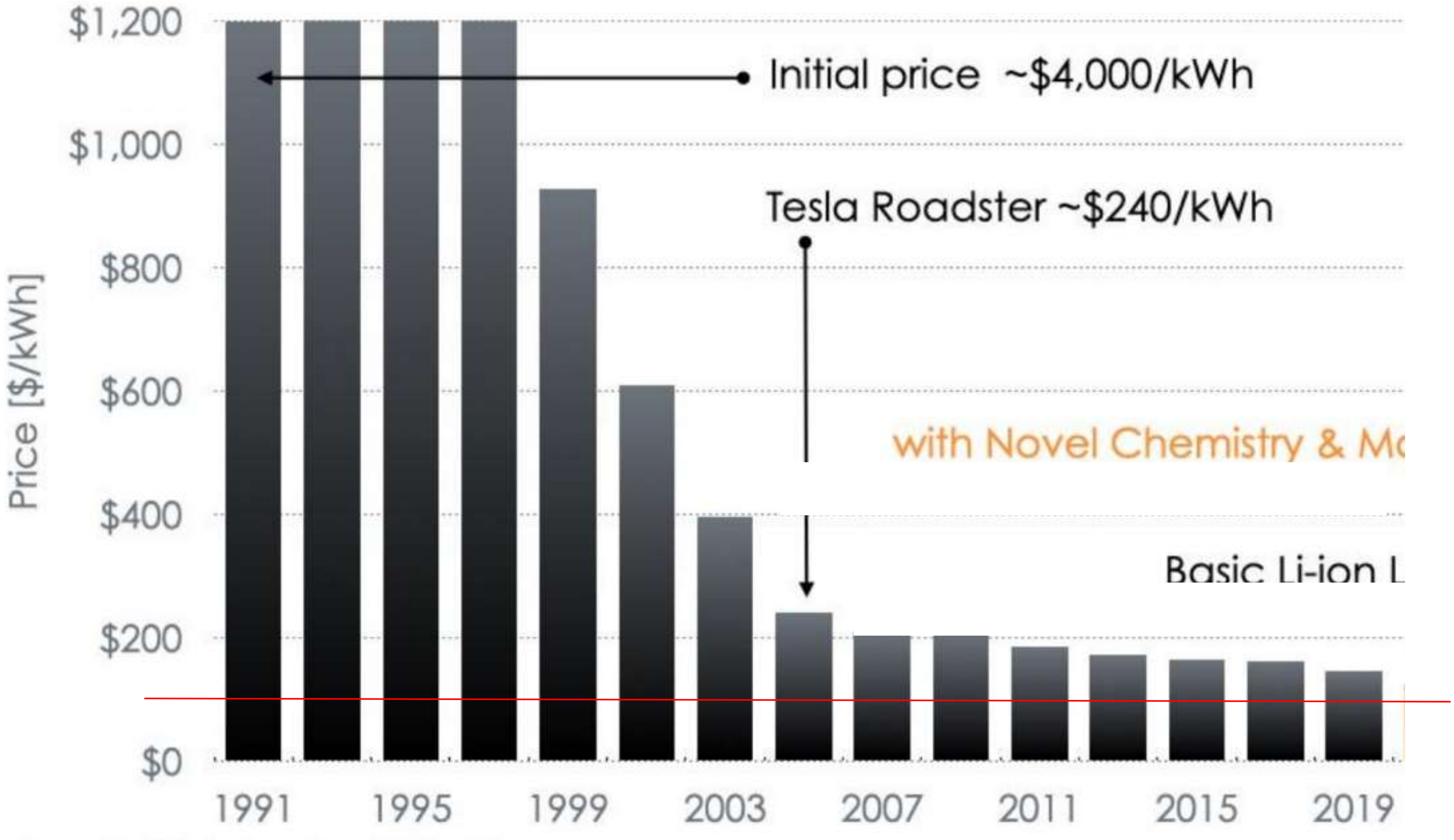
Li-ion battery: principle of operation

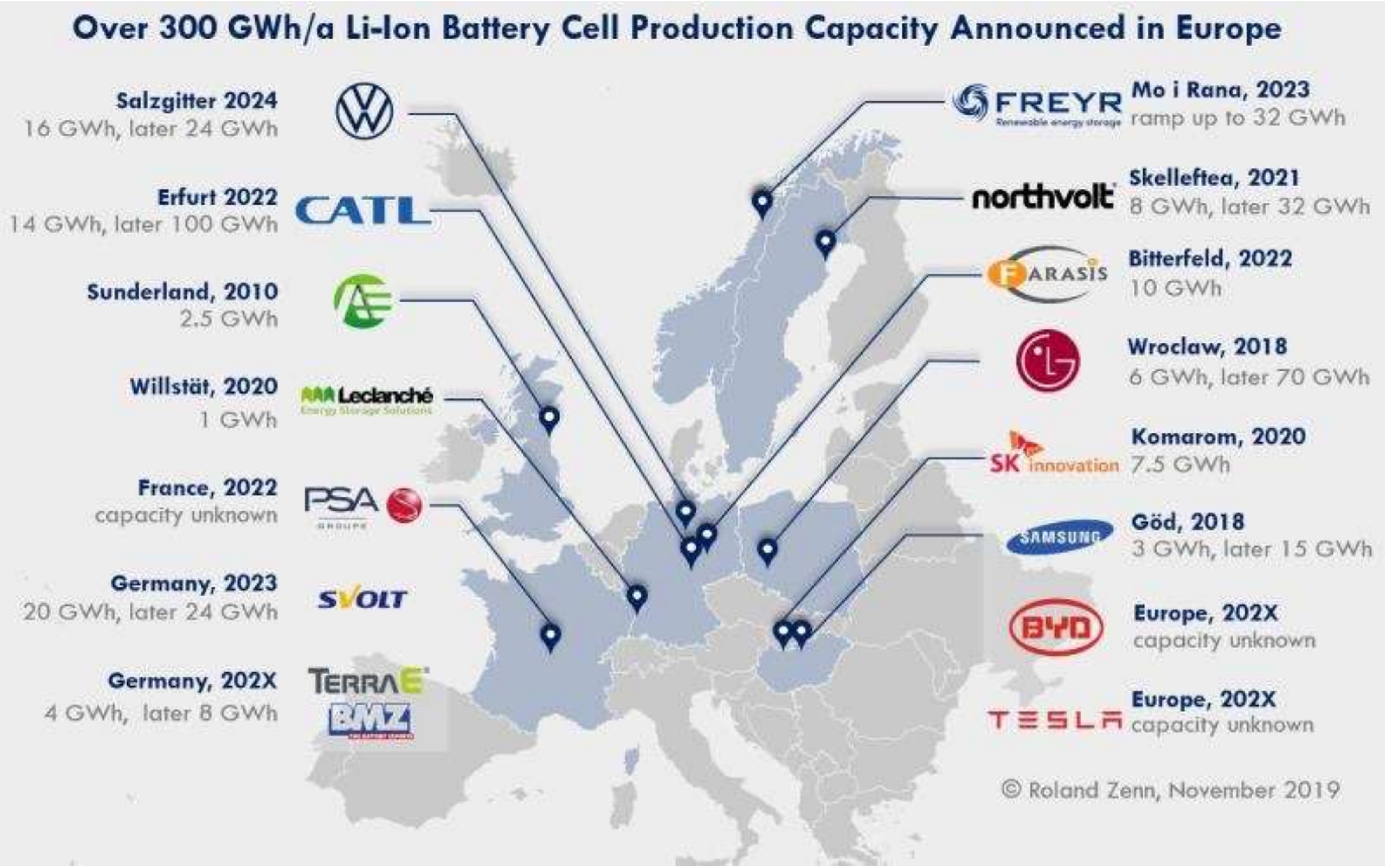


Market price $/kWh based on Li-ion technology

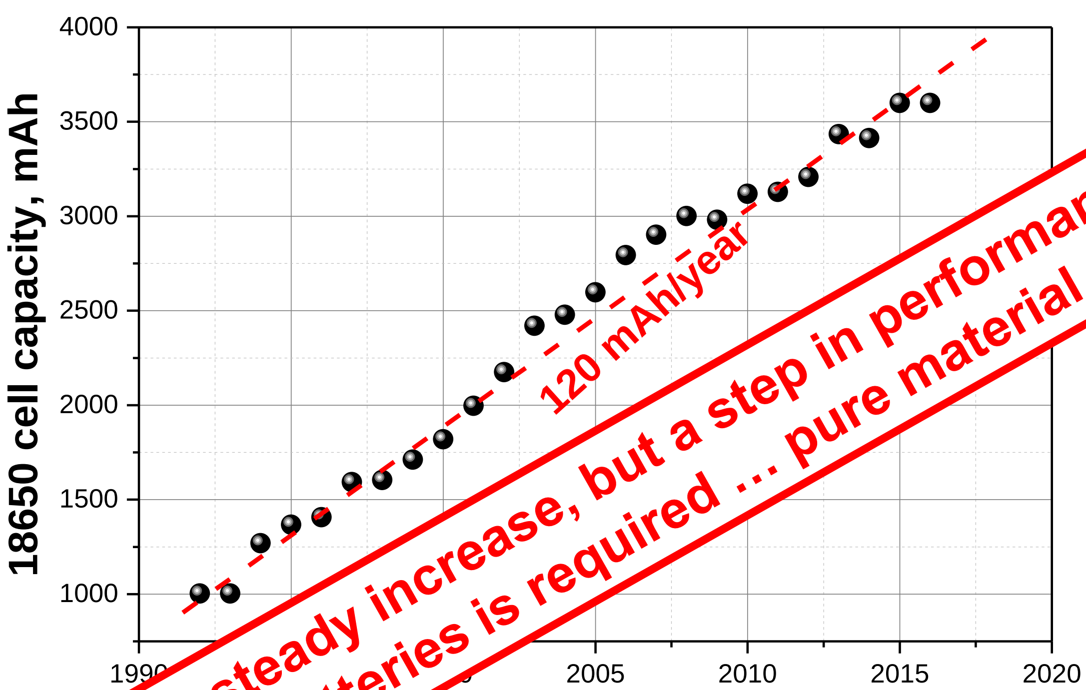


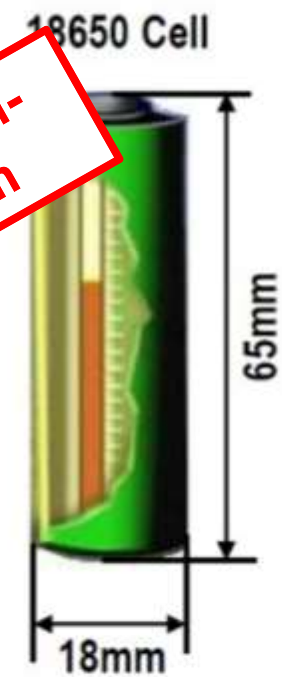
Courtesy: Gleb Yushin

Projected production of Li-ion batteries in Europe



Time evolution of 18650 cell capacity





Not steady increase, but a step in performance of Li-ion batteries is required … pure material problem

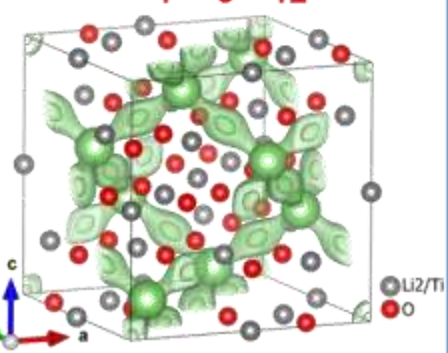
Moore's law does not hold true for battery development

- 120 mAh/annum average increase rate over almost 25 years
- ~ 3.5 %/year relative increase
- Since 2012 the capacity increase is achieved by voltage increase and introduction of Si to graphite anodes

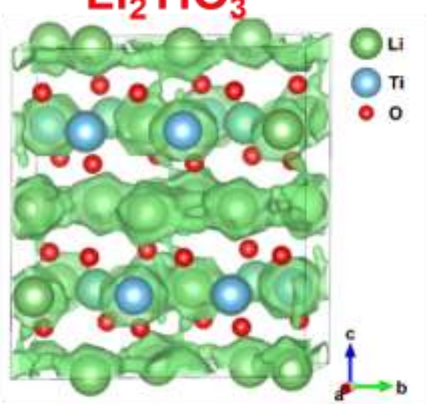
Materials for battery applications

Anode materials

$Li_4Ti_5O_{12}$

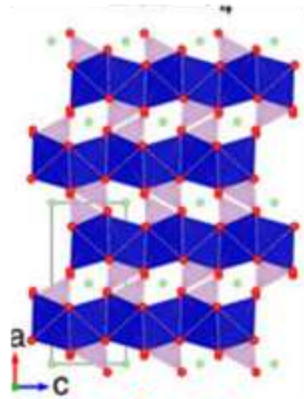


Li_2TiO_3

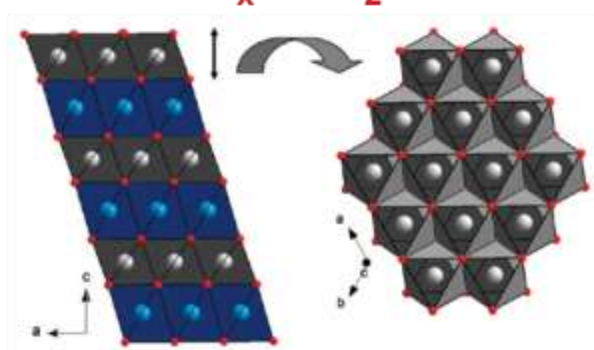


Cathode materials

$Li_{1-x}CoPO_4$

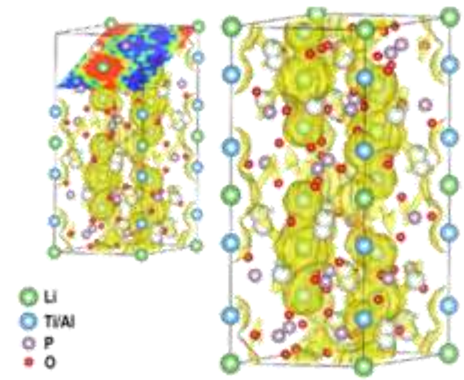


Li_xMoO_2

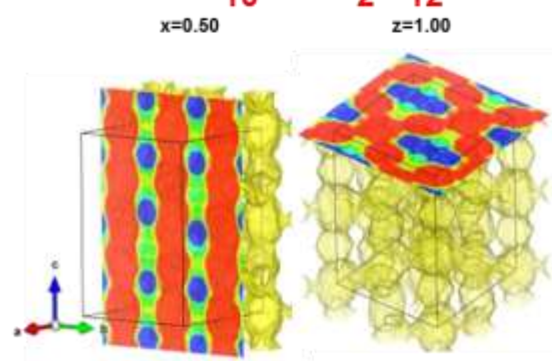


Lithium electrolytes

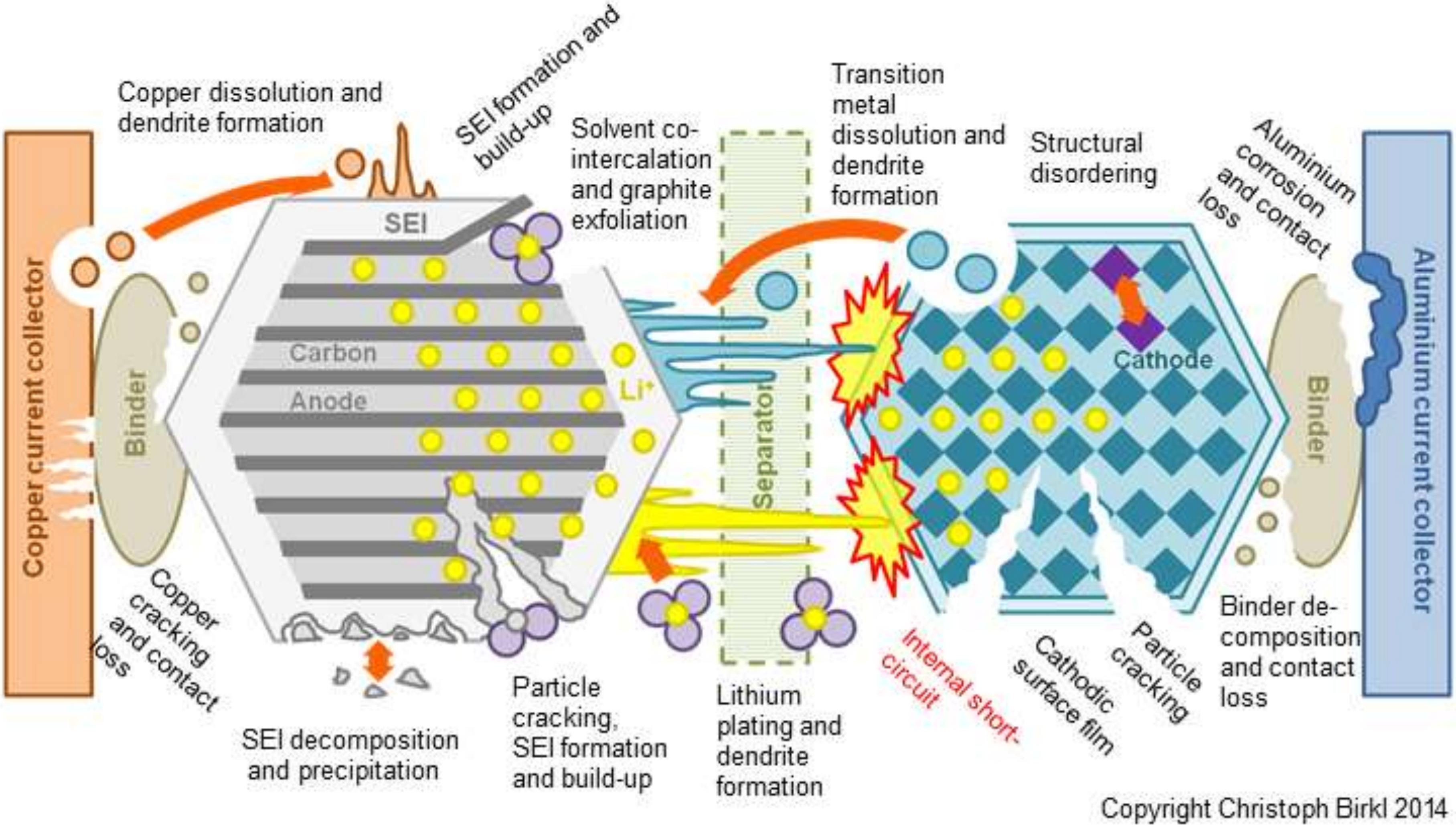
$Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$



$Li_{10}GeP_2S_{12}$



Different mechanisms of Li-ion battery degradation



Neutron-based experimental techniques with proven relevance\impact 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;

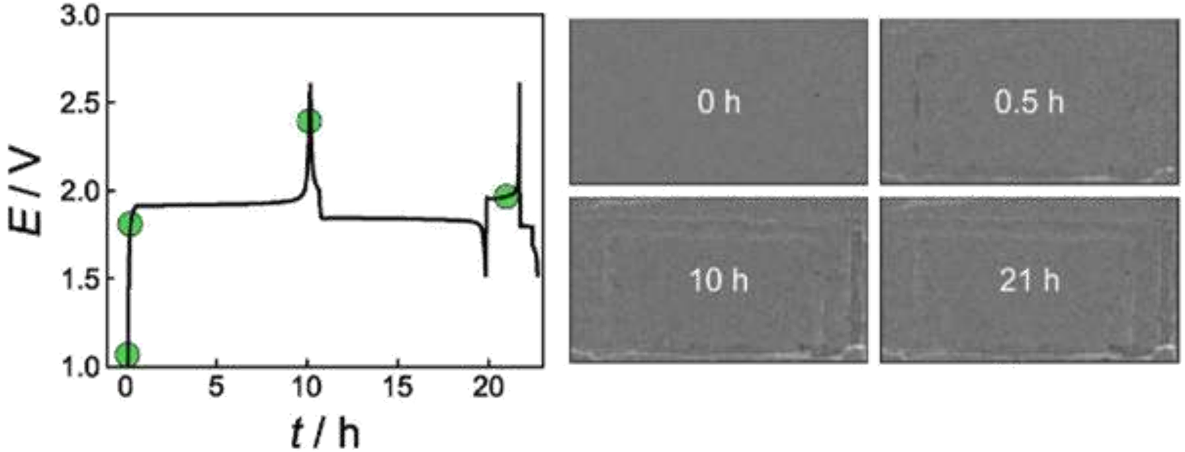
Neutron depth profiling: nanometer sensitive probe of lithium concentration in electrode materials;

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

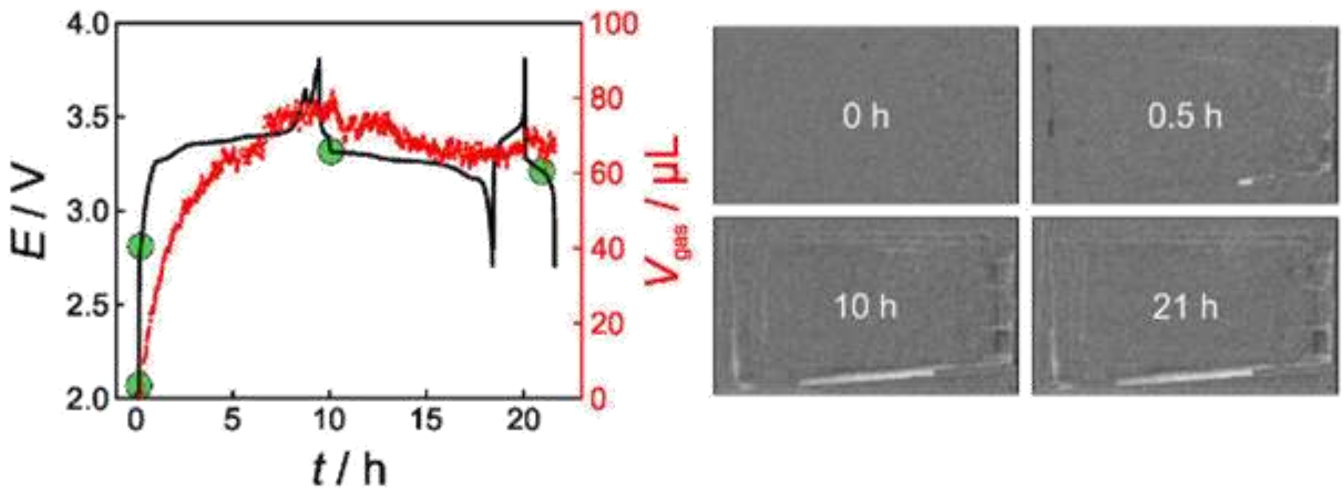
Neutron and Prompt gamma activation analysis: non-destructive and simultaneous elemental/isotope analysis;

Gas evolution in pouch cells studied by neutron radiography

LFP\LTO cell

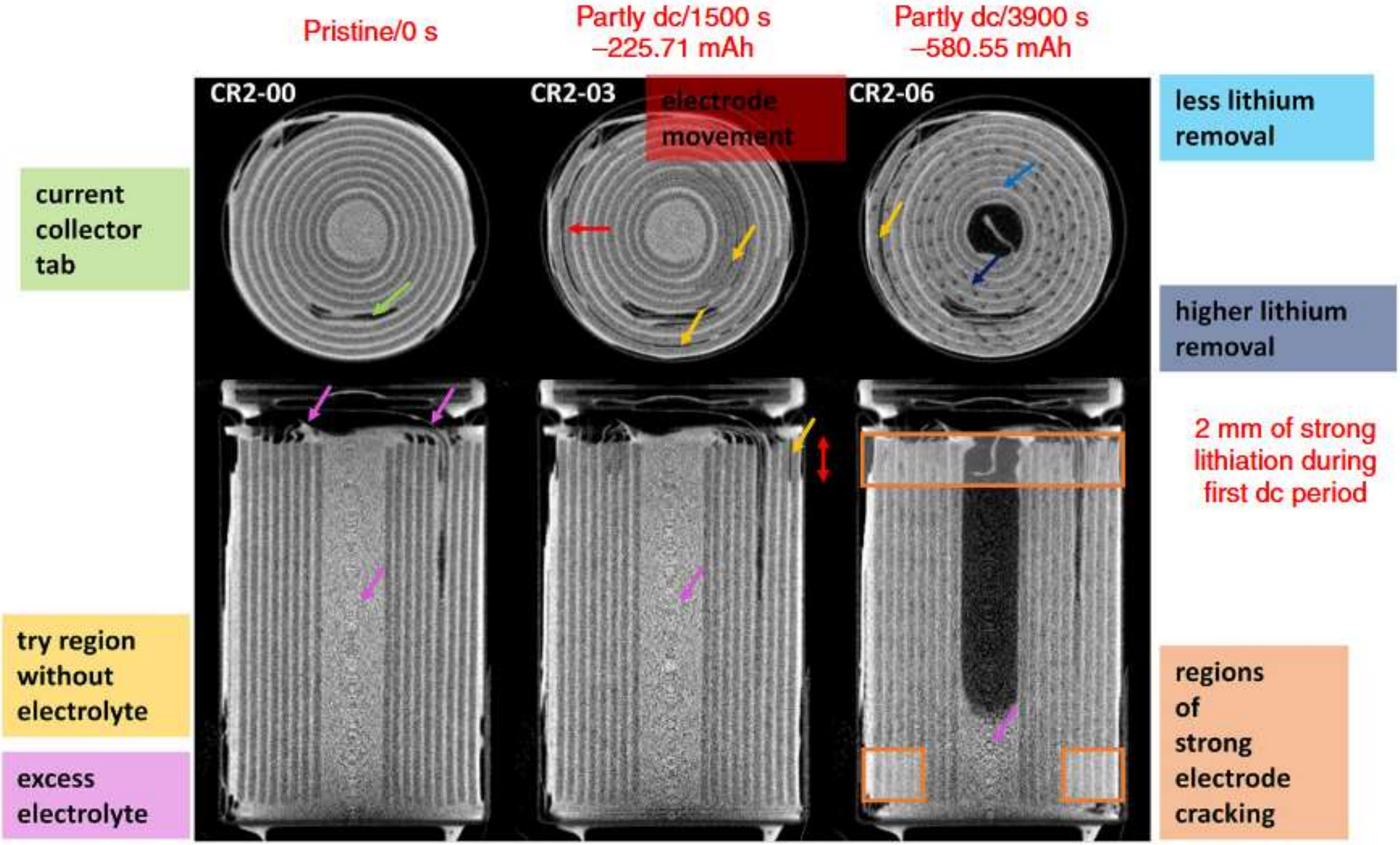


LFP\graphite cell



B. Michalak et al., Sci. Rep. 5 (2015) 15627

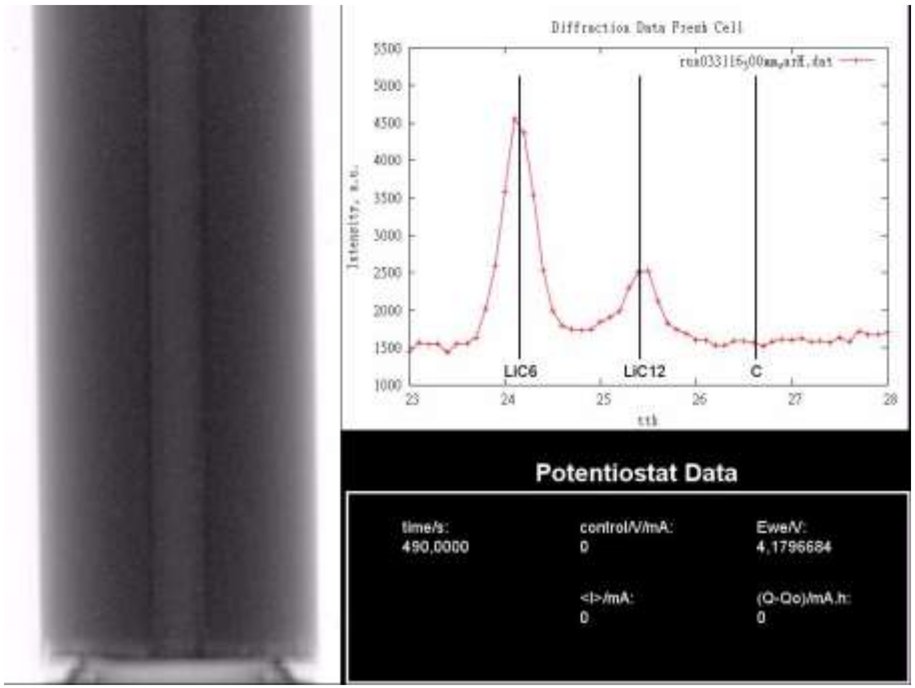
4D imaging on lithium-batteries



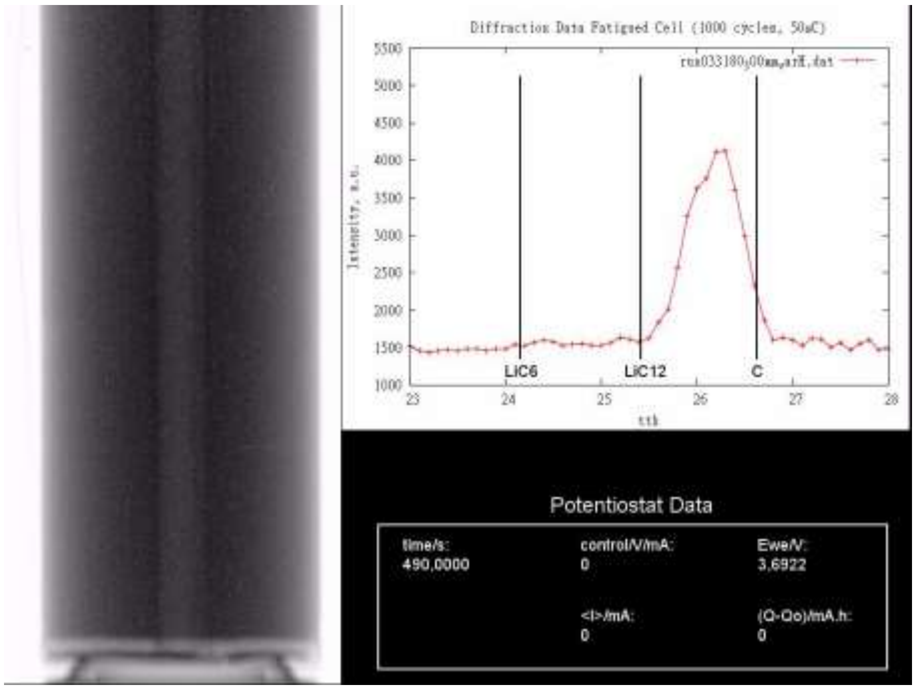
R.F. Ziesche et al., Nature Communications 11 (2020) 777

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

Fresh cell

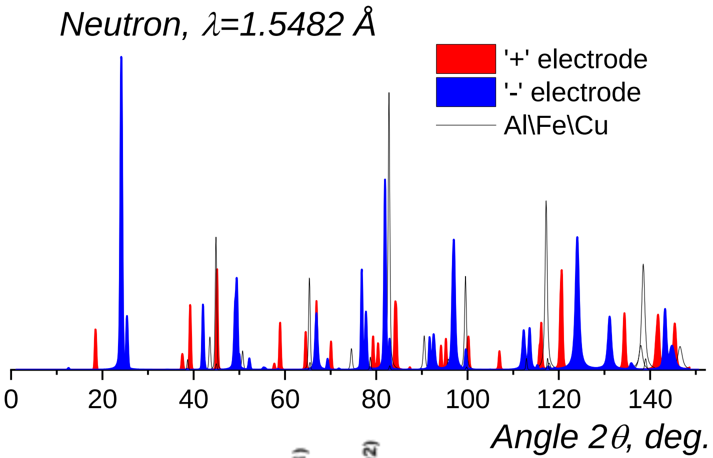


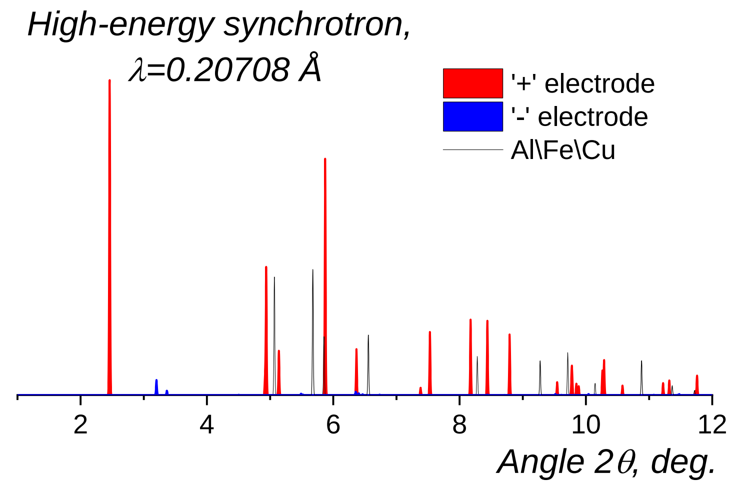
Fatigued cell

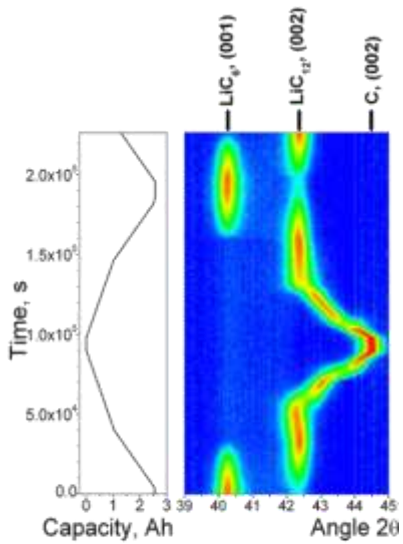


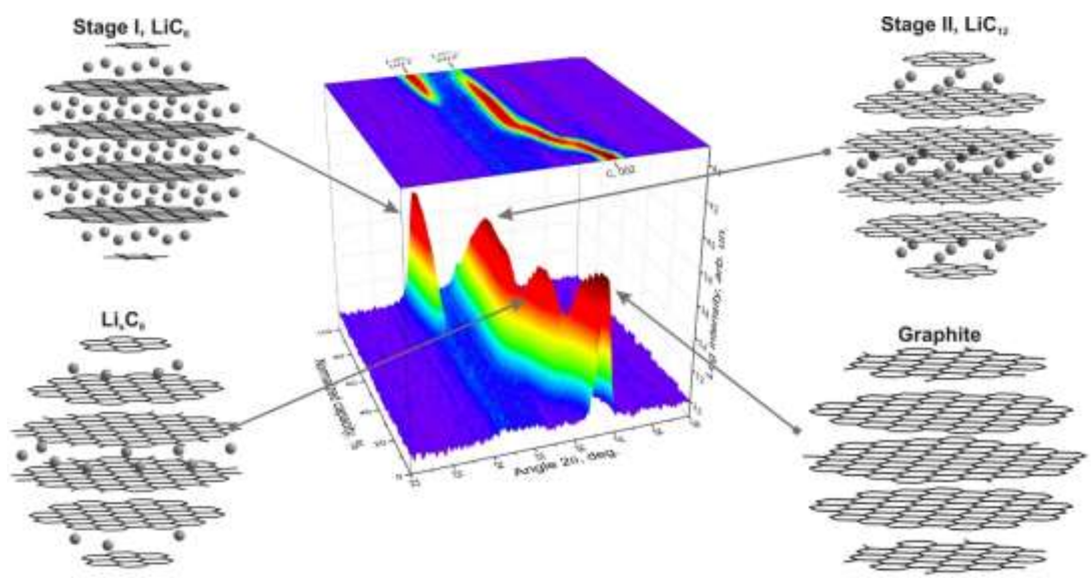
https://www.youtube.com/watch?v=ICPzHO_1nQ8

Why graphite?



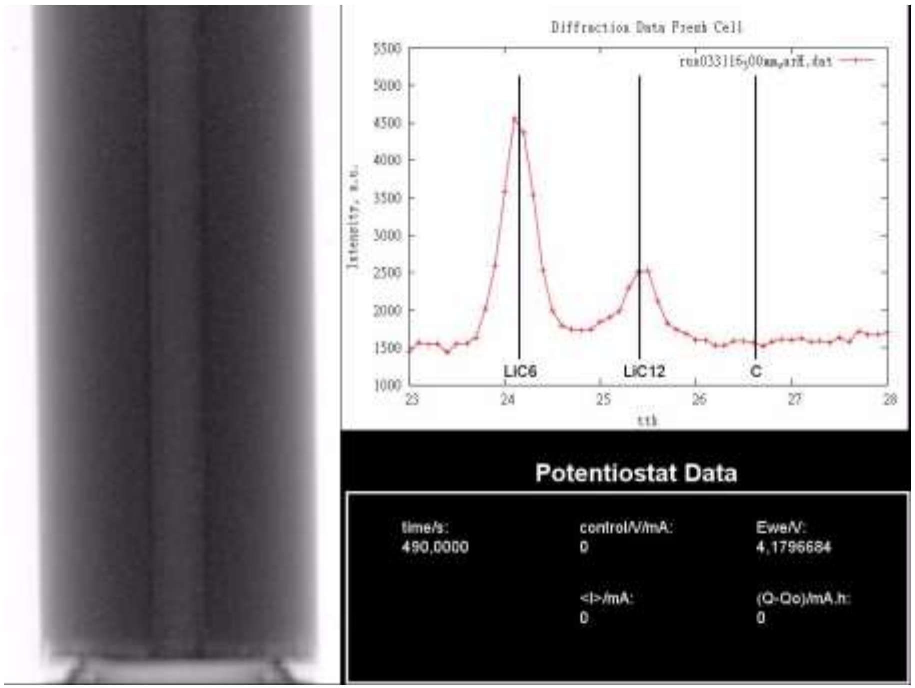




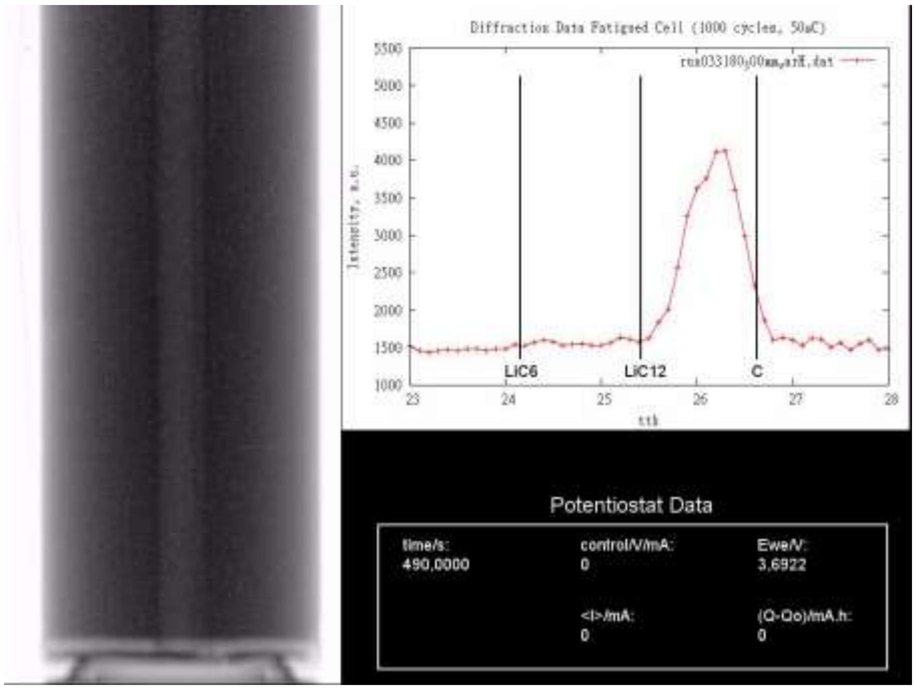


Simultaneous neutron radiography and diffraction data collection on 18650-type cell cycled up-side-down

Fresh cell

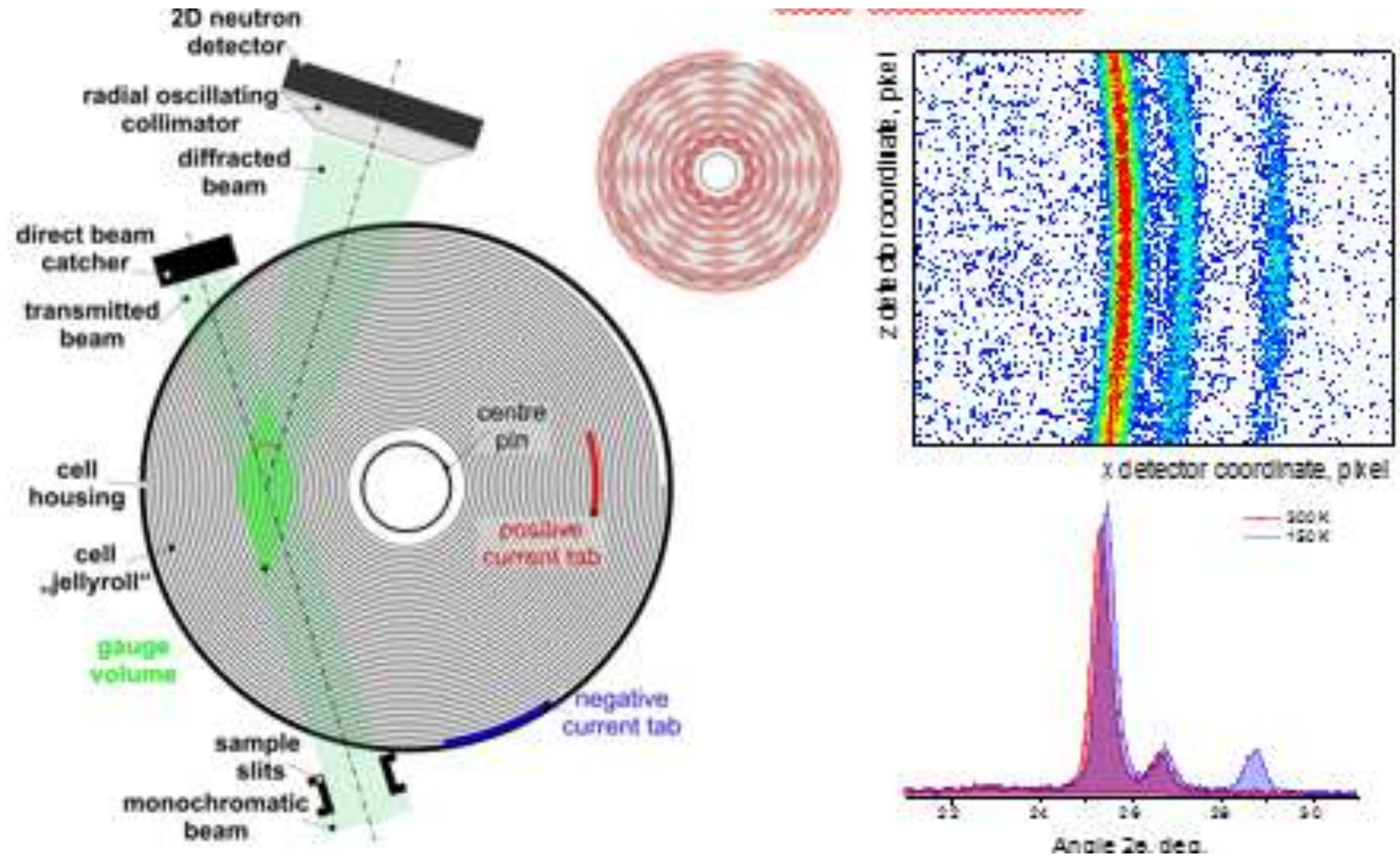


Fatigued cell

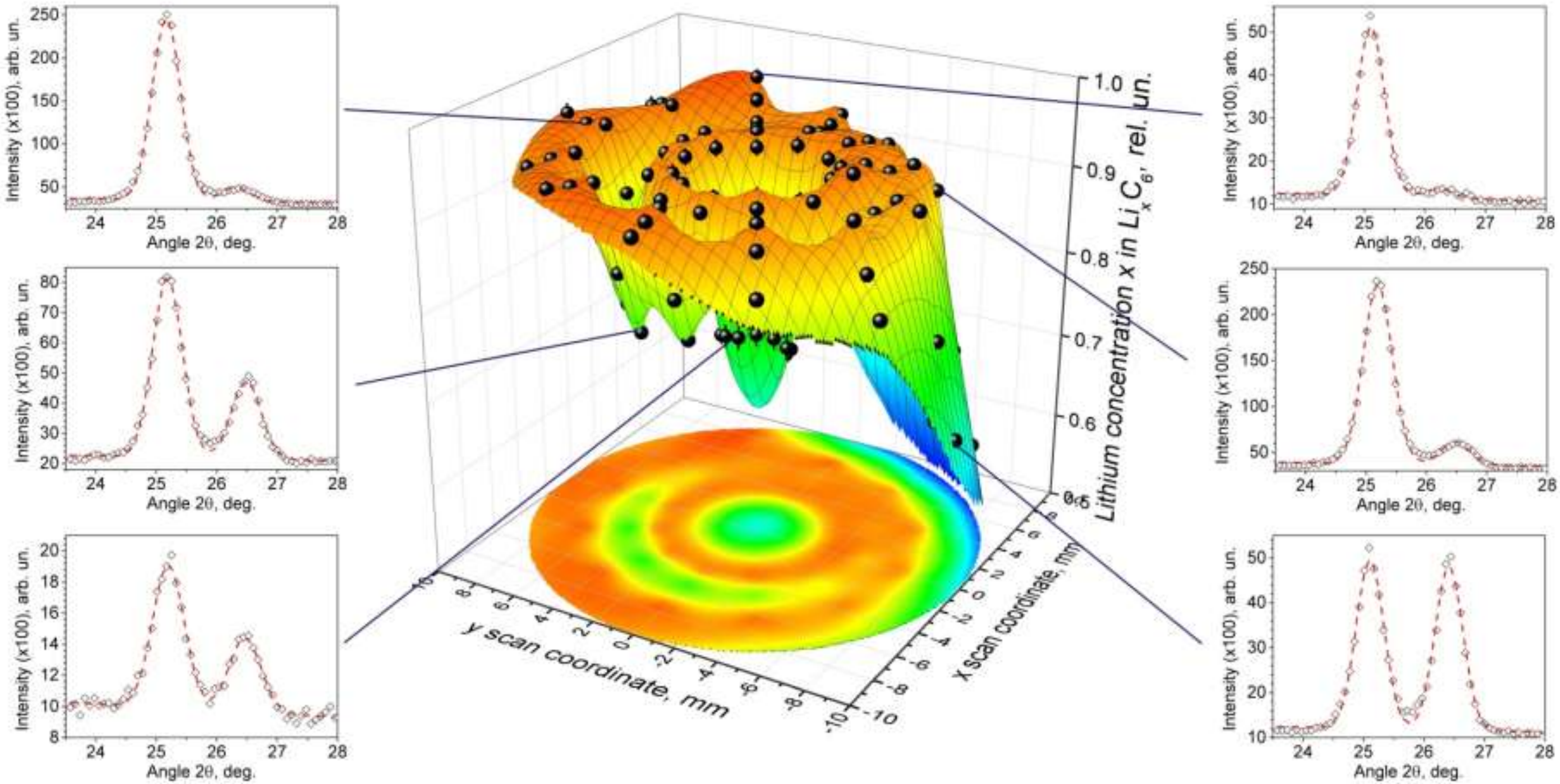


https://www.youtube.com/watch?v=ICPzHO_1nQ8

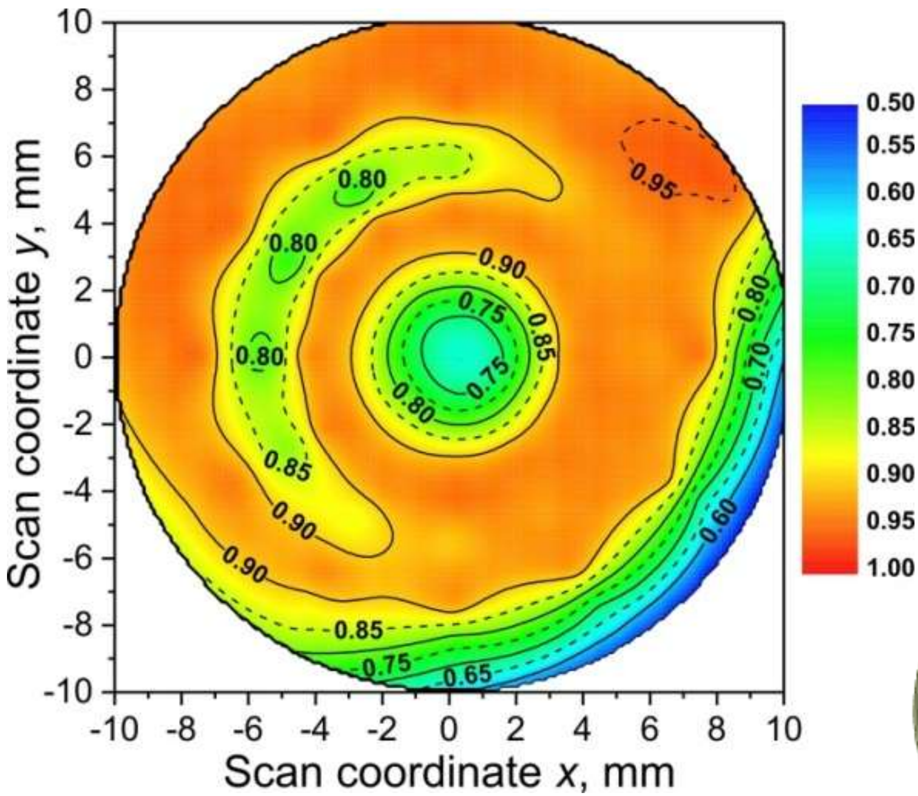
Spatially-resolved neutron diffraction and current distribution in Li-ion batteries

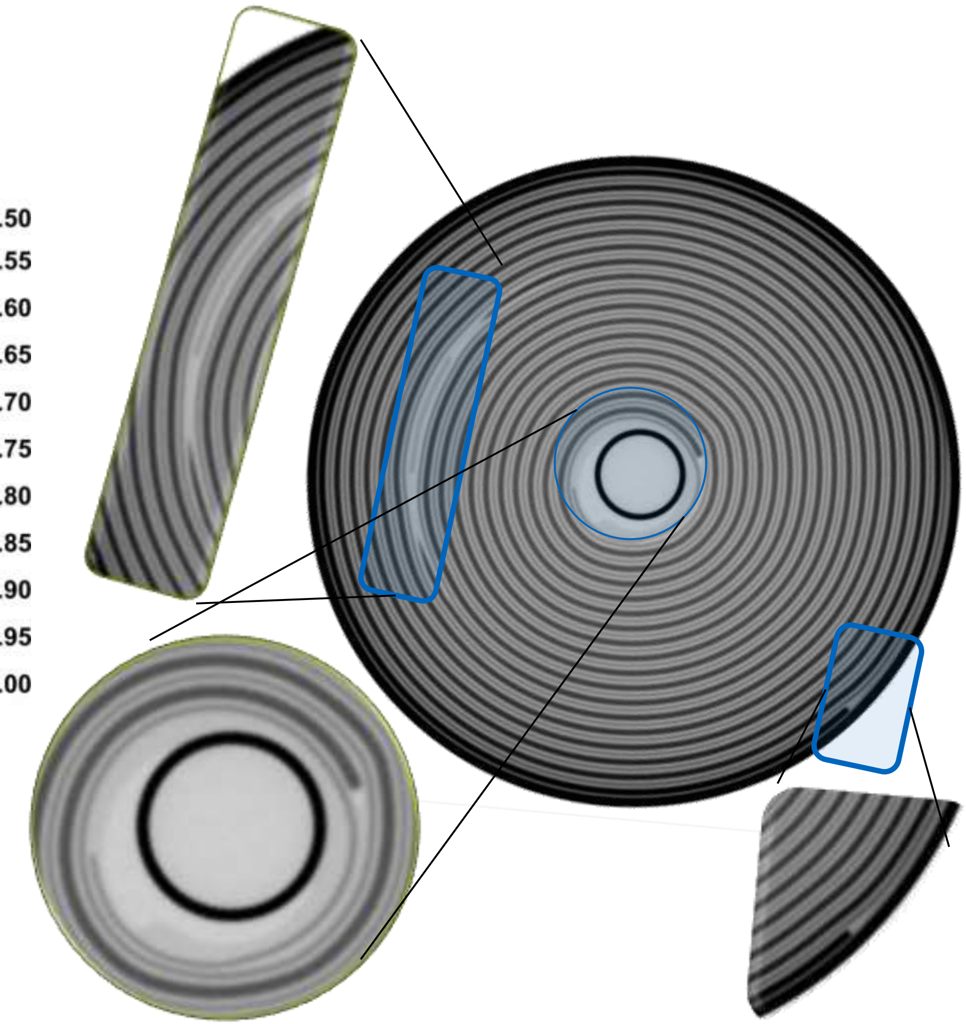


Selected diffraction patterns



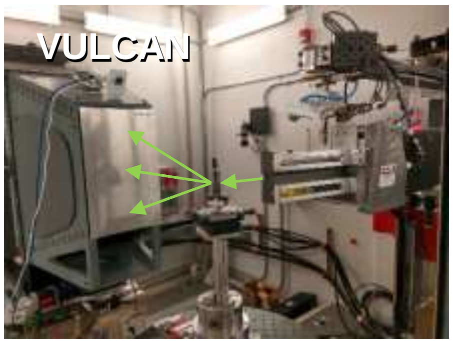
Lithium distribution in the middle of 18650-type cell

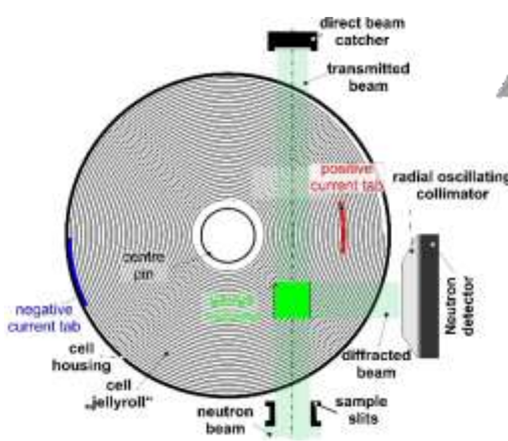


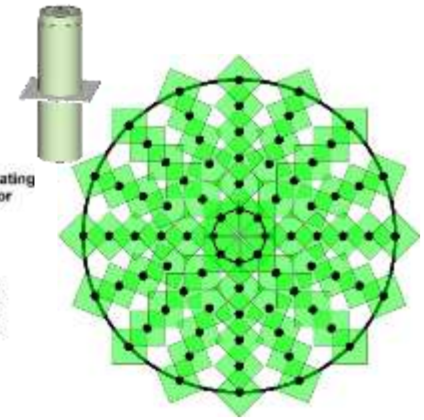


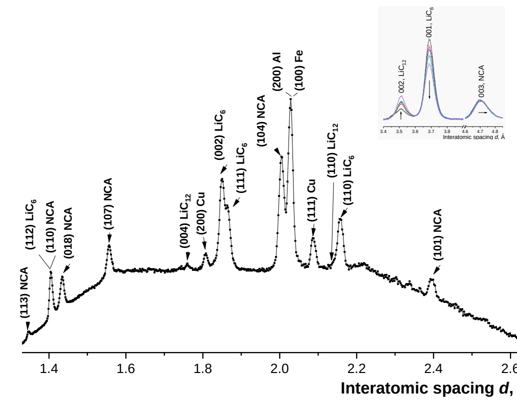
Spatially-resolved TOF neutron diffraction

OAK RIDGE National Laboratory

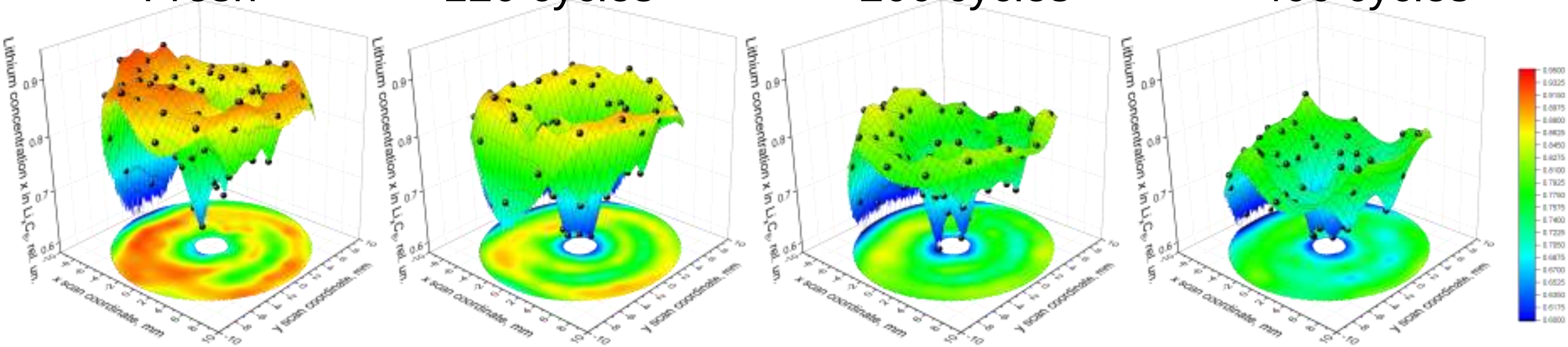








Fresh | 120 cycles | 200 cycles | 400 cycles



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

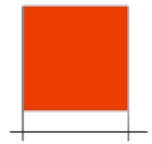
Spatially-resolved diffraction using conical slits

Gauge volume

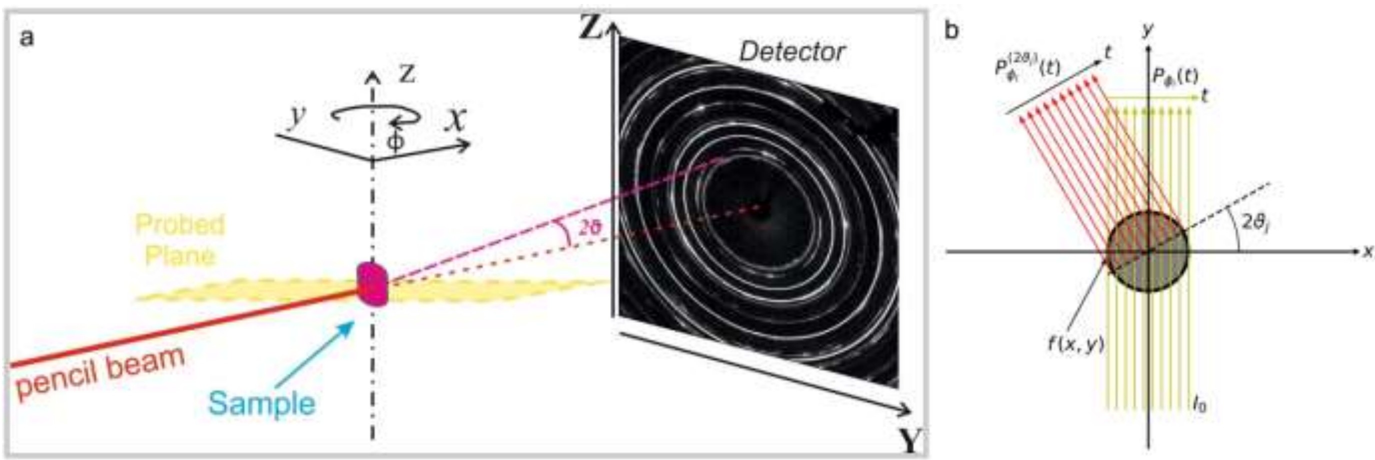
Neutron diffraction

Gauge volume

Diffraction tomography



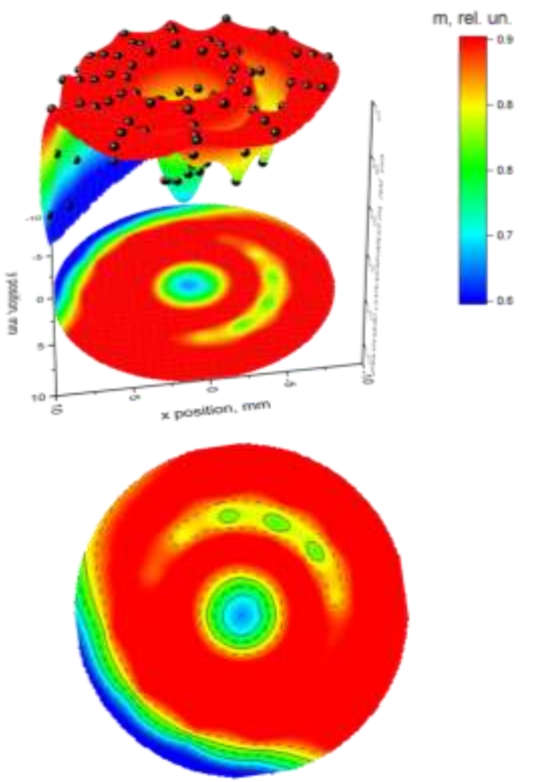
Principle of diffraction tomography



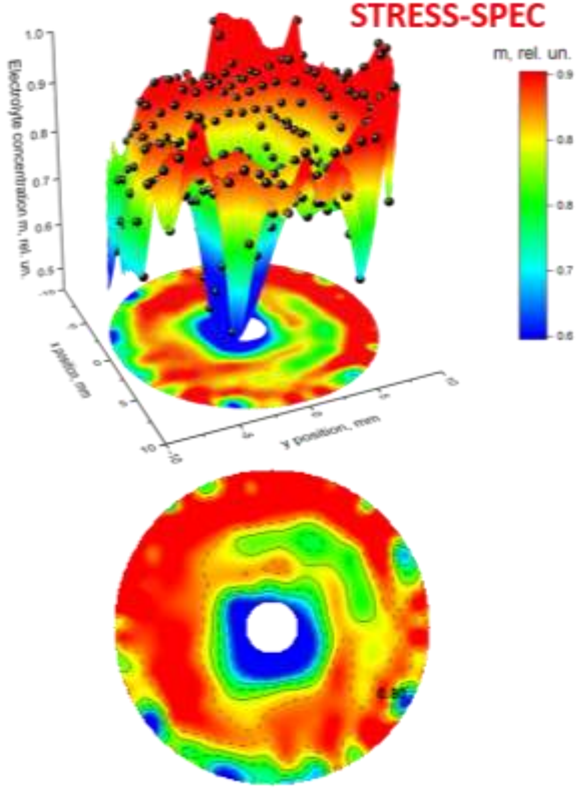
Lithium distribution in the graphite anode of 18650-type lithium ion battery

Spatially resolved neutron diffraction

STRESS-SPEC



Neutron diffraction tomography*

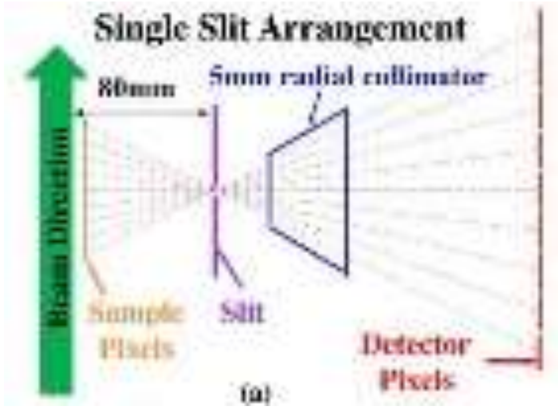


Summary

- Perspectives for neutron powder diffraction and spatially-resolved diffraction

More flux, better resolution

pinhole neutron diffraction

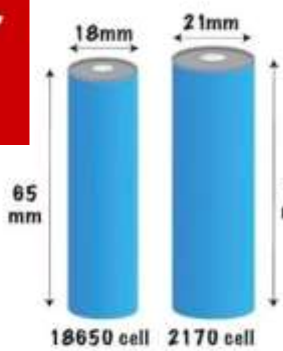


- Neutron diffraction tomography

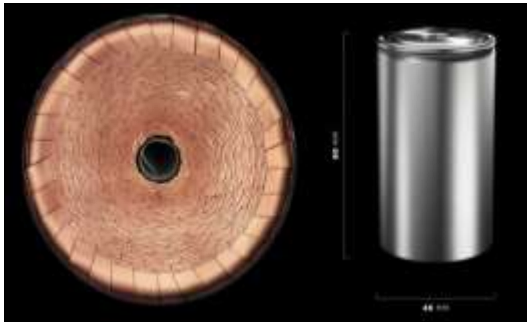
Low-divergent\parallel monochromatic neutron beam with submillimeter focusing

- Neutron imaging in battery research

More flux, better resolution, higher neutron energy



4680



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ILL: Dr. T. Pirling (SALSA, ILL)

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DFG Deutsche Forschungsgemeinschaft

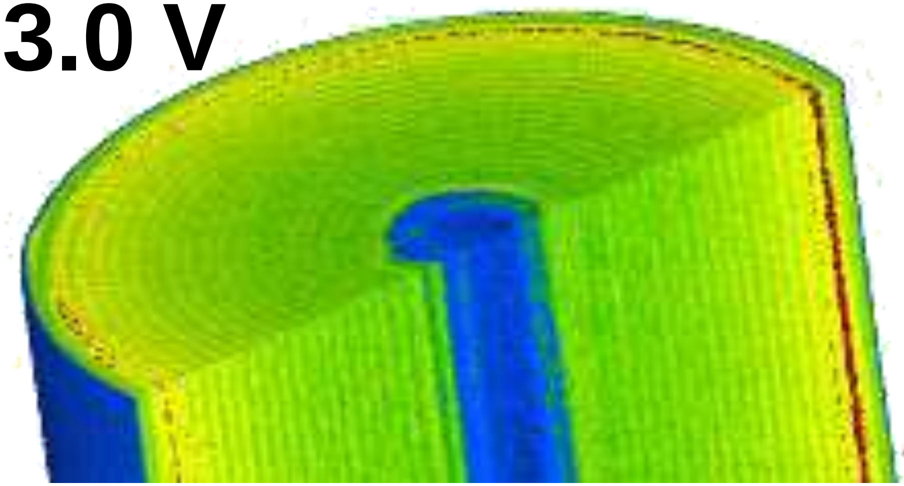
BaCaTeC

FRM II Forschungs-Neutronenquelle Heinz Maier-Leibnitz

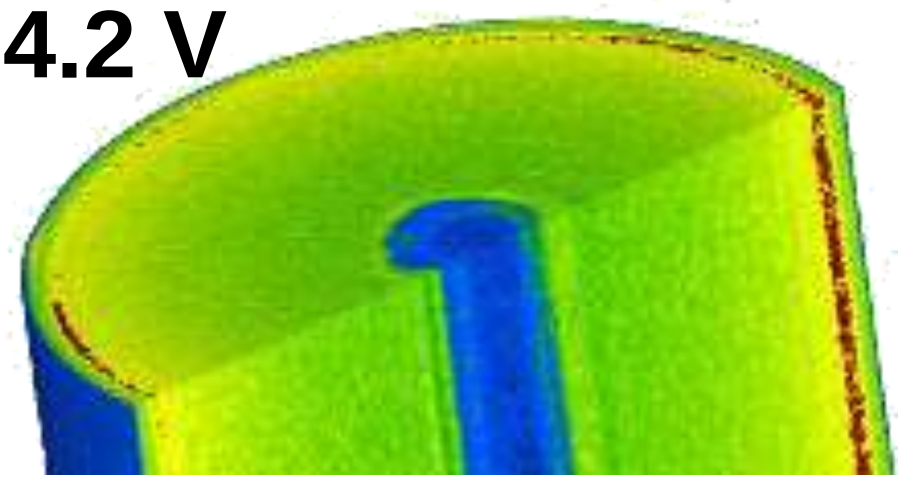
Neutron CT reconstruction from 18650-type LCO|C cell

ANTARES@FRMII

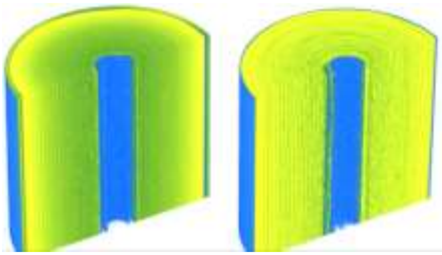
3.0 V



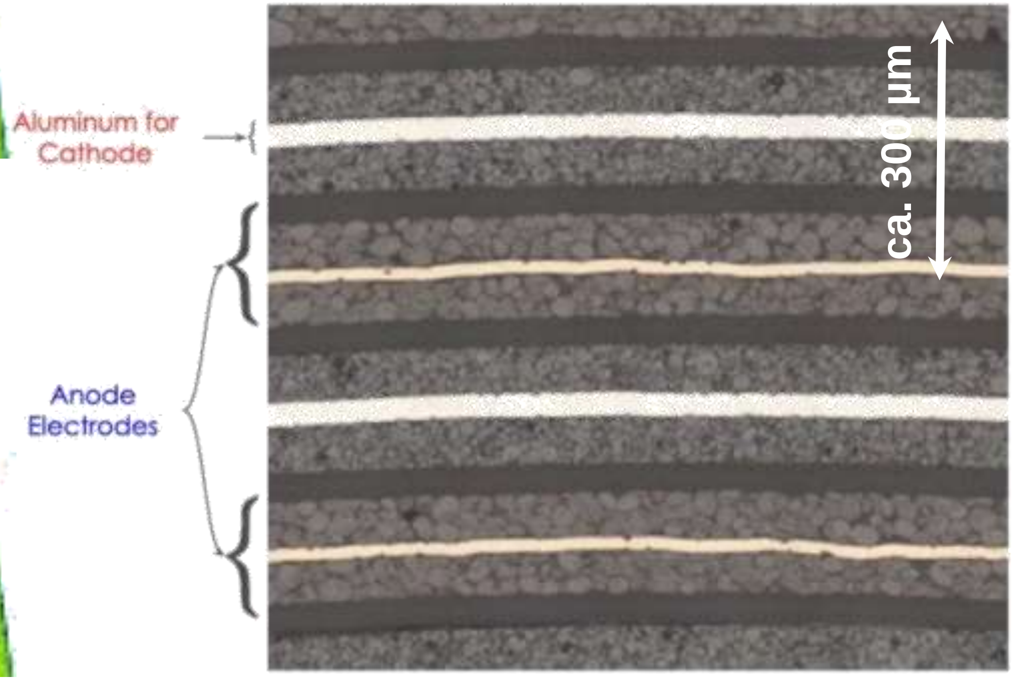
4.2 V



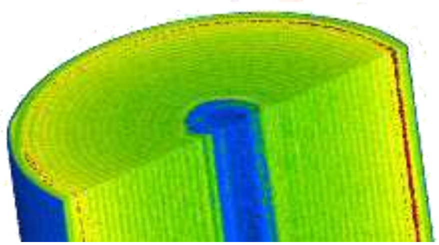
poly mono

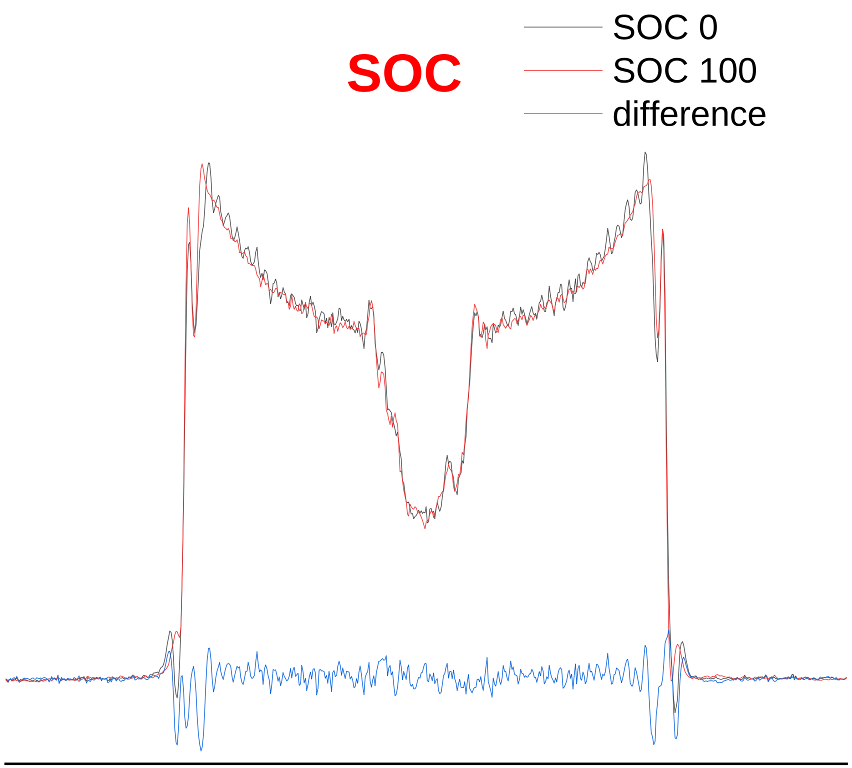


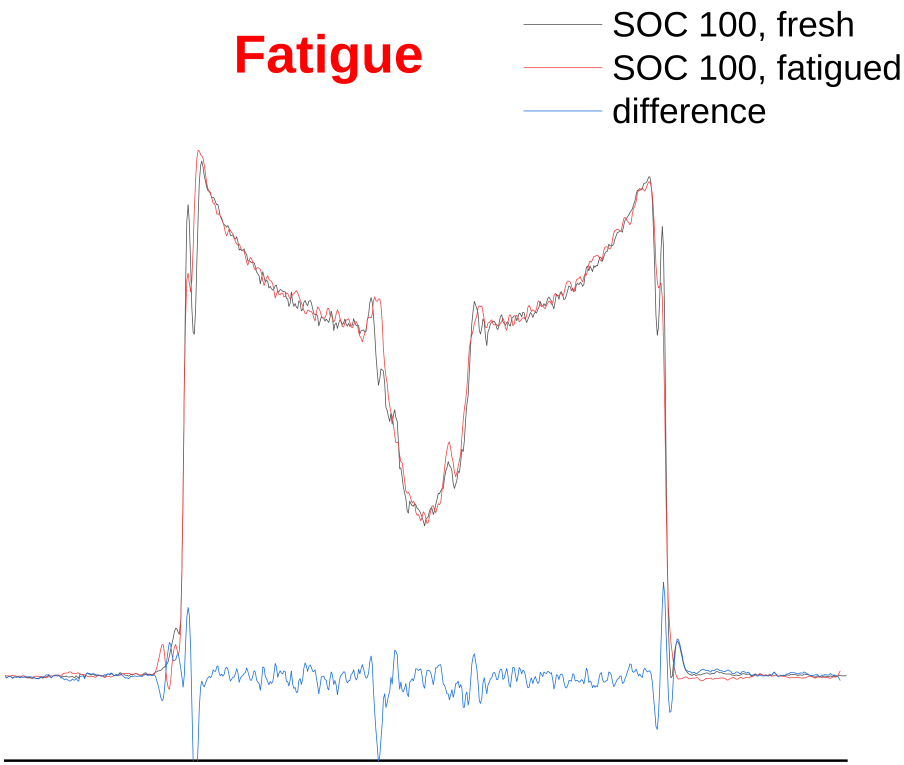
X-ray CT



Neutron CT reconstruction from 18650-type LCO|C cell

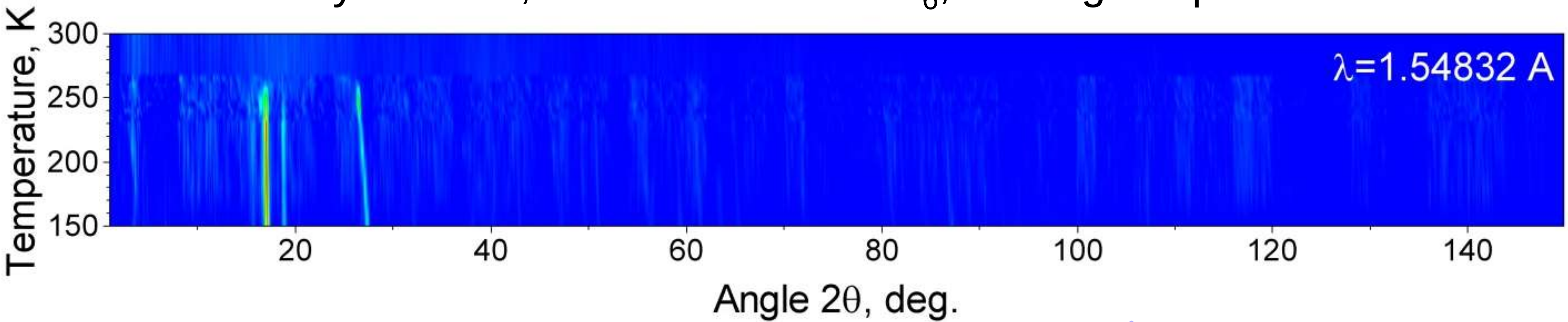


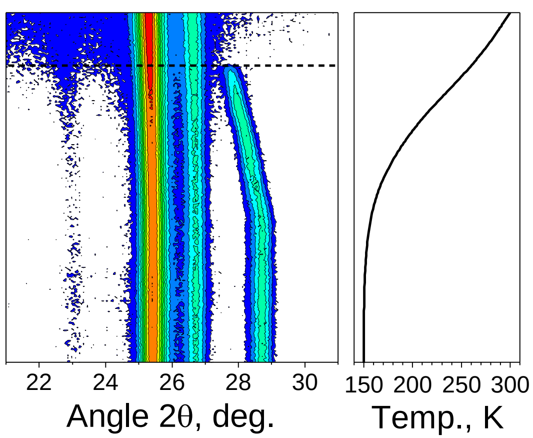


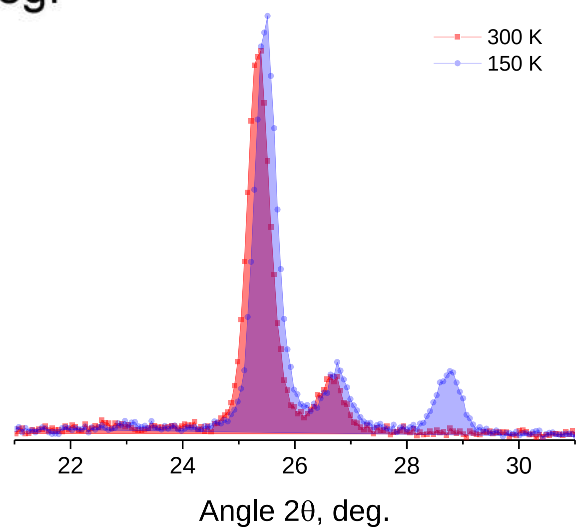


Evolution of the neutron diffraction signal (background subtracted) upon cooling of LP30 electrolyte filled in a thin-wall vanadium container.

Chosen electrolyte: LP30, EC+DMC+1M $LiPF_6$; Melting temperature: ca.250 K



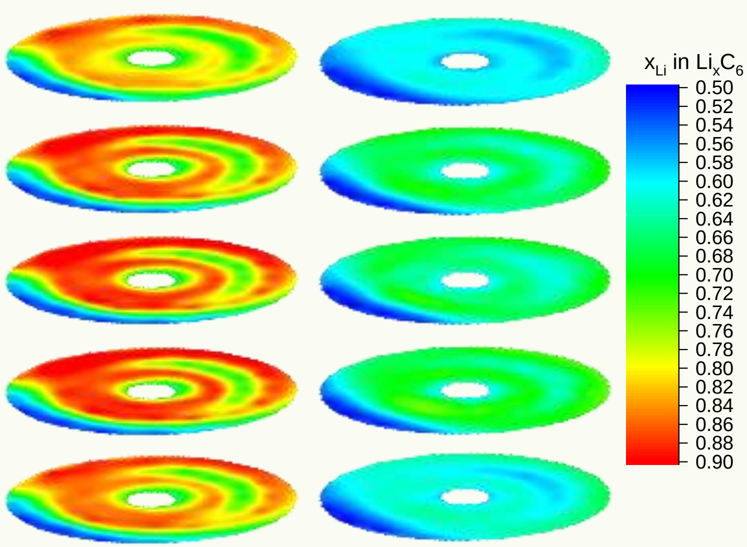


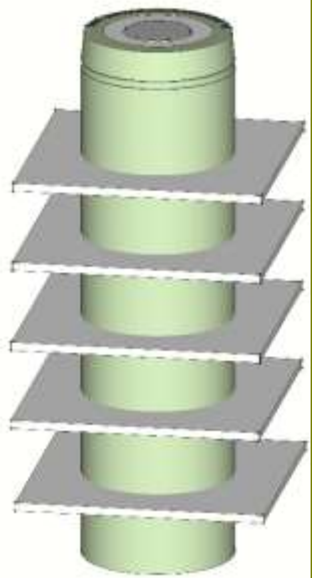


Distribution of lithium and electrolyte concentration in fresh and aged 18650-type cells

Lithium concentration x in Li_xC_6

fresh **600 cycles**





Electrolyte concentration m

fresh **600 cycles**