Studies of prismatic Li-ion batteries with neutron and high energy X-ray diffraction

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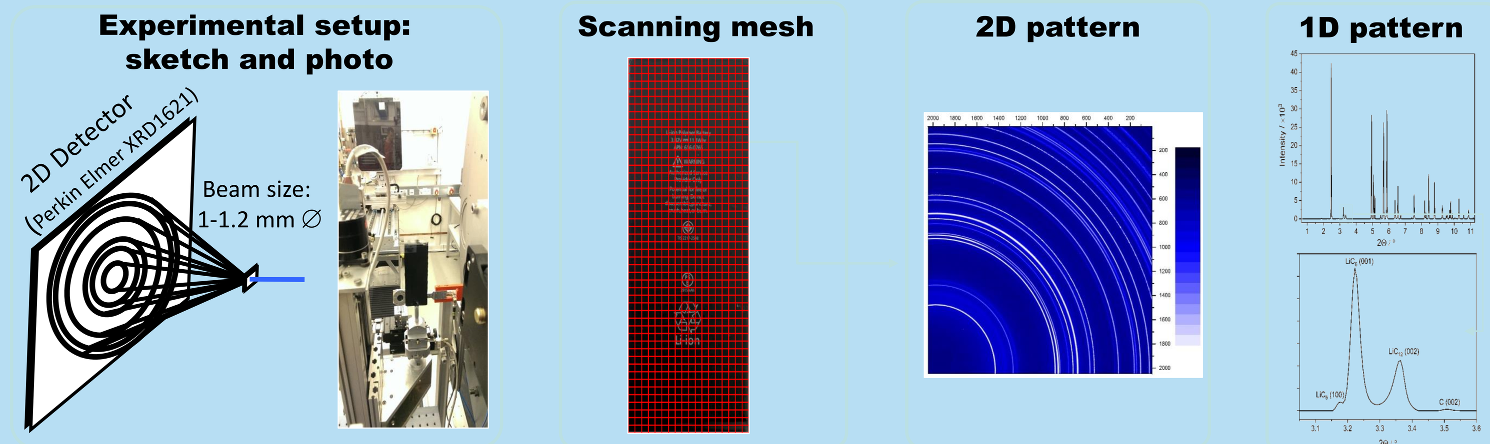
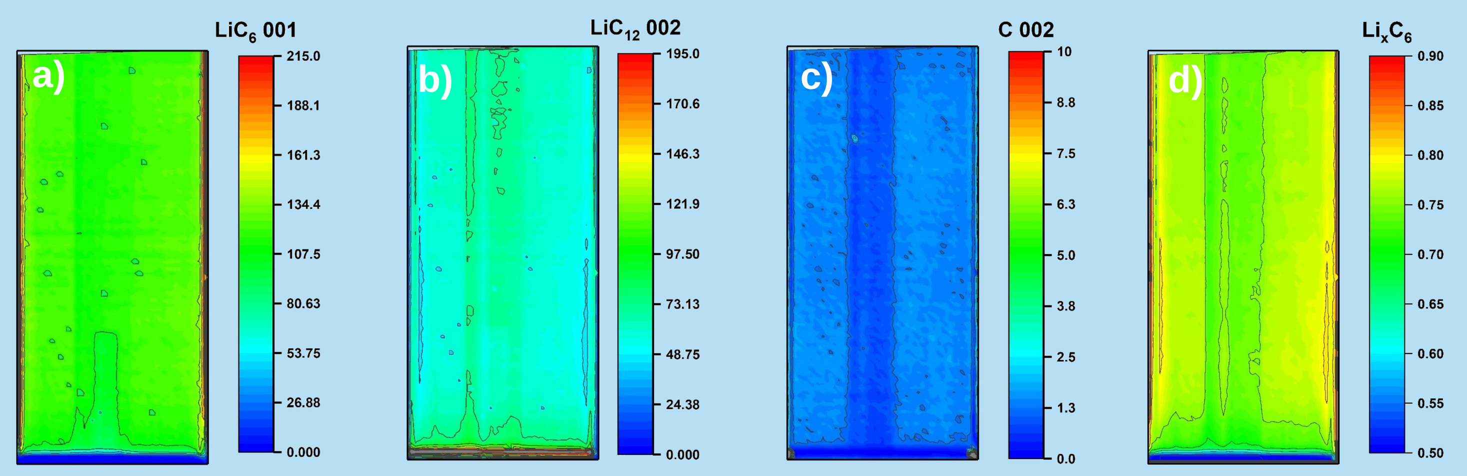
Introduction and motivation

Nowadays Li-ion batteries are widely used in powering portable devices, off-grid energy storage, and e-mobility applications. Characteristics of modern Li-ion batteries (LIBs) (high power/energy density, high mass and volumetric capacities, nearly no memory effect, low self-discharge when not in use etc.) have still a certain room for improvement which makes research on LIBs of high scientific and technological relevance.[1]
Of particular interest are methods which allow performing *in situ / operando* studies of LIBs. Powder diffraction is a well-established experimental method well suited for studies of LIBs on atomic scale.[2] Among different diffraction sources - lab X-rays, synchrotron radiation and thermal neutrons – latter two are of great relevance since they are capable to probe the structure of Li-ion cell components under real operating conditions without dismounting the cell, and can be also used for non-ambient conditions.
Recently we showed by means of high energy X-ray diffraction 2D Li distribution in the anode and the cathode of the commercial prismatic Li-ion cell.[3] For the same prismatic battery applying neutron diffraction, we find out the overall Li concentration in the cell from results of Rietveld refinement and more importantly we were able to observe phases evolution inside the cell for operando conditions.[4]
In the current contribution capabilities of these two methods for studies of prismatic Li-ion batteries will be presented on example of fresh and aged prismatic cells, which were studied using both methods: neutron diffraction was used to evaluate changes of cell constituencies where with high energy X-ray diffraction the changes in 2D Li distribution with aging were probed.
An important point is the fact that in comparison to the cylindrical cells the prismatic are simpler to manufacture with high reproducibility in the laboratory. This make them an attractive option to study new electrode materials, electrolytes and additives.

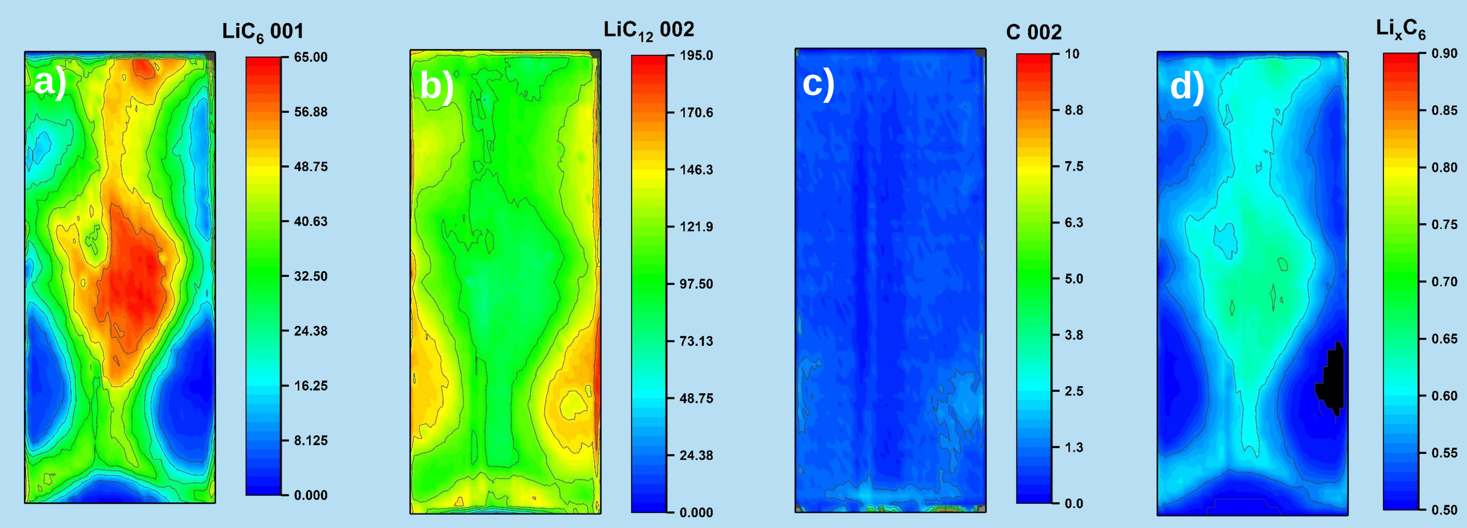
High energy synchrotron diffraction



Experimental setup used in X-ray diffraction tomography experiment



2D distribution of (001) LiC_6 (a), (002) LiC_{12} (b), (001) C (c) along with the lithium concentration in the anode (d) for the fresh cell.



2D distribution of (001) LiC_6 (a), (002) LiC_{12} (b), (001) C (c) along with the lithium concentration in the anode (d) for the aged cell.

Cell specs and aging

Dimensions	48×114×3 mm
Nominal capacity	2915 mAh
Voltage window	3.00 – 4.35 V
Cycling conditions	CH CC-CV 1000 mA ≈ C/3, cut off 150mA DCH CC 1000 mA ≈ C/3
Cathode	Li_xCoO_2
Anode	Graphite

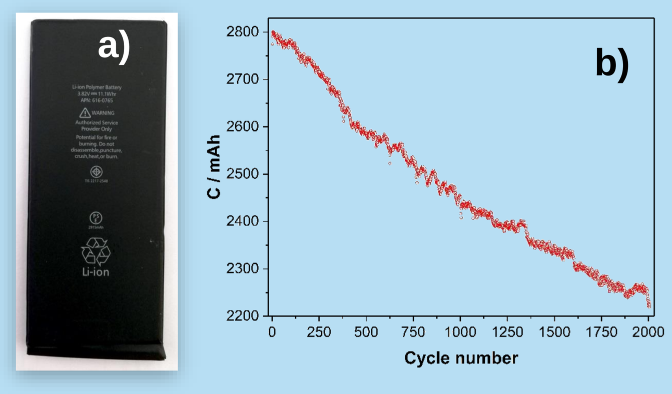
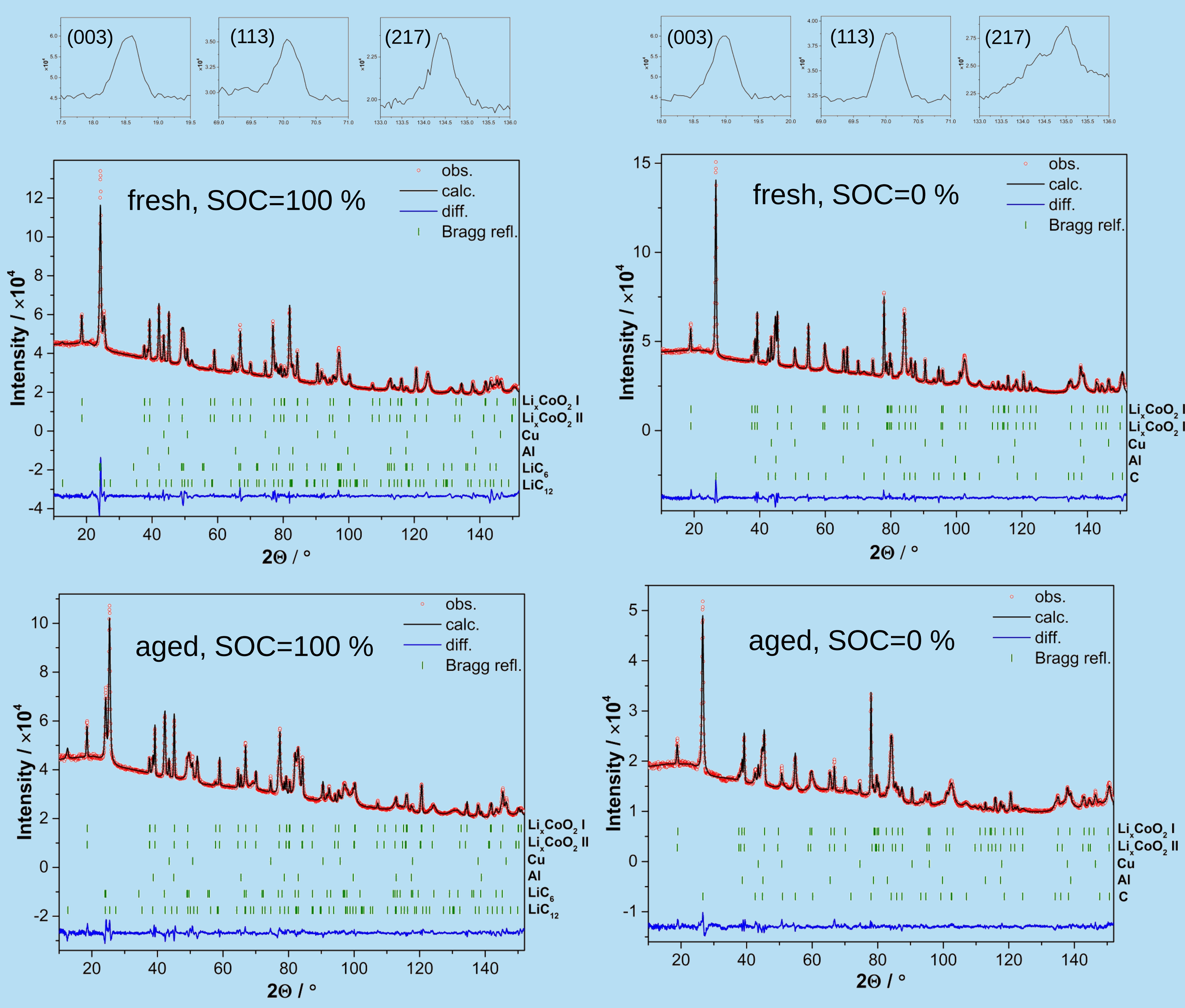


Photo of the cell (a) and capacity fade with cycling (b)

Neutron powder diffraction

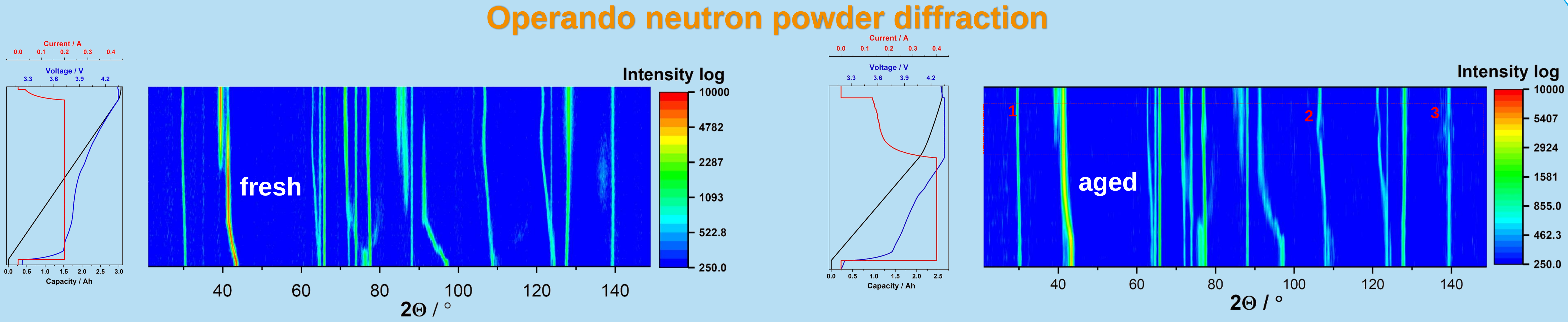
$Li_{0.89(4)}C_6$

$Li_{0.63(4)}C_6$



Rietveld refinement plots for data collected at SOC = 100% and 0 % for fresh and aged cells. The wavelength for data collection was ~1.5482 Å. The insert on the top present splitting of the peaks for the Li_xCoO_2 cathode.

Operando neutron powder diffraction



Evolution of electrochemical parameters (left) and stack of diffraction patterns (background subtracted log diffraction intensity coded in false color vs. 2Θ) collected for fresh and aged prismatic Li-ion battery under permanent rotation (right). The wavelength of data collection was λ≈2.536 Å.

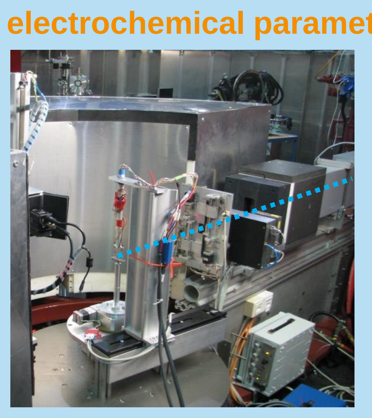
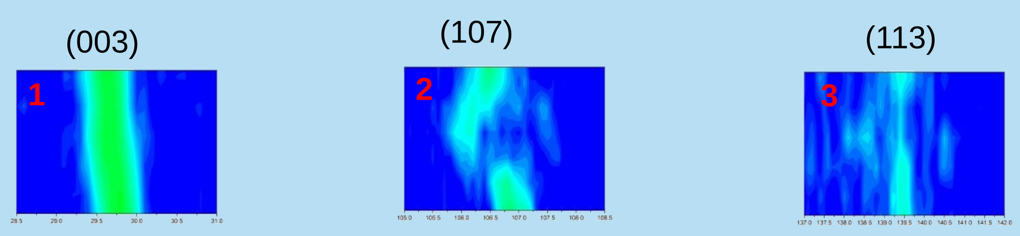


Photo of the experimental setup

Part of the cell measured during experiment



Selected cathode peaks with clear phase transition appearing at certain SOC

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[2] Harks, P.P.R.M.L., F.M. Mulder, and P.H.L. Notten, In situ methods for Li-ion battery research: A review of recent developments. *J. Power Sources*, **2015**, 288, 92-105.
[3] M. J. Muhlbauer, A. Schokel, M. Etter, V. Baran, and A. Senyshyn, *J. Power Sources,* **2018**, 403, 49-55
[4] V. Baran, M. J. Mühlbauer, M. Schulz, J. Pfanzelt, and A. Senyshyn, *J. Energy Storage,* **2019**, 24, 100772

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