Lithium and electrolyte distribution in fresh and aged 18650-type lithium-ion batteries

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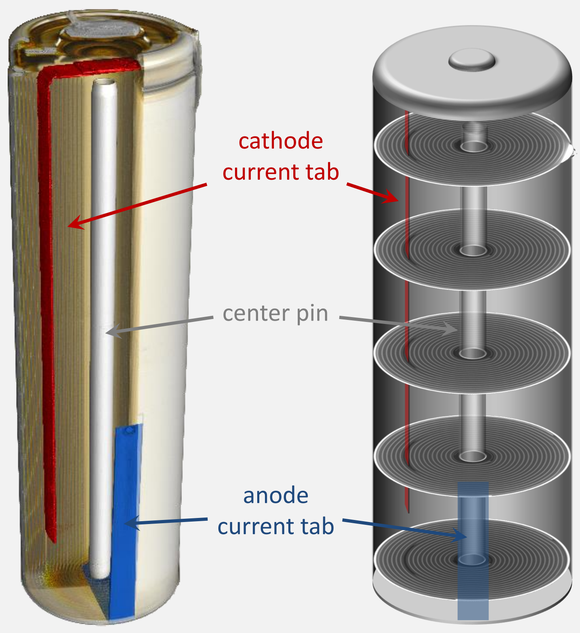
Aim and results

1. Quantification of lithium content in fully charged graphite anode
2. Characterization of electrolyte distribution and quantity
3. Correlating the lithium and electrolyte amounts with cell design/layout
4. Quantitative and qualitative aging-driven lithium and electrolyte homogeneity

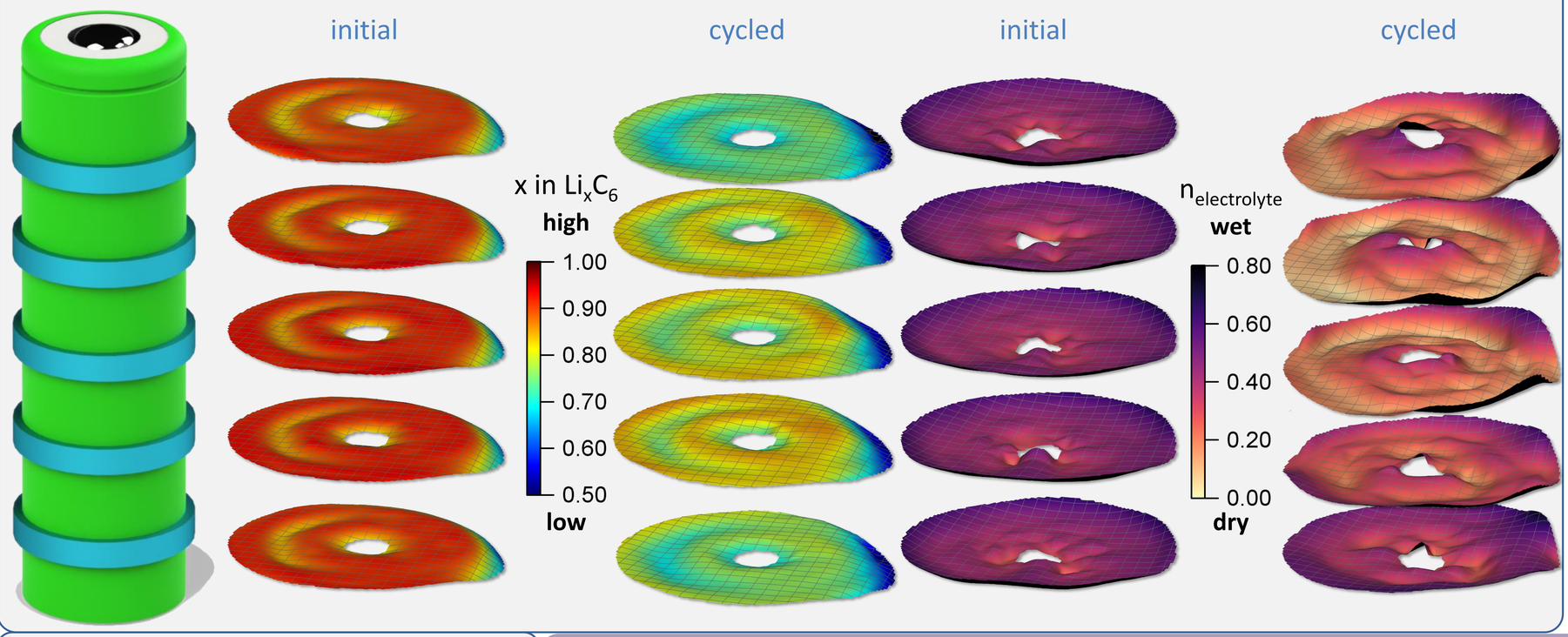
➔ Exemplary results for NCR18650B cells

Cell layout according to X-Ray CT

acceleration voltage: 130 kV		Images:	1001 (over 360°)
Cathode current:	100 µA	Exposure time:	2000 ms



Lithium concentration in the graphite anode (x in Li_xC_6) for selected cell regions

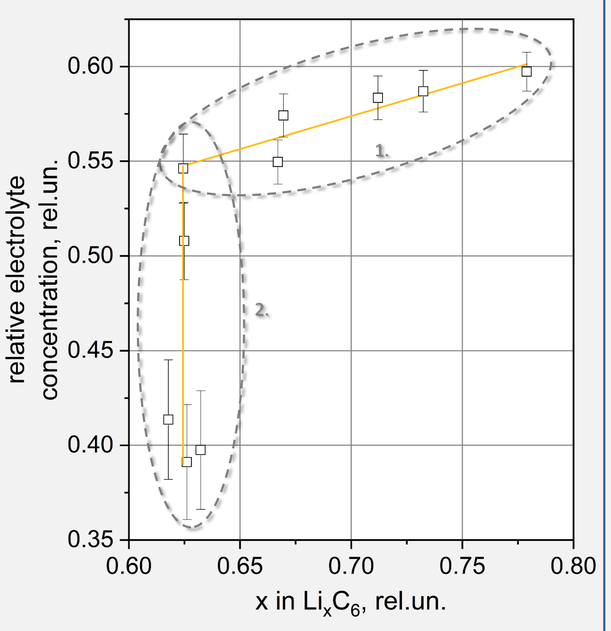


"Frozen-in" electrolyte distribution for individual cell levels

High-resolution neutron powder diffraction

SPODI (FRM II, Garching, Germany)	
wavelength: $\lambda = 1.548$ Å	angular range: 4-152°
beam size: 40×20 mm² (v × h)	angular step size: 0.05°

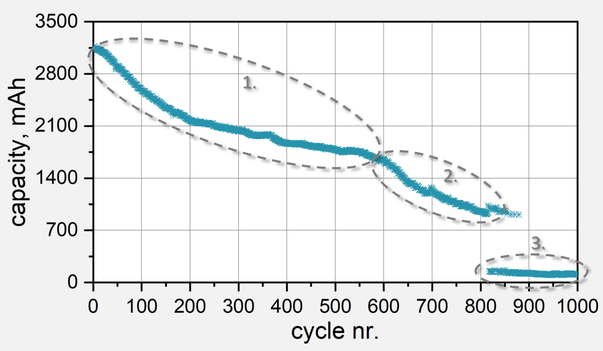
1. Correlated degradation of active lithium and electrolyte
2. Reduction of electrolyte



Electrochemical behavior

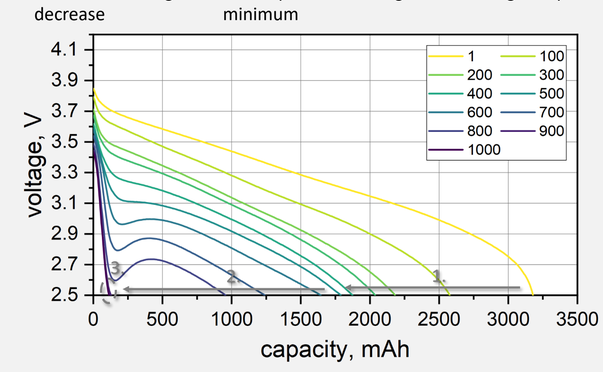
Capacity degradation

1. $\sqrt{\text{time}}$ behavior
2. Accelerated fading rate
3. Reduced capacity



Voltage characteristics

1. Monotonic voltage decrease
2. Development of voltage minimum
3. Voltage drop



Discussion

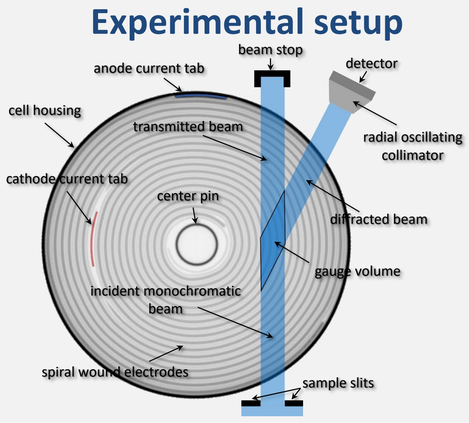
1. Geometrical characteristics of a NCR18650B cell:
   - Cathode contacting extending over ~80% of width (top, left) in the middle of the spirally wound cathode stripe; one anode contacting at the radially outer end of the electrode stripe (~ $^1/_3$ of the total electrode height)
   - Lack of active electrode material at the beginning and ending of the current collectors and at the position of the current tabs
2. State of fresh cell (as received):
   - Reduced lithium content at the location of the cathode current tab and at the beginning/ending of the anode stripe
   - Smooth and uniform electrolyte distribution over height with gentle radial gradient (higher electrolyte aggregation at cell housing)
3. State of aged cell (after cycling):
   - General decreasing in the concentration quantities → loss of active lithium + drying out of the cell
   - Formation of a height gradient in lithium content (systematically lower quantities at cell bottom/top)
   - Evolution of a height gradient in the electrolyte allocation (with higher quantities at cell bottom)
   - Radial gradient of electrolyte distribution involving the overall remaining electrolyte

Methods

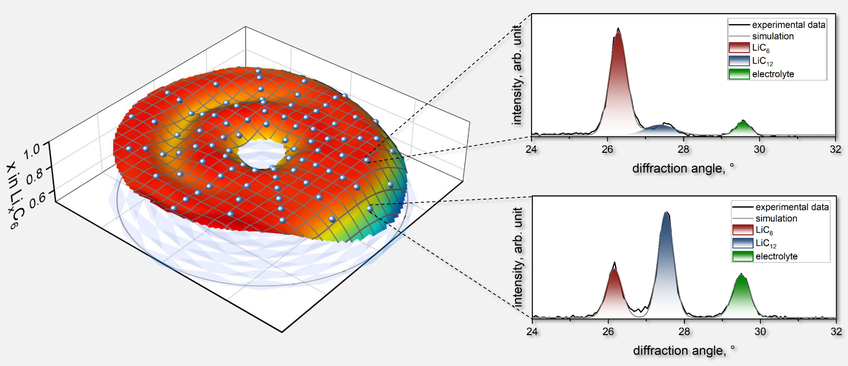
Spatially-resolved neutron powder diffraction @ STRESS-SPEC (FRM II, Garching, Germany)

monochromatic wavelength:	$\lambda = 1.615$ Å	central detector angle:	≈ 27° in 2θ
incident beam size:	2×18 mm² (h × v)	collimator field of view:	2 mm

Experimental setup



Selected example



Outlook

➔ A way to higher energy/power densities and longer lifetimes leads through new cell designs, which potentially enable a more homogeneous usage of the electrode material. As a result, regions that previously contributed less to the total capacity may become more stressed, which at the same time reduces higher current densities in other cell regions. With a more uniform distribution of the overall stress, the potential of a cell can be better exploited. First cell concepts with optimized electrical connection of the electrodes already exist, e.g. by Varta, Tesla Inc.

Literature

[1] M.J. Mühlbauer, D. Petz, V. Baran, O. Dolotko, M. Hofmann, R. Kostecki, A. Senyshyn, *J. Power Sources* **2020**, *475*, 228690.
[2] D. Petz, M.J. Mühlbauer, V. Baran, M. Frost, A. Schökel, C. Paulmann, Y. Chen, D. Garcés, A. Senyshyn, *J. Power Sources* **2020**, *448*, 227466.
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[4] D. Petz, M.J. Mühlbauer, V. Baran, A. Schökel, V. Kochetov, M. Hofmann, V. Dyadkin, P. Staron, G. Vaughan, U. Lienert, P. Müller-Buschbaum, A. Senyshyn, *Energy Storage Mater.* **2021**, *41*, 546-553

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