

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

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Various side reactions in lithium-ion batteries like the formation of the solid-electrolyte-interface (SEI), loss of active lithium, drying out of the cell [1] *etc.* lead to a partial loss of capacity during extensive electrochemical cycling. The typical profiles of these side reactions along with the temperature and current density are non-uniform in general, which in the end leads to a stabilization of heterogeneous state. The loss of active lithium can be correlated with the formation of SEI during cycling. On the other hand, the quantitative behavior of the electrolyte in cell operation and fatigue remains not fully understood yet.

Quantification of the liquid electrolyte in an electrically and environmentally isolated system such as lithium-ion batteries is not a simple task. Opening the cell would affect its state, e.g. evaporation of electrolyte. Typical X-ray and neutron-based methods used for non-destructive cell characterization are not capable to quantify the amount of liquid electrolyte with high precision. Recently it was shown, that a liquid DMC-based electrolyte exhibits a long-range order in the frozen state at temperatures $T < 260$ K [2]. Neutron diffraction displays sensitivity to this long-range order and therefore enables the quantification of the frozen electrolyte. One step further, spatially-resolved neutron powder diffraction can be used for the simultaneous quantification of the intercalated lithium in the graphite and the relative concentration of the frozen electrolyte (Figure 1).

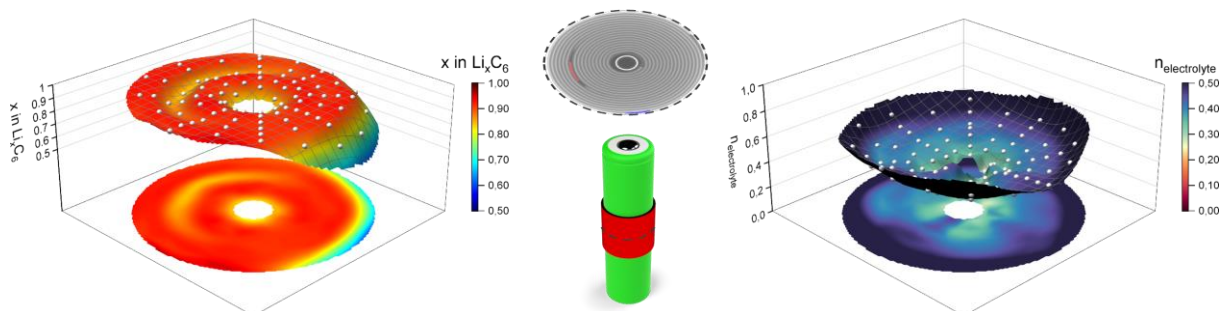


Figure 1 Lithium concentration in graphite (left) and corresponding electrolyte (right) distribution in central plane (red area, middle bottom) of an 18650-type lithium-ion battery measured with *in-situ* neutron powder diffraction and reconstruction slice of X-ray computed tomography (middle top).

The results of the current study show the non-destructive quantification of lithium and electrolyte, their spatial distribution and concentration changes induced by cell fatigue. Combined experimental studies including electrochemistry, X-ray computed tomography and neutron diffraction independently reveal a direct correlation between losses of active lithium intercalated in the graphite anode and those of liquid electrolyte averaged over the volume. The three-dimensional lithium distribution is determined with spatially-resolved neutron powder diffraction, displaying the non-trivial character of active lithium/electrolyte losses and complex profile of the cell capacity fading.

- [1] Petz D., et al., Lithium heterogeneities in cylinder-type Li-ion batteries- fatigue induced by cycling. *J. Power Sources*, 448, 227466 (2020)
- [2] Senyshyn A., et al., Low-temperature performance of Li-ion batteries: The behavior of lithiated graphite, *J. Power Sources*, 282, 235-240 (2015)