Aging-driven Composition- and Distribution- Changes of Electrolyte and Graphite Anode in 18650-type Li-ion Batteries

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Keywords: Li-ion batteries, in operando characterisation, aging

Carbonate-based esters used as solvents in real-life Li-ion battery electrolytes exhibit a long range order in a frozen state, which enables their accurate and non-destructive quantification and localisation by diffraction methods. In the current study lithium concentration inside the graphite anode and distribution of electrolyte were determined simultaneously for series of differently cycled (variously aged) Li-ion cells using neutron diffraction at low temperatures. Differently stabilized aging states was supplemented by the pronounced and systematic losses of lithium inventory, increase of internal resistance (also reflected in the increase Joule heating of the cells) as well as drying out of cells (loss of electrolyte inventory). An independent electrolyte characterization is performed via quasi adiabatic calorimetry on variously aged 18650-type lithium-ion batteries, where the shape of the thermodynamic signal has been found strongly evolving with the state of fatigue of the cells. A clear correlation of lithium losses and remaining electrolyte amount was observed, where two regimes of their consumption can be identified and attributed to a characteristic cell capacity fade. Analyzing the liquid electrolyte extracted/harvested from the studied cells reveals the decomposition of conducting salt to be the main driving factor for fatigue in the electrolyte degradation.

Figure 1. Lithium and electrolyte concentrations at different planes of fresh and aged (600 cycles) studied cylinder cells.

[1] Mühlbauer M.J., Petz D., Baran V., Dolotko O., Hofmann M., Kostecki R., Senyshyn A. (2020) J. Power Sources 475, 228690.
[2] Petz D., Baran V., Peschel C., Winter M., Nowak S., Hofmann M., Kostecki R., Niewa R., Bauer M., Müller-Buschbaum P., Senyshyn A. (2022) Adv. Energy Mat. 12, 2201652

The authors gratefully acknowledge the financial support provided by the Heinz Maier-Leibnitz Zentrum (Technische Universität München), German Federal Ministry of Education and Research (BMBF project 05K16VK2 and 05K19VK3) and Bavaria California Technology Center (BaCaTeC, project 14[2014-02]). Authors thank the Heinz Maier-Leibnitz Zentrum for the provision of beamtime and access to their infrastructure.