In-operando EPR spectroscopy of lithium ion batteries

Arvid Niemöller [a], Peter Jakes [a], Svitlana Eurich [a], Anja Paulus [a], Hans Kungl [a], Rüdiger-A. Eichel [a,b], Josef Granwehr [a,c]

[a] *Forschungszentrum Jülich GmbH, Institut für Energie- und Klimaforschung (IEK-9), 52425 Jülich, Germany*

[b] *Institut für Physikalische Chemie, RWTH Aachen University, 52056 Aachen, Germany*

[c] *Institut für Technische und Makromolekulare Chemie (ITMC), RWTH Aachen University, 52056 Aachen, Germany*

Email: a.niemoeller@fz-juelich.de

Redox mechanisms in battery cathode materials are challenging to be identified. Despite investigations using a wide range of different experimental techniques, exact mechanisms on atomic scales are still not well understood for many classes of materials. In-operando electron paramagnetic resonance (EPR) is a recently introduced technique with the potential to shed new light on oxidation states of transition metal ions in battery cathode materials. An electrochemical flat cell was developed that matches the requirements of the EPR spectrometer. It was used to cycle a $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) spinel cathode vs. lithium metal over 500 hours, proving the functionality and stability of the cell setup. EPR spectra show a broad LNMO EPR signal with weak amplitude that was recorded with sufficiently high sensitivity to unravel oxidation mechanisms in the cathode material during battery cycling. These results are compared with ex-situ SQUID measurements. In addition, the EPR linewidth varied continuously with the state of charge, suggesting the formation of a solid solution for slow cycling and a mixed model of solid solution and two-phase formation for fast cycling rates. Long-term EPR experiments complement the electrochemical measurements, allowing us to deduce a model for long-term material degradation of LNMO during battery cycling.

Reference

[1] A. Niemöller, P. Jakes, S. Eurich, A. Paulus, H. Kungl, R.-A. Eichel, and J. Granwehr, J. Chem. Phys. 148 (2018) 014705