Operando near sulfur K-edge X-ray absorption spectrometry of Li-S battery coin cells

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The complete understanding of the functionality of battery components requires the correlation with underlying physical and chemical properties which is the challenge for most analytical methods due to a lack of reference materials. Lithium Sulfur (Li-S) batteries are promising candidates for improved batteries offering up to 5 times higher capacity than conventional lithium ion batteries. The main degradation is caused by polysulfides formed during cycling which are soluble in the electrolyte solution. For a better understanding of this process in-situ and operando characterization techniques are required [1].

We use CR-2032 coin cell formed Li-S batteries with DOL/DME (1:1 wt.%) 1 Mol TFSI electrolyte modified with thin cathode current collector and thin window enabling the transmission of excitation and fluorescence radiation. Traceable X-ray spectrometric measurements were performed using radiometrically calibrated instrumentation in the PTB laboratory at BESSY II synchrotron radiation facility. By means of operando near sulfur K-edge X-ray absorption spectrometry (NEXAFS) recorded during galvanostatic cycling with potential limitation (GCPL) measurements we could determine the different sulfur species in the cell.
To investigate fluid systems such as electrolyte solutions and ionic liquids we use a fluid cell with ultra thin entrance window that enables soft X-ray studies under ultra high vacuum conditions to probe even light elements.

For 8 full charge/discharge cycles (0.1 C) operando sulphur K-edge NEXAFS could be recorded. After spectra deconvolution the different sulfur species and their behavior over time are analyzed. While for the first cycles a reversible formation of polsulfides is visible further cycles show a steady increasing of polysulfides due to the solubility in the electrolyte solution and thus the loss of cathode active material and capacity fading.

The investigation of polysulfides for different states of charges (SOC) and state of health (SOH) enables a deeper understanding of the main degradation process. These information help to improve the battery system by modify its materials e.g. with binder components or by choosing an optimal (dis-)charge current. The simple set up enables also investigations from the anode side. In addition, the set up can be adapted for different types of batteries with other active materials, e.g. NCM Li-Ion batteries.

References: [1] M. Müller, S. Choudhury, K. Gruber, V. Cruz, B. Fuchsbichler, T. Jacob, S. Koller, M. Stamm, L. Ionov, B. Beckhoff, Spectrochim. Acta B 94-95, 2014, 22-26