Investigating the ageing of different sulfur composite electrodes in lithium sulfur cells using electrochemical impedance spectroscopy and the distribution of relaxations times method

Dominik Steckermeier [a], Paul Titscher [a,b], Prof. Dr. A. Kwade [a,b]
[a] Institute for Particle Technology, Technische Universität Braunschweig, Volkmaroder Str. 5, 38104 Braunschweig, Germany

[b] Battery LabFactory Braunschweig, Technische Universität Braunschweig, Langer Kamp 19, 38106 Braunschweig, Germany

E-mail: d.steckermeier@tu-braunschweig.de

Lithium-sulfur batteries promise to improve gravimetrically sensitive applications in terms of energy storage due to its high theoretical specific energy. However, poor cycling stability due to the redox shuttle effect and dendrite formation hinder commercialization. To overcome these challenges the comprehension of internal processes during cycling is essential. Electrochemical impedance spectroscopy (EIS) offers valuable insights into assembled cells. Being a quasi-stationary method EIS does not affect cyclic aging and, combined with the distribution of relaxation times (DRT) method, reveals the nature of various polarization processes, which are relevant for the cycling stability.

Lithium-sulfur cells are assembled in an El-Cell setup with a lithium reference electrode as well as in the form of CR2032 coin cells without reference electrode. Cathodes are made with 60:30:10 weight-% (sulfur/carbon/binder) recipe and various binders (CMC, PVDF, PEO). The cells are assembled with DME/DOL 50/50 (v/v) as electrolyte. The cells are formatted with three cycles at C/10. The coin cells are aged for 100 cycles obtaining EIS data every twentieth cycles. Electrode resolved EIS data is obtained from the El-Cells at different temperatures and the DRT method is applied to these spectra. The temperature dependence of the underlying polarization processes is used to calculate the activation energy of the processes and thus identify the said processes. The DRT functions of the coin cells are calculated employing the knowledge of the cathode's characteristic frequencies out of the electrode resolved EIS measurements. A suitable equivalent circuit is chosen accordingly to the DRT functions. Based on this, the dependence of the polarization processes on cyclic age and state of charge is quantified.

The presented results show that the overall impedance of the cells is dominated by cathodic processes. The DRT of the cathodes reveal two unique signals with different relaxation times. One signal represents an SEI like film formation on the cathode surface. The other signal represents the phase transfer reaction. The increase of the total internal resistance of the cell during the aging process is mainly associated with a change of the charge transfer resistance at the cathode. The results promise that the aging-induced effect of both the film resistance and phase transfer resistance are strongly depending on the used binder. In this regard, CMC based cathodes show the most distinct results.

Category 6. Advanced Analytical Tools