

Next generation battery electrochemistry analyzed –
towards a validated computational model of the
lithium/sulfur cell

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The lithium-sulfur (Li/S) battery is among the most promising next-generation systems for electrochemical energy storage and recent advances have brought the Li/S battery even closer to the verge of commercialization [1]. The complex redox chemistry of sulfur, the large number of soluble intermediates and the dissolution and precipitation of solid phases, however, still present a major challenge to understanding and mastering Li/S electrochemistry.

The goal of this work is to contribute to the understanding of the Li/S battery and its limitations by investigating the internal state of a battery by experimental observations and simulations with a physically-based electrochemical model of the Li/S cell. The computational model used for this work is based on our recently published model [2] of the Li/S cell including a multi-step reaction mechanism, a detailed model of the evolution of solid phases [3] as well as multi-component (Li^+ , PF_6^- , S_8 , S_8^{2-} , S_6^{2-} , S_4^{2-} , S_2^{2-} ,

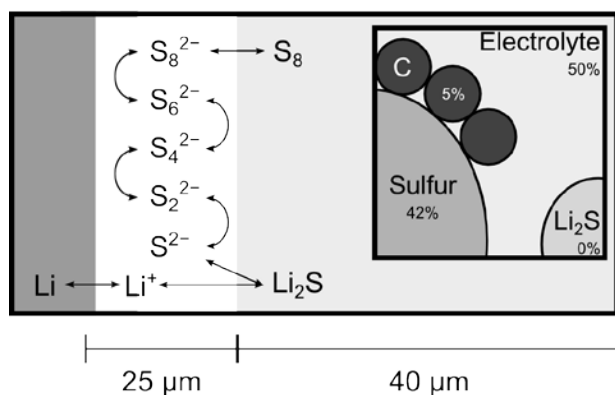


Fig. 1: Cell compartments in the 1D-model. Left to right: negative electrode (lithium metal), electrolyte-filled separator, positive electrode. Illustrated are the proposed reaction mechanism and the composition of the positive electrode.

S^{2-}) mass and charge transport.

To parameterize and refine the model, experimental data were obtained from Li/S coin cells operated under various conditions. The cells used for this study are composed of Li metal anodes, an ionic liquid based electrolyte and positive electrodes made from a carbon/binder/lithium sulfide composite, cf. Ref. [4]. As a first step, they were further optimized by substituting some of the conductive carbon with more effective components and by modifying the electrolyte composition.

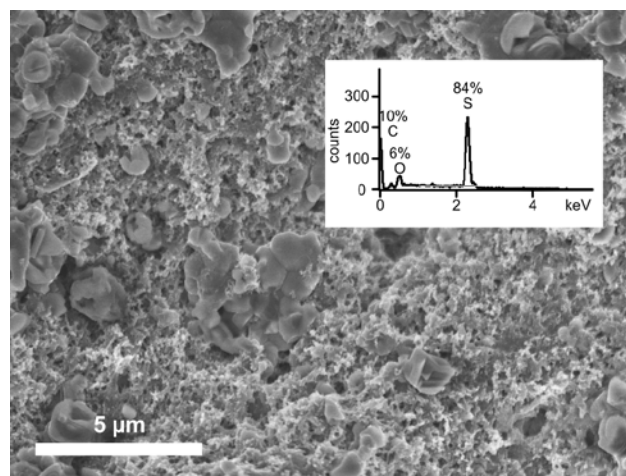


Fig. 2: Information on the microstructure of the sample is obtained from SEM images. Inset: The atomic composition of the sample is analyzed by EDX.

The techniques used for data collection include electrochemical methods, i.e. short and long term cycling at different charge/discharge rates, cyclic voltammetry, impedance spectroscopy (also during cycling) as well as ex situ methods, e.g. SEM imaging at various states of charge and states of health.

Along with prior knowledge about the materials used and the geometrical properties of the cells, these data were used to determine all parameters required for the model.

Using the refined model, most experimental results can be reproduced with good agreement. Validated in such a way, the model is used to simulate properties of the Li/S cell that are not easily accessible by experiments, e.g. lithium and polysulfide concentration gradients within the electrolyte and electrode volume expansion during cycling.

Results include simulations of charge/discharge curves and electrochemical impedance spectra [5] as well as mass distribution and concentration profiles. The results confirm that the discharge behavior for the most common type of Li/S cell is governed by the presence of solid reactant and product phases in exchange with the dissolved sulfur poly-anions. The first and second discharge stages are characterized by the presence of solid S_8 and Li_2S , respectively, while all sulfur compounds are dissolved in the electrolyte during an intermediate stage. Simulated electrochemical impedance spectra indicate that the contributions of various processes to the cell's overpotential are significantly different for different stages of charge.

These and other findings help to understand what is happening in the cell during operation, which in turn helps to identify optimized operation conditions and improve cell design on the electrode and material level.

References

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