Insights on the Formation of Solid Charge & Discharge Products in Lithium-Sulfur Batteries

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A major driving force for the development of electrochemical storage technology with high energy density is the electrification of the mobility sector. High expectations rest on the development of beyond Li-Ion battery systems [1]. Especially, lithium-sulfur batteries (Li/S) are believed to be a promising candidate already in the near future. Despite the increasing efforts to realize a large-scale commercialization several fundamental properties of Li/S batteries are still a matter of intensive research. Recently, several groups investigated the influence of surface properties at the positive electrode, like the affinity towards polysulfides or surface roughness, on the morphology and spatial distribution of solid charge and discharge products [2]–[4]. The results indicate that a spatial control of the formation of solid Li_2S is able to improve battery performance, however, additional design guidelines are needed to optimize this approach. Simulations on the continuum scale give the opportunity to interpret the measurements, improve our understanding of relevant processes, and allow for an optimization of interface, electrode and, cell designs.

In our contribution we will present simulation results of a detailed model describing the nucleation, growth, and dissolution of the solid end-products S_8 and Li_2S in Li/S batteries. In our calculations we simulate the dynamic evolution of the corresponding particle size distributions at various positions in the cell and take into account their effect on transport properties and active surface areas. The model is integrated in our framework for the simulation of metal-sulfur (Me/S) batteries which handles the reaction and transport of dissolved sulfur species on cell level [5]. This multiscale approach allows us to track the concentration and volume fraction of sulfur species during cycling and additionally gives the opportunity for a systematic study of the polysulfide shuttle. The simulated evolution of solid volume fractions and particle size distributions are in good qualitative agreement with data of X-ray in-operando measurements recently published in the literature [6] and correlate the morphological properties of the electrode to the electrochemical characteristics. In a next step the model will be used to investigate the influence of additional positive electrode materials with different specific surface area and/or affinity towards sulfur species in order to assess their impact on battery performance.

This approach provides mechanistic insights on the operation of Li/S batteries and will contribute to the understanding and, therefore, improvement of next-generation batteries.

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