Continuum Modelling as Tool for Optimizing the Cell Design of Mg-Ion and Mg-S Batteries

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Regarding energy density, safety, cost, and sustainability rechargeable magnesium batteries (RMBs) are a very promising next-generation energy storage technology. However, for a successful commercialization of magnesium batteries there are still some fundamental and technical challenges to overcome, which are mainly caused by the high charge density of the bivalent cation and the consequential strong coulomb interactions with anions and solvent molecules.[1,2] A decisive bottleneck of the RMB technology is to establish a highly reversible, high voltage / high capacity cathode.

Up to date Chevrel phase (CP) Mo_6S_8 is still considered as benchmark intercalation cathode. By understanding of beneficial and limiting processes of this model electrode the development of novel high-capacity / high-voltage cathodes may be accelerated. Thereby, it is well-known that the morphology of an intercalation material can strongly influence the battery performance and smaller particles as well as thinner electrodes are common strategies for avoiding adverse effects of transport limitations.[3] Nevertheless, the low theoretical capacity and redox potential of CP intrinsically limits the reachable energy density of the battery, which is a major issue regarding practical applications. Therefore, high capacity conversion cathodes based on sulfur are a promising strategy for making RMBs attractive candidates for emerging energy storage markets. However, self-discharge and shuttling of dissolved polysulfides are major issues of Mg-S batteries, which cause loss of active material on the cathode side and surface passivation of the Mg anode. Consequently, the dissolution and diffusion of sulfur and polysulfides strongly limits the cycling stability, capacity retention, reversibility and lifetime of Mg-S batteries. Strategies to mitigate the polysulfide shuttle and its adverse effects include the design of novel sulfur hosts, electrolytes and functional separators. Besides spatial confinement by encapsulating the sulfur into the cathode, chemical interactions like covalent bonds and adsorption are a promising approach to reduce the migration of sulfur containing species to the Mg anode. Interestingly, CP is not only electrochemically active itself but it can also strongly adsorb polysulfides and moreover, enhance the electrochemical kinetics of the conversion reaction, which significantly enhances the performance of Mg-S batteries.[4]

In our contribution we carefully study Mg-ion batteries with a CP cathode as well Mg-S batteries with CP additive as adsorbent and redox mediator to get a better understanding of how to overcome undesired limitations as well as how to maximize beneficial effects. Therefore, we present a newly developed continuum model for CP and its integration into a simulation framework for metal-sulfur batteries. The parameterization and validation of the model is based on DFT calculations and experimental data. Different kind of (transport) limitations and their impact on the battery performance are studied in detail. Thereby, we focus on the influence of the battery design and especially the 3D microstructure. Moreover, different ways to incorporate CP into Mg-S batteries and different ratios of S to CP are analyzed. All in all, the combination of different modelling techniques with experimental measurements provides important insights into the operation of RMBs and enables an optimization of the cell design.

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