Continuum Modelling as Tool for Optimizing the Cell Design of Magnesium Batteries

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Magnesium-based next-generation batteries are of great interest since magnesium is not only very abundant, which allows economic and sustainable applications, but also less prone to dendrite formation than many other metals. Together with the bivalency of the magnesium cations the resulting possibility to safely use a metal anode enables batteries with high specific capacities.
However, for a successful commercialization of magnesium batteries there are still some challenges to overcome. The high charge density of the bivalent cation causes strong coulomb interactions with anions and solvent molecules. Therefore, magnesium salts are prone to form ion pairs and bigger clusters – especially at high concentrations, which may adversely affect the transport in the electrolyte and the electrochemical reaction at the electrode.[1] Moreover, energetic barriers for desolvation and solid-state diffusion of the double-charged magnesium ion are usually very high, which can have a crucial impact on the battery performance. Former can significantly hinder the electron-transfer reaction,[2] whereas latter makes the choice of suitable cathode materials very challenging.
Consequently, a good understanding of the limiting processes in rechargeable magnesium batteries is key to develop novel high-capacity / high-voltage cathode materials. For instance, 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. However, high mass loadings as well as suitable separators are still essential bottlenecks for commercialization of magnesium-ion batteries.
Up to date Chevrel phase (CP) Mo_6S_8 is considered as benchmark intercalation cathode and $Mg[B(hfip)_4]_2$ / DME is seen as most promising chloride-free magnesium electrolyte.[3,4] In our contribution we carefully study this model system of a magnesium-ion battery to get a better understanding of how to overcome undesired limitations. Therefore, we present a newly-developed continuum model, which is able to describe the complex intercalation process of magnesium cations into a CP cathode. The model considers not only the different thermodynamics and kinetics of the two intercalation sites of Mo_6S_8 and their interplay but also the impact of the desolvation on the electrochemical reactions and possible ion agglomeration. 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. All in all, the combination of different modelling techniques with experimental measurements provides important insights into the operation of magnesium ion batteries and enables an optimization of the cell design.

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