

Modelling of Magnesium Intercalation into Chevrel Phase Mo₆S₈

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Regarding energy density, safety, cost, and sustainability rechargeable magnesium batteries are a very promising next-generation energy storage technology. However, the high charge density of the bivalent magnesium 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 a suitable cathode material very challenging.

Chevrel phase (CP) Mo₆S₈ was the first material to show reversible magnesium insertion with reasonable kinetics.^[3] Up to date CP still is often used as benchmark system and a good understanding of the limiting processes 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 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.

In our contribution we will present a newly developed 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 Mo₆S₈ and their interplay but also the impact of the desolvation on the electrochemical reactions and possible ion agglomeration. The continuum model is then applied to the state-of-the-art chloride-free Mg[B(hfip)₄]₂ / DME electrolyte,^[4] whereby DFT calculations and experimental data are the basis for parameterizing and validating the model. 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.

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