Modelling of Magnesium Intercalation into Chevrel Phase

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Regarding energy density, safety, cost, and sustainability rechargeable magnesium batteries are a very promising next-generation energy storage technology. However, for a successful commercialization of Mg batteries there are still some challenges to overcome. Generally, the high charge density of the bivalent cation causes strong coulomb interactions with anions and solvent molecules. Therefore, energetic barriers for desolvation and solid-state diffusion are usually very high, which can have a crucial impact on the battery performance. Former can significantly hinder the electron-transfer reaction,[1] whereas latter makes the choice of suitable cathode materials very challenging. 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. Moreover, the presence of chlorides can influence the intercalation process.[2]

Up to date Chevrel phase (CP) Mo_6S_8 is considered as a benchmark intercalation cathode. 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 (Fig. 1). 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. The impact of different electrolytes as well as the role of electrolyte constituents, especially chlorides, on the battery performance are studied in detail. All in all, the combination of modelling with experimental measurements provides important insights into the operation of magnesium ion batteries and enables an optimization of the cell design.

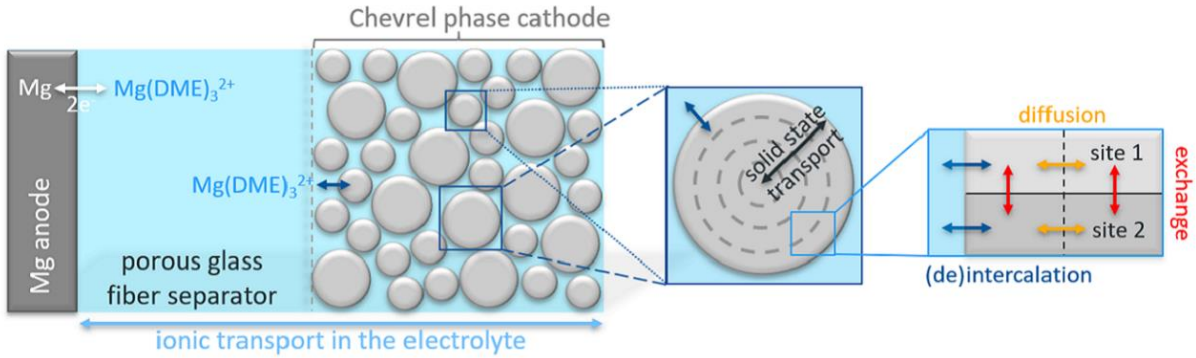

Figure 1: Schematic illustration of the 1+1D continuum model for a Mg / $Mg_2Mo_6S_8$ battery.

1. Drews, J.; Jankowski, P. et al. *ChemSusChem* **2021**, *14* (21), 4820-4835. DOI: 10.1002/cssc.202101498
2. Attias, R; Chae, M.S. et al. *ACS Catalysis* **2020**, *10 (14)*, 7773-7784. DOI: 10.1021/acscatal.0c01956

Acknowledgements: This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 824066 (E-MAGIC). The simulations were carried out at JUSTUS 2 cluster supported by the state of Baden-Württemberg through bwHPC and the German Research Foundation (DFG) through grant No INST 40/575-1 FUGG.