

Modelling of electron-transfer kinetics in magnesium electrolytes: Influence of the solvent on the battery performance

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The possibility to store electricity from renewable sources is a key component of a sustainable energy supply system. Thereby, batteries based on metal anodes possess a considerably higher theoretical energy density than state-of-the-art Li-ion-technology. Taking into account additional requirements for economic, sustainable and safe applications, it becomes apparent, that magnesium-metal based next-generation batteries are of great interest.

However, the processes in the electrolyte and at the magnesium metal surface are not yet properly understood. The bivalency of the magnesium cations leads to strong coulomb interactions with the anion as well as with the solvent. It was found that 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 plating behaviour at the electrode.[1] Consequently, a good solvation is important for the dissociation of the magnesium salts, which is in turn crucial for a high ionic conductivity of the electrolyte. At the same time, the desolvation of double charged magnesium cations usually goes along with high energetic barriers, which can have a crucial impact on the deposition process. This can lead to significantly higher overpotentials for magnesium deposition compared to magnesium dissolution.

In our contribution we will present a newly developed kinetic model for electrochemical reactions at metal electrodes, which explicitly couples desolvation to electron transfer and, furthermore, qualitatively considers effects of the electrochemical double layer. By including this kinetics into our general transport model [2] the impact of five different solvents on the battery performance is studied for the state-of-the-art, chloride-free Mg[B(hfip)₄]₂ electrolyte salt [3]. The parametrization of the model is mainly based on DFT calculations [4] and the simulation results are validated and supported by experimental data. It becomes apparent that the desolvation of one coordination site of the solvated cation is limiting the overall magnesium deposition. Consequently, the thermodynamics of this initial desolvation, which are determined by the solvent, play a crucial role for the battery performance. However, the impact of the electrochemical double layer is equally important to reproduce the non-intuitive qualitative trends observed in the experiments with different solvents. All in all, the combination of different modelling techniques with experimental measurements provides extensive insights into the deposition mechanism of magnesium and enables to identify the general properties, which are relevant for fast kinetics and consequently small overpotentials. These fundamental insights on the operation of magnesium batteries are key to further optimize their performance.

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