

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

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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 processes in the electrolyte and at the electrode 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)<sub>4</sub>]<sub>2</sub> 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 measurements. 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 important insights into the operation of magnesium batteries.

## Keywords:

Continuum modelling, kinetics, rechargeable magnesium batteries, desolvation, deposition mechanism, electrochemical double layer.

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