

First steps towards a model of Mg-S batteries

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The use of alkaline/alkaline earth metal as anode material, such as Li, Na, Mg, or Zn offers many benefits compared to conventional intercalation chemistry based battery technologies. Lithium-sulfur batteries are one of most investigated systems of that type. In recent years magnesium-sulfur batteries are highly discussed as a next-generation energy storage system. Magnesium can be directly used as anode material due to its dendrite-free deposition and thus increases the safety as well as energy density of such a cell. Two electrons are stored per Mg atom which compensates the rather low discharge potential of magnesium-sulfur cells of 1.7 V and provides a high capacity of 3832 mAh/cm³ and 2230 mAh/g [1]. The system offers a theoretical energy density of over 3200 Wh/l, which is beyond that of lithium-sulfur batteries and is therefore very promising for automotive and stationary applications [2]. Furthermore magnesium and sulfur are both naturally abundant, low in price and non-toxic. However, magnesium-sulfur batteries are in a very early stage of research and development. The first proof of concept was reported by Kim et al. in 2011. Critical issues of this first cell were a short lifetime of only two cycles and an initial discharge potential of only 1 V indicating side reactions [3]. A new electrolyte recently developed by Zhao-Karger et al. pushed the system to the next level and a cell with a lifetime of more than 50 cycles and a discharge potential near the theoretical value was demonstrated. However, analogous to lithium-sulfur batteries magnesium-sulfur batteries show polarization effects during charging, low cyclic stability, initial capacity fading, and a polysulfide shuttle. The reaction mechanism is proposed analogous to those of lithium-sulfur batteries but is still not investigated in detail.

To the best of our knowledge there are no continuum models of magnesium-sulfur batteries in the literature. Therefore, we present the first step towards a mechanistic model of magnesium-sulfur cells. Our aim is to provide more insight in the operation of Mg-S batteries and to support the experimental progress. We use a continuum model based on porous electrode and dilute solutions theory. The transport of dissolved species is described by the Nernst-Planck equation where transport occurs via diffusion and migration. Our kinetic model includes a reduced reaction mechanism from our previous work on Li-S cells which was able to reproduce the key experimental results [4]. In this work we additionally take into account adsorption and desolvation effects [5] which are expected to be prominent for Mg cations. In close collaboration with experimentalists we aim at guiding new developments of the Mg-S system.

References:

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