

Investigation of Magnesium-Sulfur Batteries using Electrochemical Impedance Spectroscopy

**J. Häcker^{*1}, C. Danner¹, Z. Zhao-Karger², B. Sievert¹,
N. Wagner¹ and K. A. Friedrich^{1,3}**

¹German Aerospace Center, Institute of Engineering Thermodynamics,
Pfaffenwaldring 38-40, 70569 Stuttgart, Germany

²Helmholtz Institute Ulm (HIU) Electrochemical Energy Storage,
Helmholtzstrasse 11, 89081 Ulm, Germany

³University of Stuttgart, Institute for Energy Storage,
Pfaffenwaldring 31, 70569 Stuttgart, Germany

*E-mail: joachim.haecker@dlr.de

The combination of magnesium and sulfur in an electrochemical cell is a promising candidate to cope the need of high-energy batteries for future applications like electric vehicles. Due to the abundance and non-toxicity of both elements it is not only a low cost and environmentally friendly couple but also ensures safety as magnesium offers dendrite-free deposition. Theoretically, a cell voltage of 1.77 V and an energy density of 3200 Wh l⁻¹ can be achieved. However, the Mg-S system suffers from fast capacity decay in the first cycles and poor cycle life. Nevertheless, significant research progress is gained since the first report by Kim et al. in 2011 [1], especially in the development of suitable electrolytes. Recently, Zhao-Karger et al. synthesized a chloride-free Mg(BH₄)₂-derived electrolyte [2] with enhanced properties in terms of electrochemical and thermal stability as well as cycling performance. Still, despite sophisticated studies the mechanisms leading to fast cell degradation are not well understood.

To identify intrinsic processes electrochemical impedance spectroscopy (EIS) was applied to Mg-S cells as a function of open cell voltage (OCV), state of charge (SOC) and temperature. As the occurring reactions are difficult to be separated also symmetrical cells were examined by the means of the distribution of relaxation times (DRT). From these insights an electric equivalent circuit based on R-CPE circuits was developed in which each circuit is assigned to a specific intrinsic process. Overall, these results indicate that the magnesium electrode features surface layers, which cause overpotentials and limited cycle life. In addition, the retention of polysulfides in the sulfur electrode is crucial as they not only cause loss of active material but also are incorporated in forming passivating layers on the magnesium anode.

References

- [1] Kim, H; Muldoon, J. Structure and compatibility of a magnesium electrolyte with a sulphur cathode. *Nat. Commun.* **2011**, 2, 427.
- [2] Zhao-Karger, Z; Fichtner, M. A new class of non-corrosive, highly efficient electrolytes for rechargeable magnesium batteries. *J. Mater. Chem. A*, **2017**, 5, 10815-10820.