

EIS investigation of intrinsic processes in Mg-S batteries

Joachim Häcker^a, Christian Danner^a, Norbert Wagner^a, K. Andreas Friedrich^{a,b}

^a *German Aerospace Center, Institute of Engineering Thermodynamics,
Pfaffenwaldring 38-40, 70569, Stuttgart, Germany*

^b *University of Stuttgart, Institute for Energy Storage,
Pfaffenwaldring 6, 70569, Stuttgart, Germany*

E-mail: joachim.haecker@dlr.de

Sulfur is one of the most promising cathode materials due to its high theoretical capacity of 1672 mAh g⁻¹, its low cost and environmental friendliness. In combination with a negative magnesium electrode (Mg-S) a cell voltage of 1.77 V and an energy density of 3200 Wh l⁻¹ can be theoretically achieved. In contrast to lithium metal, magnesium features significant advantages as it is abundant and shows no dendrite formation during cycling, which ensures superior safety.

However, the Mg-S system is still in an early stage of research (first report by Kim et al. in 2011 [1]) and suffers from fast capacity decay in the first cycles and poor overall cycle stability. Especially the search for a suitable electrolyte emerged to be difficult as it inter alia has to be non-nucleophilic and capable of reversible Mg deposition/stripping. Very recently Zhao-Karger et al. published a Mg(BH₄)₂-derived electrolyte with enhanced cycling properties [2] which allows further detailed investigation of Mg-S cells.

To identify the origin of the fast degradation electrochemical impedance spectroscopy (EIS) was applied to full Mg-S cells as a function of state of charge (SOC) and temperature. As the occurring processes 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 four R-CPE circuits was developed in which each circuit is assigned to a specific intrinsic process.

As some of the processes like the formation of a solid electrolyte interphase (SEI) on the Mg electrode occur specifically in the first stages of galvanostatic cycling, the focus was on the first discharge and charge cycle, respectively. A large SOC and temperature dependence for the derived resistances was observed whereupon especially the thermal activated reduction to short chain magnesium polysulfides is accompanied by a large decline in overpotential of the second reduction plateau. Furthermore, it can be concluded that the first cycle represents a formation cycle, which strongly determines the further cell performance.

References:

- [1] H. S. Kim, T. S. Arthur, G. D. Allred, J. Zajicek, J. G. Newman, A. E. Rodnyansky, A. G. Oliver, W. C. Boggess, J. Muldoon, Nat. Commun. 2 (2011), 427.
- [2] Z. Zhao-Karger, M. E. G. Bardaji, O. Fuhr, M. Fichtner, J. Mater. Chem. A, 5 (2017) 10815-10820.