Modeling and Simulation of Metal-Sulfur Battery with Sulfurized Polyacrylonitrile (SPAN) Cathodes

Esther Kezia Simanjuntak[1,2,4], TimoDanner[1,2,4], Peiwen Wang[3], Michael R. Buchmeiser[3], Arnulf Latz[1,2,4]
[a]German Aerospace Center (DLR), Institute of Engineering Thermodynamics, Pfaffenwaldring 38-40, 70569, Stuttgart, Germany
[b]Helmholtz Institute Ulm for Electrochemical Energy Storage (HIU), Helmholtzstraße 11,89081, Ulm, Germany
[c]Institute of Polymer Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569, Stuttgart, Germany
[d]University of Ulm, Institute of Electrochemistry, Albert-Einstein-Allee 47, 89081, Ulm, Germany
esther.simanjuntak@dlr.de

The increasing demand for rechargeable and high-energy density batteries for portable devices, electric vehicles, and large-scale stationary storage systems has driven the intensive research to find more sustainable and economical materials. Lithium–sulfur (Li–S) batteries have been considered as a promising material for next-generation batteries with very high theoretical capacity (2,062 mAh/cm^3). However, repeated plating and stripping of Li can lead to the growth of dendrites that potentially cause short circuits and battery failure. In recent years, magnesium (Mg) was proposed as anode material for Metal-Sulfur (Me-S) batteries due to its reduced tendency to dendrite formation and high volumetric capacity (3,837 mAh/cm^3) [1]. Unfortunately, similarly to Li-S batteries, Mg-S batteries show a low coulombic efficiency and fast self-discharge due to the polysulfide shuttleSeveral mitigation strategies to reduce the polysulfide shuttle effect, have been developed for Li-S batteries and some of these concepts have been also transferred to Mg-S batteries [2]. One of the promising approaches is to covalently bind the sulfur to a polymer backbone. Long cycle life and high specific capacities have been demonstrated for sulfurated poly(acrylonitrile) (SPAN) cathodes in lithium-based batteries and, more recently, the proof-of-concept was also shown for Mg-SPAN batteries [3,4].

In our contribution, we present a novel continuum model for SPAN electrodes and demonstrate its application to Me-SPAN batteries. Within our simulation framework we include both red/ox reactions of sulfur covalently bound to the polymeric backbone of SPAN and transport as well as electrochemical reactions of the polysulfides in solution. Model parameters are extracted from structural and electrochemical characterization of SPAN composite electrodes and we demonstrate that we were able to reproduce the measured discharge curves. Starting with this standard configuration we perform simulation studies to investigate the influence of electrode geometric parameters such as electrode thickness and tortuosity on Li-SPAN cell performance. Finally, we apply our model for the simulation of Mg-SPAN batteries with dual salt electrolyte and investigate the kinetic mechanism in this complex electrochemical system. In collaboration with our experimental partners, we aim on providing more insights into the degradation mechanisms and limiting factors for battery performance, which are able to guide new developments for Me-SPAN batteries.

Acknowledgements
Financial support by the German Federal Ministry of Education and Research (BMBF) within the project MagSiMal (project number 03XP0208) is gratefully acknowledged.

References:
[1] Z. Zhao-Karger, M. Fichtner: “Magnesium–sulfur battery: its beginning and recent progress”, MRS Commun. 2017, 770 - 784.
[2] P. Wang, M. R. Buchmeiser: “Rechargeable Magnesium–Sulfur Battery Technology: State of the Art and Key Challenges”, Adv. Funct. Mater. 2019, 1905248.
[3] P. Wang, M. R. Buchmeiser: “High-Performance Magnesium-Sulfur Batteries Based on a Sulfurated Poly(acrylonitrile) Cathode, a Borohydride Electrolyte and a HighSurface Area Magnesium Anode”, Batteries & Supercaps 2020, 10.1002/batt.202000097.
[4] P. Wang, M. R. Buchmeiser: “Characteristics of magnesium-sulfur batteries based on a sulfurized poly(acrylonitrile) composite and a fluorinated electrolyte”, Electrochimica Acta 2020, 361, 167024.
[5] R. Richter, A. Latz: “Insights into Self-Discharge of Lithium– and Magnesium–Sulfur Batteries”, ACS Applied Energy Materials. 2020, 3, 9, 8457-5474.