

# Understanding Mg/S Batteries: The Different Electrochemistry of Lithium and Magnesium Polysulfide Solutions

Georg Bieker<sup>a</sup>, Kirsi Jalkanen<sup>a</sup>, Diddo Diddens<sup>b</sup>, Martin Kolek<sup>a</sup>,  
Martin Winter<sup>a,b</sup>, Peter Bieker<sup>a</sup>

<sup>a</sup> *MEET Battery Research Center, University of Muenster,  
Corrensstr. 46, 48149 Muenster, Germany*

<sup>b</sup> *Helmholtz-Institute Muenster (HI MS), IEK-12, Forschungszentrum Juelich GmbH,  
Corrensstr. 46, 48149 Muenster, Germany*

E-mail: georg.bieker@uni-muenster.de

Lithium/sulfur batteries are considered as promising post-lithium-ion battery systems, because the high specific capacity of sulfur drastically outranges the capacities of Li-ion insertion cathodes. However, at the Li metal anode, dendrite formation and a high reactivity with the electrolyte lead to lifetime and safety concerns.[1] In order to circumvent these issues while maintaining high specific capacities, magnesium/sulfur batteries are increasingly studied.[2] In contrast to Li, the Mg metal anode enables homogeneous Mg deposition and dissolution at up to 100% Coulombic efficiency. In addition, Mg is much cheaper and highly abundant. In Li/S and Mg/S cells, charge and discharge of the sulfur cathode proceeds through a cascade of  $S_x^{2-}$  and  $S_y^-$  polysulfide intermediates. The individual polysulfide chemistries thus determine the accessibility and performance of both battery systems.

For the first time, both the electrochemical behavior as well as the solubility and stabilization of Mg polysulfides were studied. In order to reveal the influence of  $Li^+$  and  $Mg^{2+}$ , their polysulfide solutions were systematically compared in a broad variety of solvents. At first, solutions of “ $Li_2S_8$ ” and “ $MgS_8$ ” in DMSO, DMF, ACN, THF, DME, TEGDME, and Pyr<sub>1,4</sub>TFSI were investigated in UV/Vis spectroscopy.[3] Afterwards, the influence of additional LiTFSI and MgTFSI<sub>2</sub>, respectively, was examined and the red/ox processes of these polysulfide-containing electrolytes were studied in CV experiments. Finally, quantum mechanical calculations were conducted.

It could be shown that Mg polysulfides form similar disproportionation and dissociation equilibria as Li polysulfides. The stabilization of different polysulfide species is not only determined by the solvents' relative dielectric permittivity and donor number, but also depends on the coordination by either Li or Mg cations. Accordingly, the red/ox behavior of Li and Mg polysulfide solutions differ strongly. It is demonstrated that the overvoltages during charge and discharge of Mg/S cells are related to the electrochemistry of Mg polysulfides. The achieved insights into the fundamentals of the Li/S and Mg/S cell chemistries might lead the way towards new electrolyte designs and play a key role in increasing the reversibility and lowering the overvoltages of Mg/S cells.

Acknowledgements:

Funding by the German Federal Ministry of Education and Research (BMBF) within the projects ‘ACHiLiS’ (03XP0037A) and ‘MgMeAnS’ (03XP0140) is gratefully acknowledged.

References:

[1] G. Bieker, M. Winter, P. Bieker, Phys. Chem. Chem. Phys. 17 (2015) 8670-8679.

[2] Z. Zhao-Karger, M. Fichtner, MRS Comm., (2017) 1-15.

[3] G. Bieker, J. Wellmann, M. Kolek, K. Jalkanen, M. Winter, P. Bieker, Phys. Chem. Chem. Phys. 19 (2017) 11152-11162.