Supporting Information

Investigation on the Formation of Mg metal Anode/Electrolyte Interfaces in Mg/S Batteries with Electrolyte Additives

Vinayan Bhaghavathi Parambath^{a*}, Zhirong Zhao-Karger^b, Thomas Diemant^c, Markus Jäckle^d, Zhenyou Li^a, Torsten Scherer^b, Axel Gross^{a, d}, R. Jürgen Behm^{a c}, Maximilian Fichtner^{a, b*}

^a Helmholtz Institute Ulm (HIU) Electrochemical Energy Storage, Helmholtzstr. 11, D-89081 Ulm, Germany

^b Karlsruhe Institute of Technology (KIT), Institute of Nanotechnology, P.O. Box 3640, D-76021 Karlsruhe, Germany

^c Institute of Surface Chemistry and Catalysis, Ulm University, Albert-Einstein-Allee 47, D-89081 Ulm, Germany

^d Institute of Theoretical Chemistry, Ulm University, Albert-Einstein-Allee 11, D-89081 Ulm, Germany

* Corresponding author



Fig. S1: (a) S2p XP spectra of bulk sulfur and (b) S2p XP spectra of Mg polysulfides adsorbed on carbon matrix.



Fig. S2: (a) Evolution of the overpotential with respect to the cycling numbers for symmetric Mg||Mg cells in Mg electrolyte with low and high amounts of polysulfides additives. (b) Comparison of stripping/plating profiles for Mg electrolyte with low and high amounts of polysulfides additives after 300 cycles.



Figure S3: XP surface spectra for fresh Mg metal anode after soaking (30 minutes) in different electrolytes. The XPS data clearly show the deposition of MgS_x species on Mg metal surface along with MgO and MgF₂, for PS containing Mg electrolytes. Meanwhile the formation of MgI₂ species on Mg metal surface is confirmed in iodine containing Mg electrolytes.



Fig. S4: XP spectra recorded on a Mg electrode, cycled for prolonged time in Mg electrolyte, after different sputtering times.



Fig. S5: XP spectra recorded on a Mg electrode, cycled for prolonged time in iodine containing Mg electrolyte, after different sputtering times.



Fig. S6: XP spectra recorded on a Mg electrode cycled for prolonged time in Mg electrolyte with a low polysulfide concentration, after different sputtering times.



Fig. S7: Development of the atomic concentrations of different elements at the surface of Mg electrodes, which were cycled in (a) pure Mg electrolyte, and (b) in iodine containing Mg electrolyte, as a function of the sputtering time.



Fig. S8: Comparison of Mg 2s XP spectra recorded on a Mg electrode cycled in (a) pure Mg electrolyte, (b) Mg electrolyte containing iodine as additive, (c) Mg electrolyte containing polysulfide species as additive, (d) Mg electrolyte containing both polysulfide and iodine as additive, after different sputter times.



Fig S9: Scanning electron microscopic (SEM) images of an extensively cycled (700 h) Mg electrode in Mg electrolyte with a high amount of polysulfides additive.