Supporting Information

Existence of Solid Electrolyte Interphase in Mg Batteries: Mg/S Chemistry as an Example

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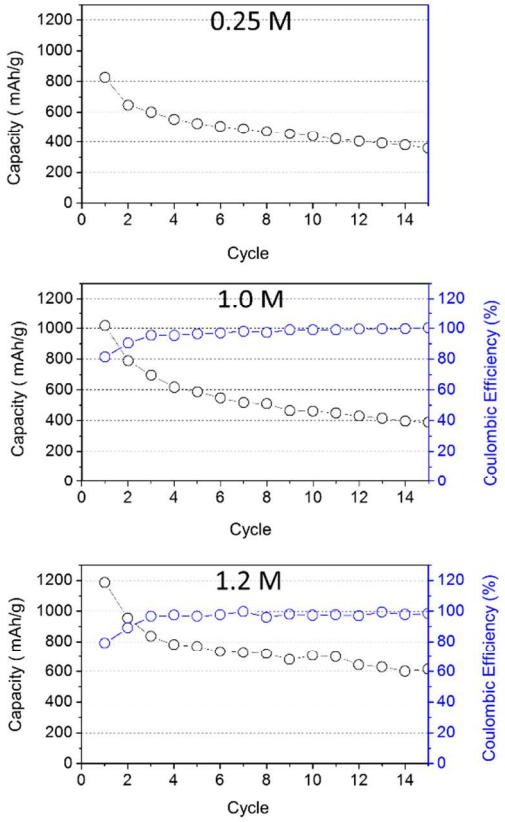


Figure S1. Cycling stabilities and coulombic efficiencies of three-electrode Mg/S cells in electrolytes with different concentrations. Coulombic efficiency in 0.25 M electrolyte is not shown since it is cut off by time. Note the cycling stability here is not comparable with our previous work[1] because in three-electrolyte set-up here the electrolyte amount is 1 mL, which is much more than that used in a two-electrode cell (< 100 uL).

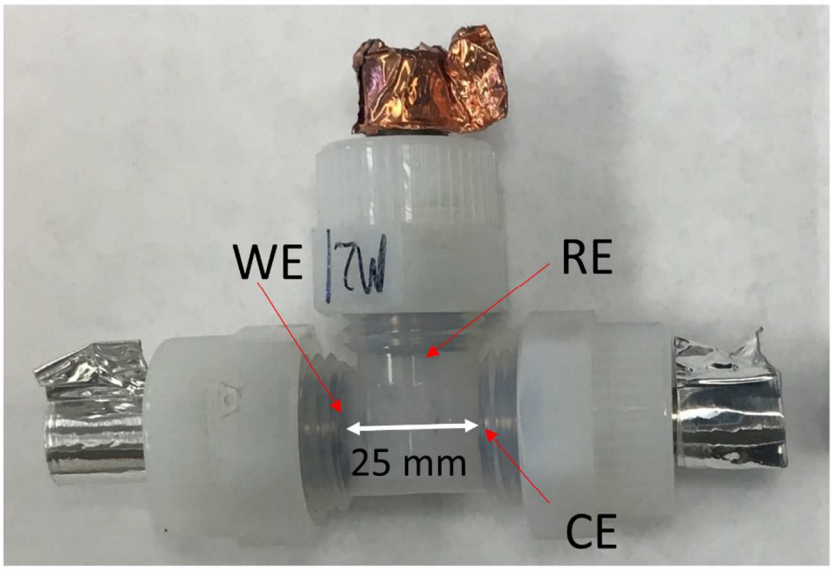


Figure S2. A S|Mg|Mg three-electrode cell before cycling.

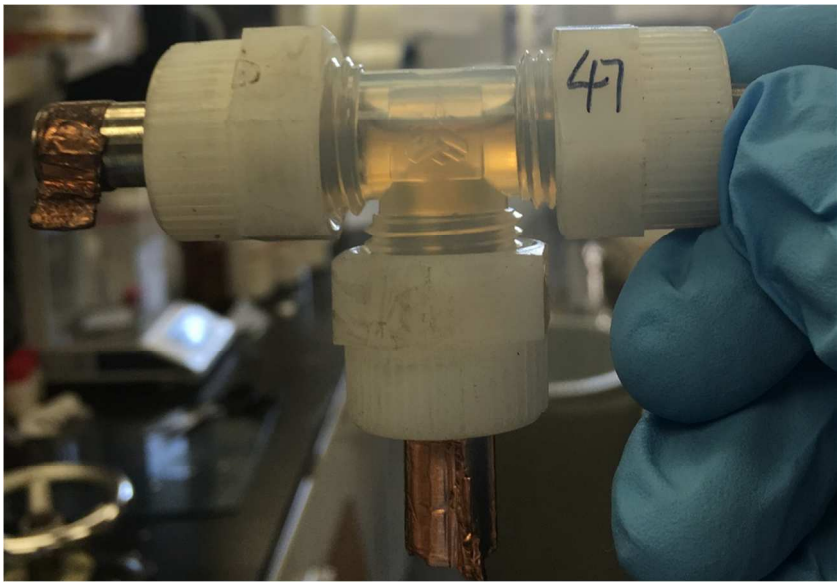


Figure S3. A Mg|Mg|Mg three electrode cell with electrolyte dissolved with 50 mM sulfur after first discharge. The color of the electrolyte turns to yellowish from transparent, which signals the formation of polysulfide.

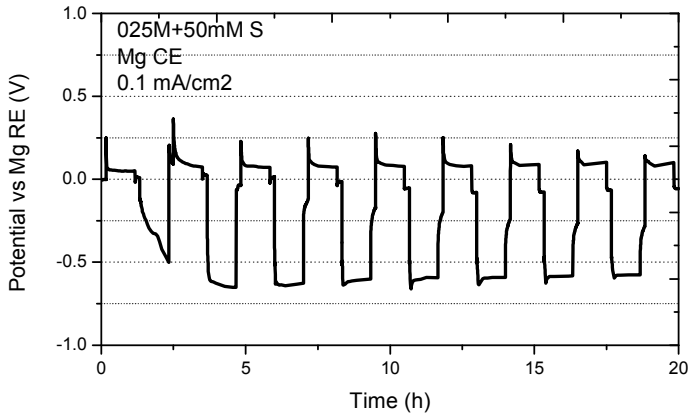


Figure S4. The potential of Mg CE in Mg|Mg|Mg three-electrode cell with sulfur containing electrolyte.

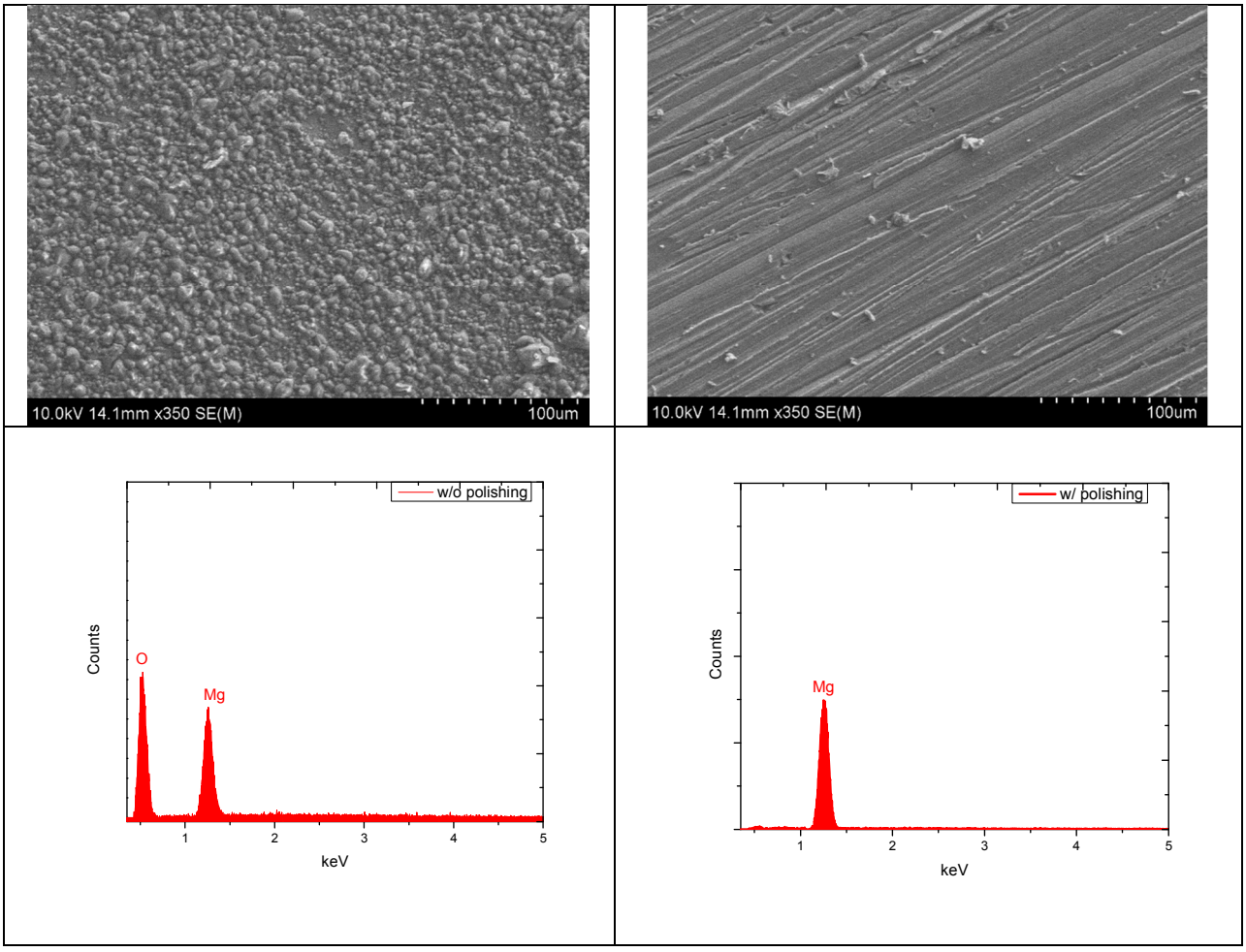
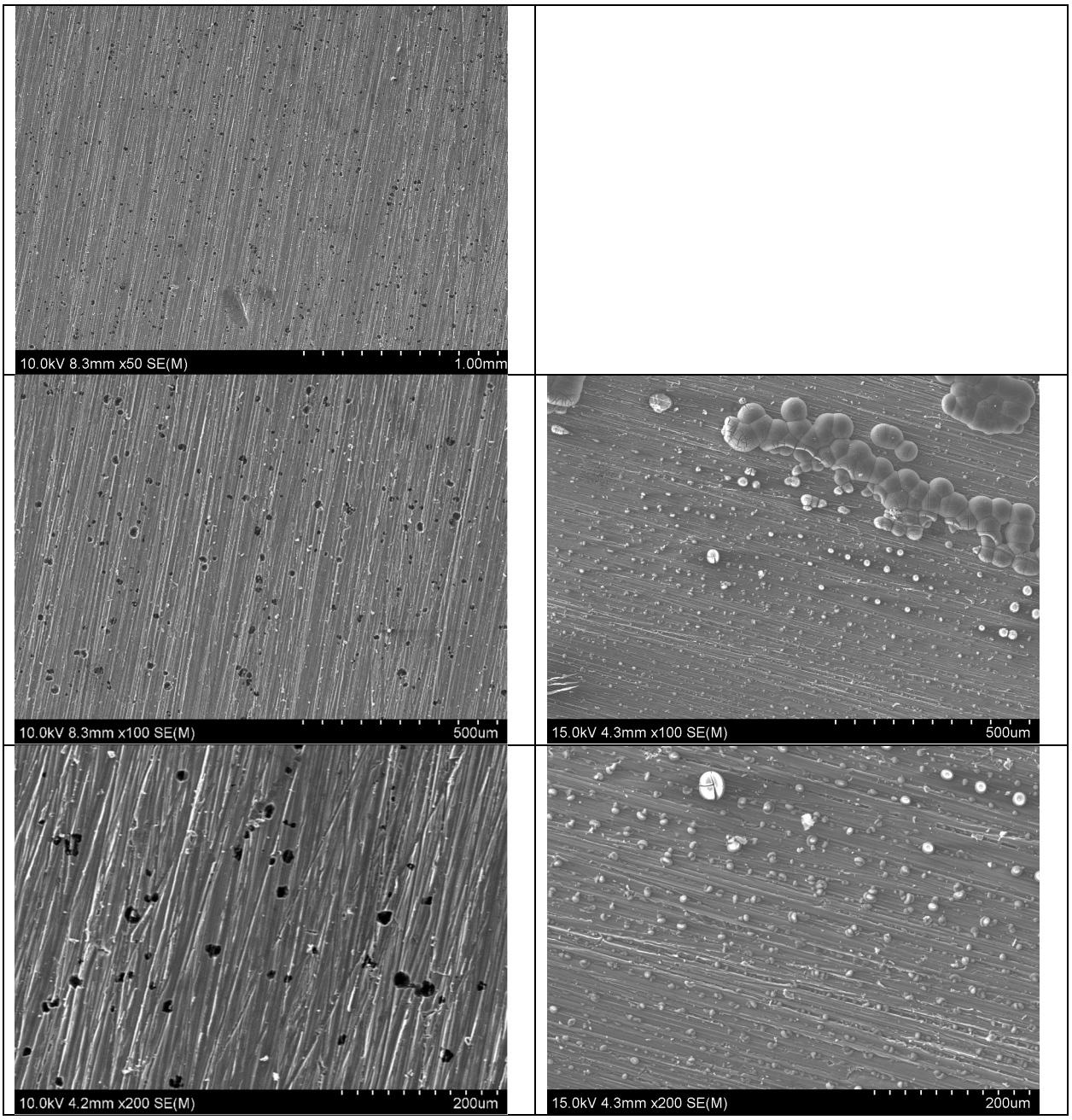


Figure S5. The morphology and EDX spectra of Mg disks before (left) and after polishing (right). Other than the Mg peak, EDX spectrum of pristine Mg electrode (before contacting electrolyte) (Fig. S5, left) is featured by a strong O peak due to the natural oxide layer on its surface. Sandpaper polishing can

remove this layer to a level that is not detectable by EDX (Fig. S5, right); however, a thin oxide layer (< 1.5 nm) detectable by X-ray Photoelectron Spectroscopy (XPS)[2] forms as long as fresh Mg surface is exposed even in glove box.[3]



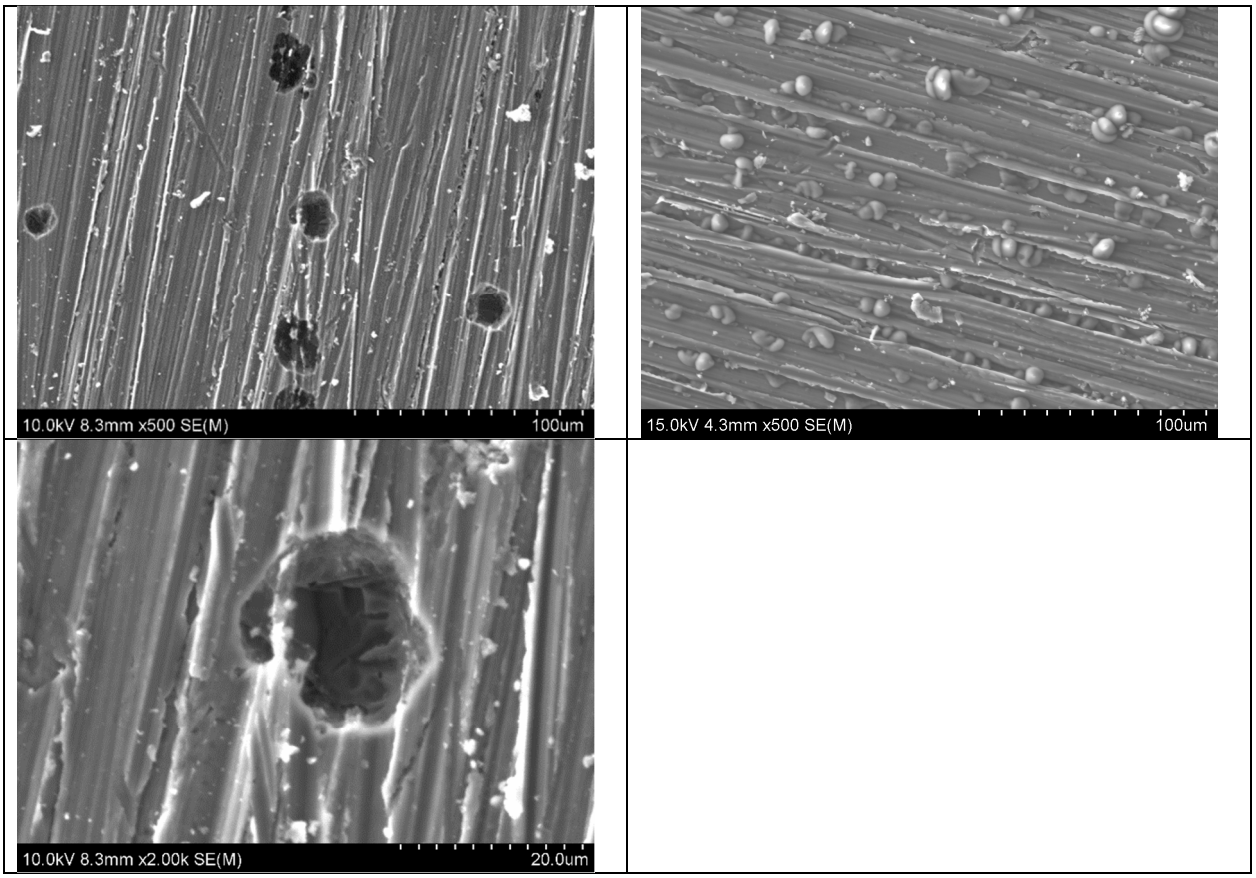


Figure S6. The morphology of Mg electrode after charging for 1 hour (left) and discharging for 3 hours (right) in sulfur containing electrolyte at different magnifications. Left: These uniformly distributed holes have similar sizes (~20 µm) and almost span the whole Mg surface. Right: The deposits have sizes ranging from several micron to tens of microns.

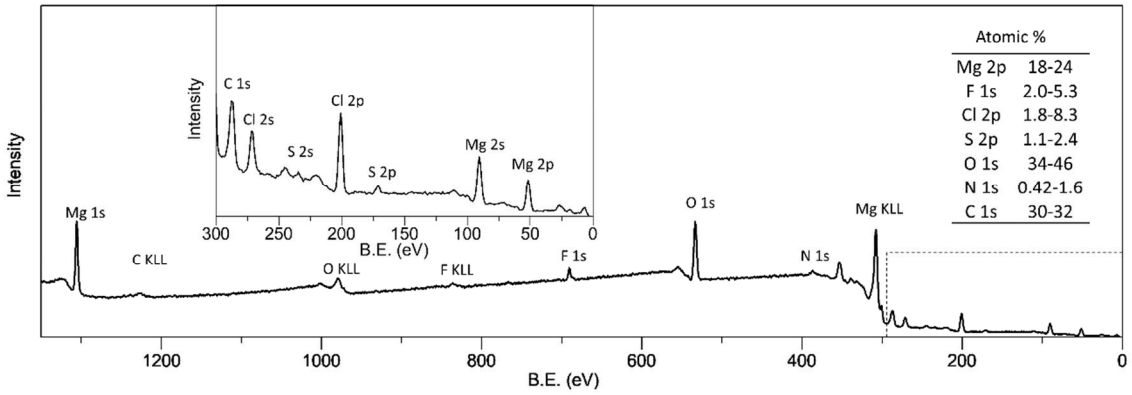


Figure S7. X-ray photoelectron spectroscopy (XPS) of Mg electrodes cycled in sulfur containing electrolyte. Survey spectroscopy before Ar^+ sputtering. Inset: Zoomed-in region between 0 and 300 eV and the atomic composition.

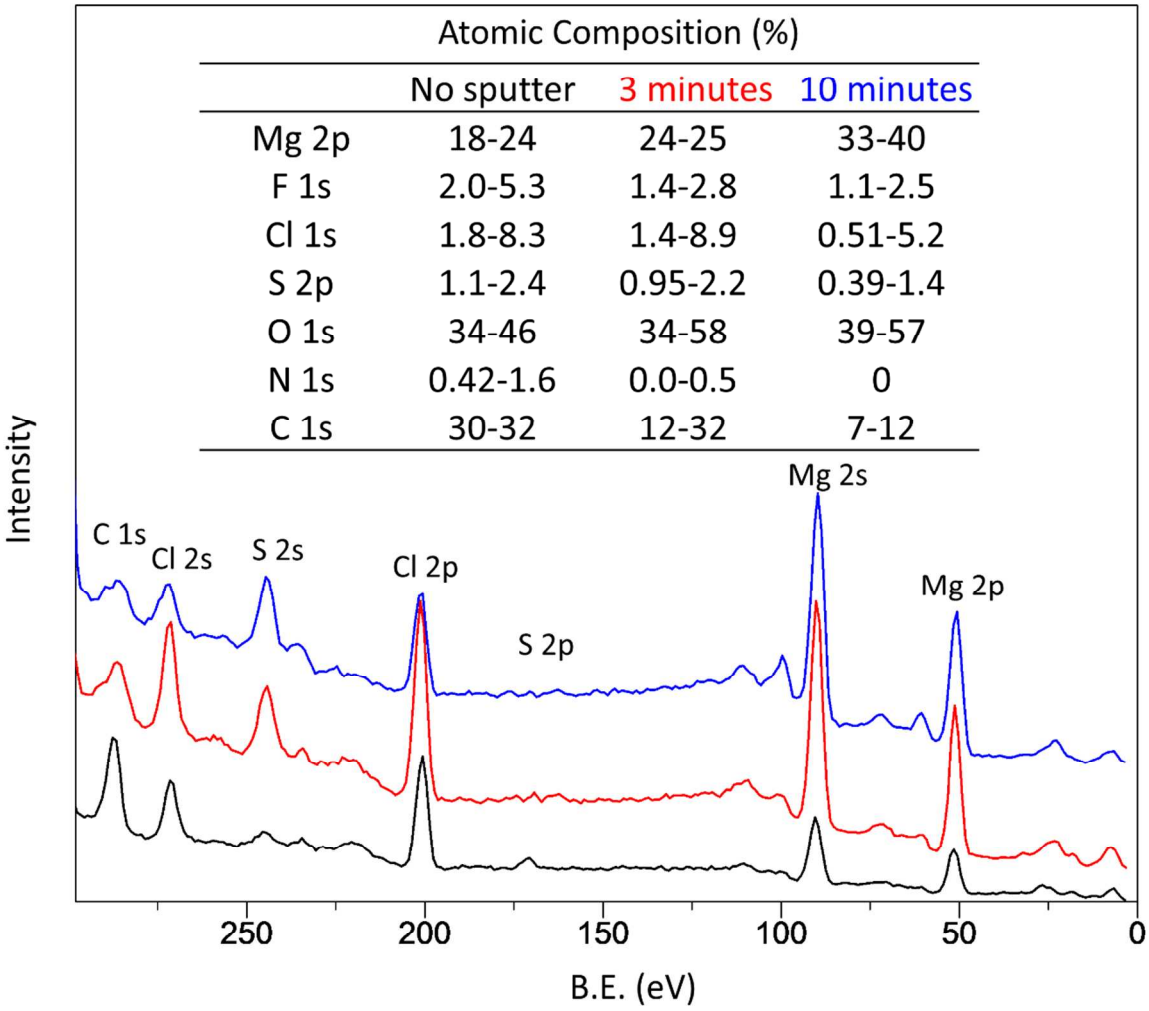


Figure S8. Survey XPS scans and atomic composition of Mg electrode cycled in sulfur containing electrolyte sputtered for different durations.

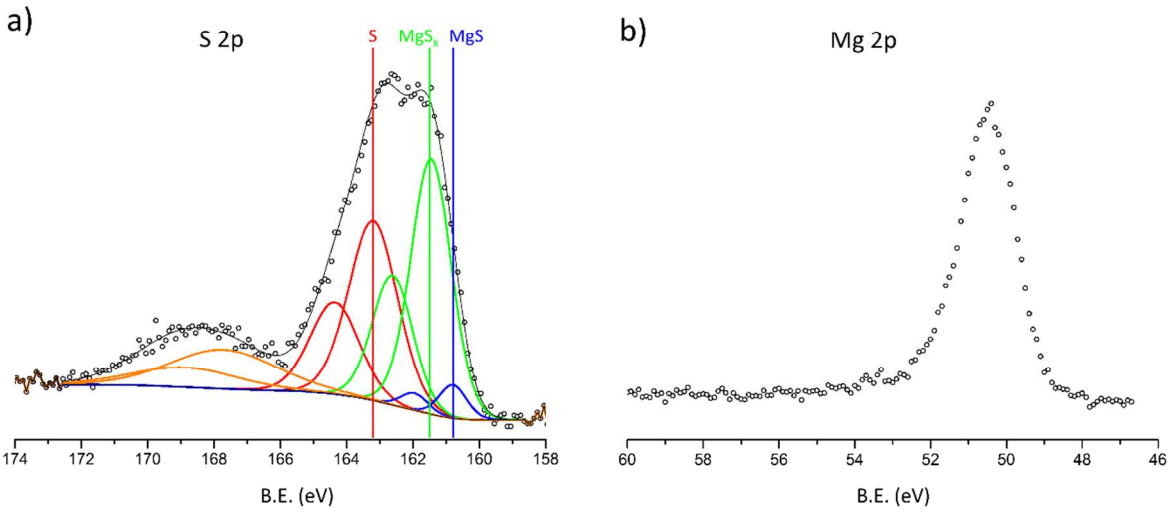


Figure S9. High resolution XPS of sulfur cathode discharged in Mg/S batteries for 985 mAh/g (corresponding to 1.18 e^- transfer per S). a) S 2p spectra. Three peaks can be observed at 163.3, 161.5 and 160.8 eV, corresponding to S, MgS_x and MgS; b) Mg 2p spectra. Peaking position: 50.4 eV. The XPS data is calibrated with reference to C 1s of adventitious carbon (284.8 eV).

References.

(1) Gao, T.; Hou, S.; Wang, F.; Ma, Z.; Li, X.; Xu, K.; Wang, C. Reversible S0/MgSx Redox Chemistry in MgTFSI2-MgCl2 Electrolyte for Rechargeable Mg/S Battery. *Angew. Chemie Int. Ed.* **2017**, DOI: 10.1002/anie.201708241.

(2) Fournier, V.; Marcus, P.; Olefjord, I. Oxidation of Magnesium. *Surf. Interface Anal.* **2002**, *34* , 494–497.

(3) Yoo, H. D.; Han, S.-D.; Bolotin, I. L.; Nolis, G. M.; Bayliss, R. D.; Burrell, A. K.; Vaughey, J. T.; Cabana, J. Degradation Mechanisms of Magnesium Metal Anodes in Electrolytes Based on (CF3SO2)2N– at High Current Densities. *Langmuir* **2017**, *33* , 9398–9406.