

Supporting Information for:

Mg Anode Passivation Caused by Reaction of Dissolved Sulfur in Mg-S Batteries

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Section 1. Characterizing the Ag₂S Quasi Reference Electrode

The Ag₂S quasi reference electrode is suitable for experiments in Mg|MACC|Mg cells. Although the Ag₂S quasi reference electrode does not have a well-defined Nernstian potential, it exhibits acceptable stability over time (Figure S1). The Ag₂S quasi reference electrode allows current-voltage characteristics of the WE electrode to be separated from those of the CE.

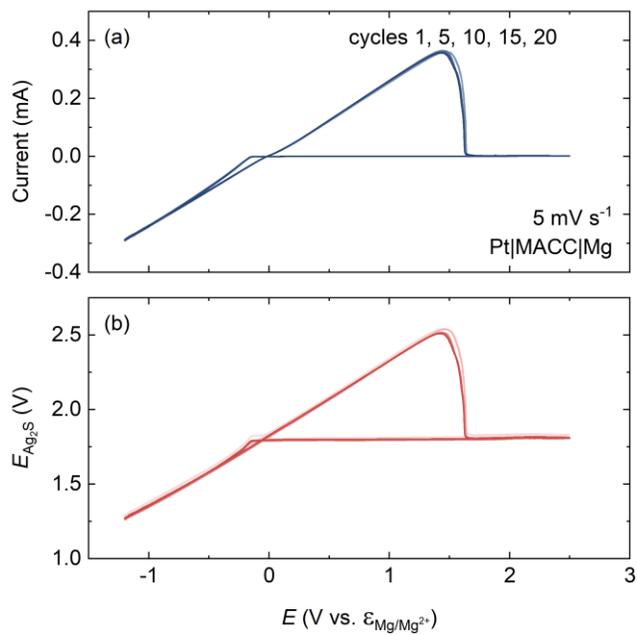


Figure S1. Monitoring the Ag₂S potential during cyclic voltammograms in a Pt|MACC|Mg cell. (a) The current-voltage characteristics of the cell for cycles 1, 5, 10, 15, and 20. **(b)** The corresponding potential of the Ag₂S quasi reference electrode as referenced to the Mg counter electrode. The results show that the quasi-reference electrode remains stable from cycle-to-cycle.

We note that the Ag_2S quasi reference electrode introduces some noise in the data. In Figure S2 we show the data from Figure 1a of the main text alongside the same data referenced to the Mg CE. While both representations are similar, the potential plotted against the Ag_2S quasi reference electrode (Figure S2b) is noisier and exhibits ~ 20 mV drift over the 48 h period.

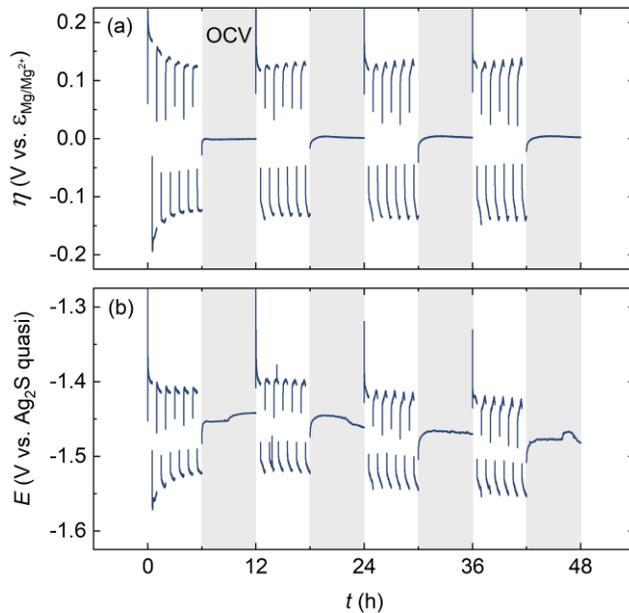


Figure S2. The standard electrochemical cycling experiment for an Mg|MACC|Mg cell referenced against a (a) Mg CE and (b) Ag_2S reference electrode . The trends are comparable between both panels but referencing to the Ag_2S reference electrode introduces some drift over time.

Addition of S_8 to Mg|MACC|Mg cells causes a change in the open circuit potential vs. the Ag_2S quasi reference electrode. The change in open circuit potential is attributed to a change in Ag_2S quasi reference electrode's electrochemical potential. To illustrate the point, the potential of an Ag_2S quasi reference electrode was monitored before and after S_8 addition in a Pt|MACC|Mg cell (Figure S3). The typical J-V behavior for the Pt|MACC|Mg cell is shown in Figure S3a. Pt cannot support plating of Mg in the presence of S_8 (*vide infra*). However, if Mg is plated onto Pt before introduction of S_8 (Figure S3b – solid blue curve) then Mg can be stripped after S_8 is dissolved (Figure S3b – solid red curve). For reference, the subsequent poor stripping/plating behavior for the Pt|MACC|Mg system is shown in Figure S3c. While Mg stripping occurs at the expected potential in the initial cycle (Figure S3b – solid red curve), the Ag_2S quasi reference electrode exhibits an immediate ~ 1 V decrease in potential vs. the Mg counter electrode (Figure S3d). The result demonstrates that the Ag_2S reference electrode has a decreased electrochemical potential in the presence of dissolved S_8 .

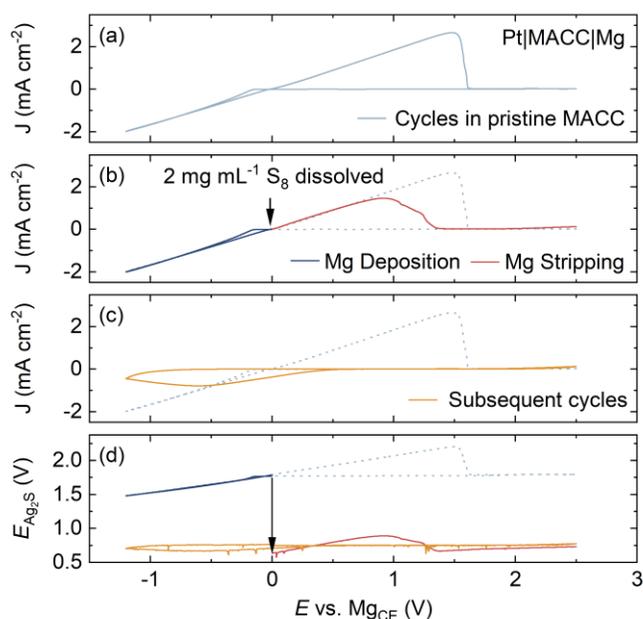


Figure S3. Plating and stripping of Mg in a Pt|MACC|Mg cell while monitoring the potential of a submerged Ag_2S quasi reference electrode. (a) Cyclic voltammograms for the Pt|MACC|Mg cell without S_8 . **(b)** Mg is plated onto the Pt WE without any S_8 dissolved in solution (solid blue line). After plating, the cyclic voltammogram was paused, 2 mg mL⁻¹ S_8 was introduced into the electrolyte, and the S_8 was stirred to dissolve for 1 h. The experiment was then resumed to observe Mg stripping (solid red line). **(c)** A characteristic cyclic voltammogram is shown after 2 mg mL⁻¹ is dissolved – reversible plating/stripping is not observed. **(d)** The submerged Ag_2S reference electrode's potential is shown for each experiment in a-c. The Ag_2S potential immediately decreases by ~ 1 V upon dissolution of S_8 .

Section 2. Mg Film Characteristics from SEM & EDS

SEM results were collected for Mg plating (-0.1 mA cm^{-2}) with and without S_8 presence in Mg|MACC|Mg cells (Figure S4). Without S_8 dissolved in MACC, Mg deposits in hemispherical islands on the surface of the Mg electrode. Plating in the presence of dissolved S_8 yields a more uniform deposition with emergence of cracks on the surface.

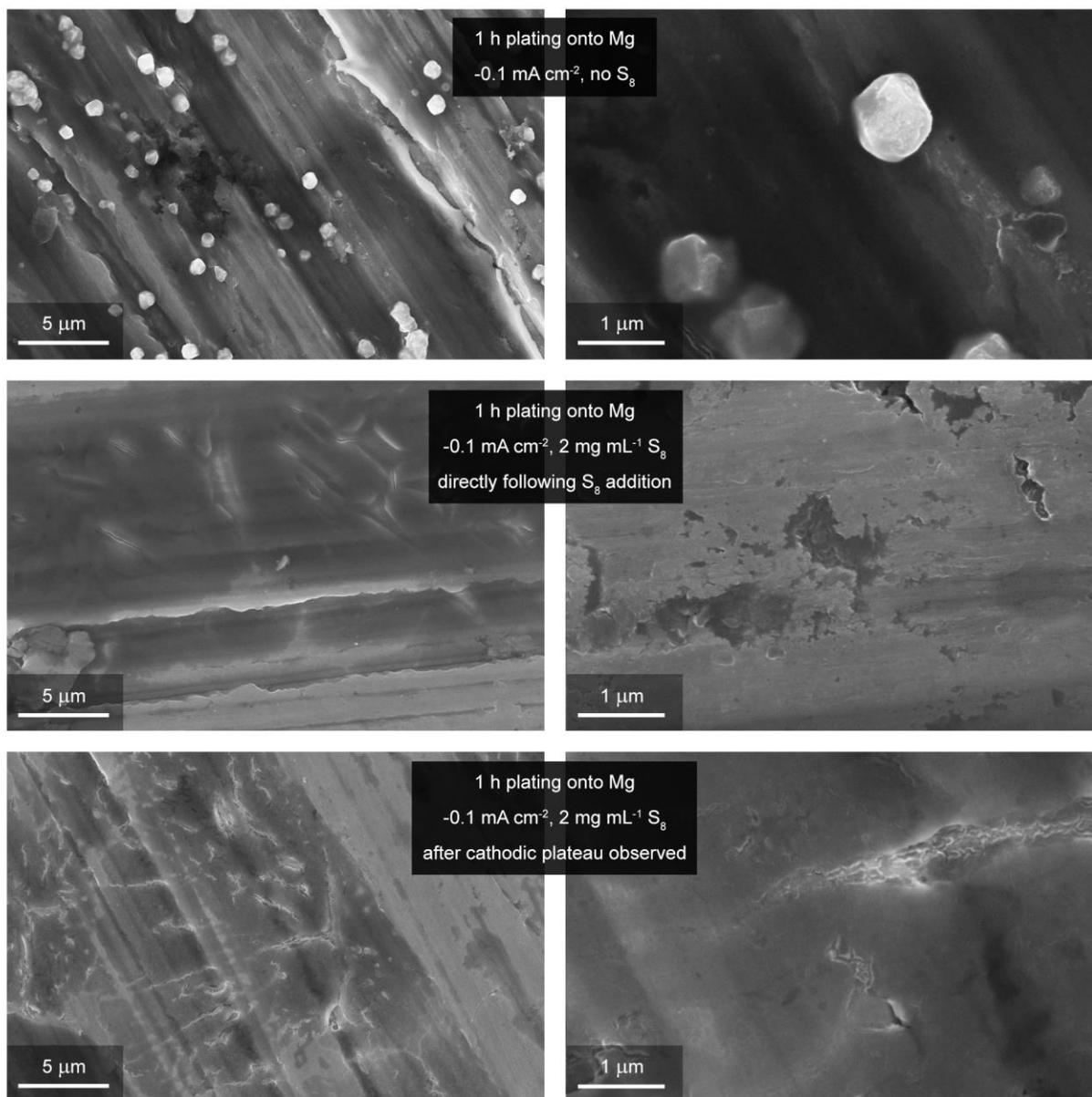


Figure S4. Morphology for 1 h of Mg plating onto an Mg metal electrode in various electrolytes. (top) Deposition in activated MACC without any S_8 dissolved in the electrolyte. **(mid)** Deposition in activated MACC immediately after $2 \text{ mg mL}^{-1} \text{ S}_8$ was dissolved. **(bottom)** Deposition in activated MACC after 2 mg mL^{-1} was dissolved and after the electrolyte was conditioned in a Mg|MACC|Mg cell until the cathodic plateau was observed.

SEM images were also collected after a Mg|MACC|Mg cell reached the cathodic plateau, during the standard cycling procedure (Figure S5). To attempt to better visualize any deposition, the cell was polarized for 6 h at the cathodic plateau potential. Small spotting is evident; however, subsequent EDS characterization indicated a homogenous Mg-covered surface (Figure S6).

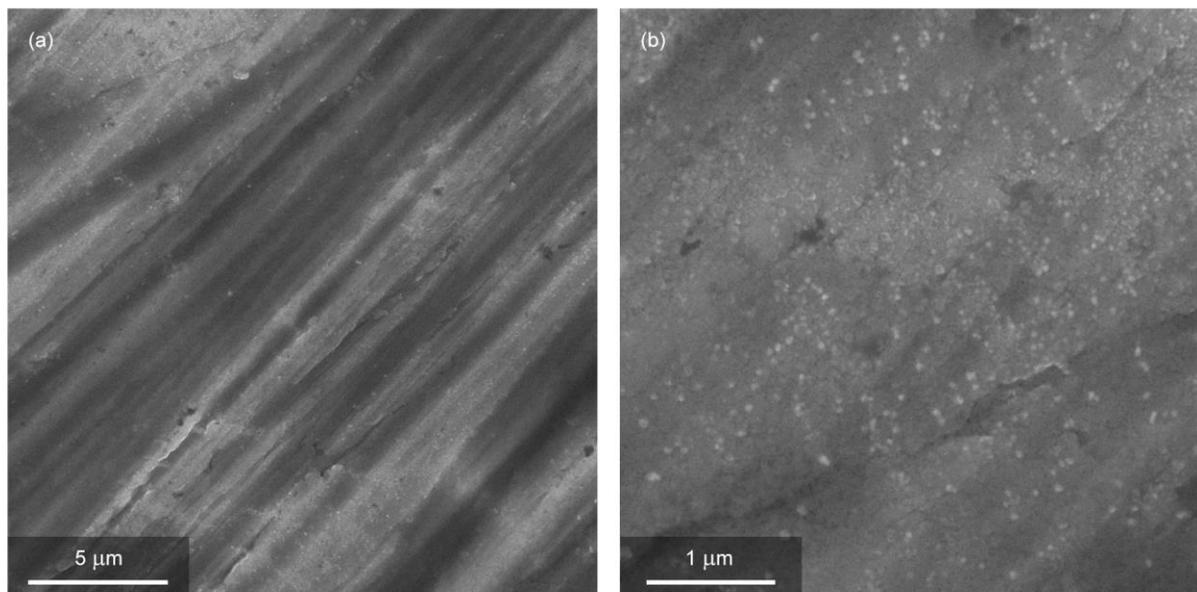


Figure S5. Morphology for 6 h deposition of Mg onto Mg metal in MACC after the cathodic plateau was reached.

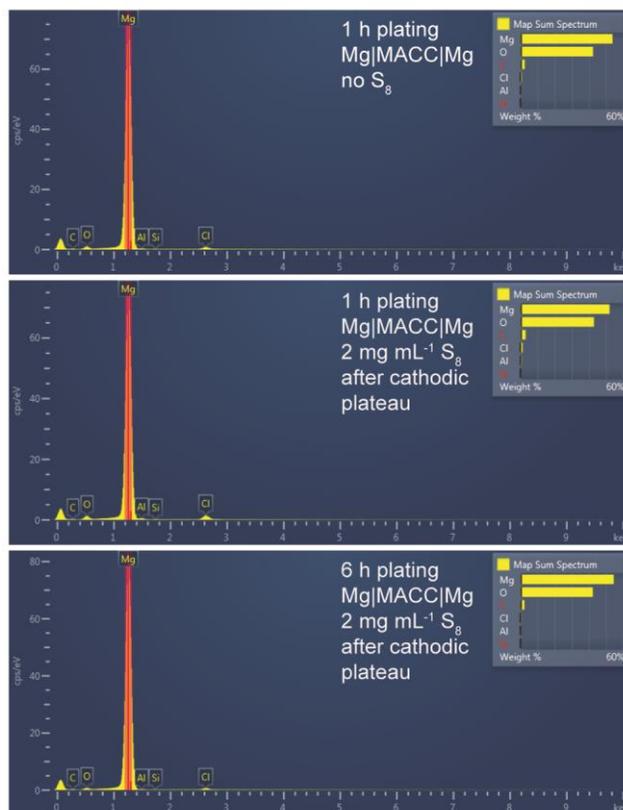


Figure S6. EDS Data for various Mg plating experiments. The collected EDS spectra are similar for all deposition conditions – exhibiting primarily Mg character. The electrodes were rinsed 3x with MACC to remove any absorbed species.

Section 3. UV-vis of the MACC Electrolyte with Dissolved S₈

The main text experiments employ MACC solutions containing 2, 5, and 10 mg mL⁻¹ S₈. After 12 h of stirring, the solutions containing 2 and 5 mg mL⁻¹ are visibility transparent whereas the 10 mg mL⁻¹ solution remains cloudy. UV-vis spectra were collected for all three solutions (Figure S7). The results show an increase in signal in the 200-320 nm range. Absorbance peaks at 260 and 280 nm have previously been attributed to dissolved S₈.¹

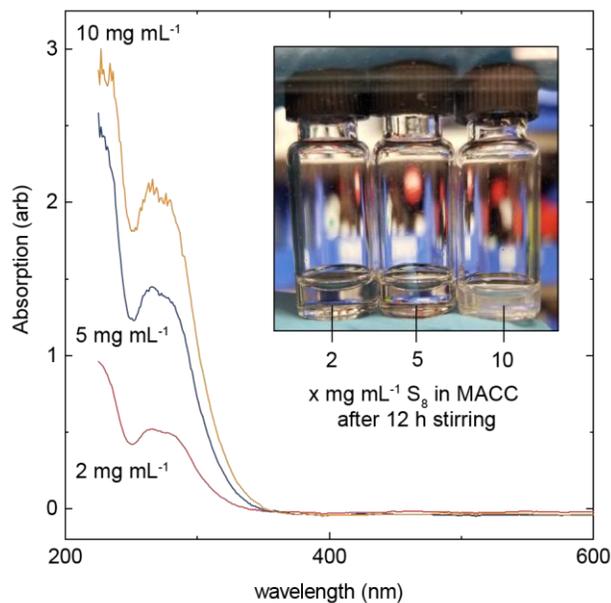


Figure S7. The UV-vis spectra of MACC with 2, 5, and 10 mg mL⁻¹ S₈. The spectra show a systematic increase in absorbance in the 200-320 nm range. UV-vis cuvettes were prepared by diluting each solution 10:1 in activated MACC as to achieve a detectable quantity of S₈. The cuvettes had a path length of 1 mm and the shown spectra are background subtracted using a MACC sans S₈ background spectrum.

Section 4. Additional Electrochemical Results

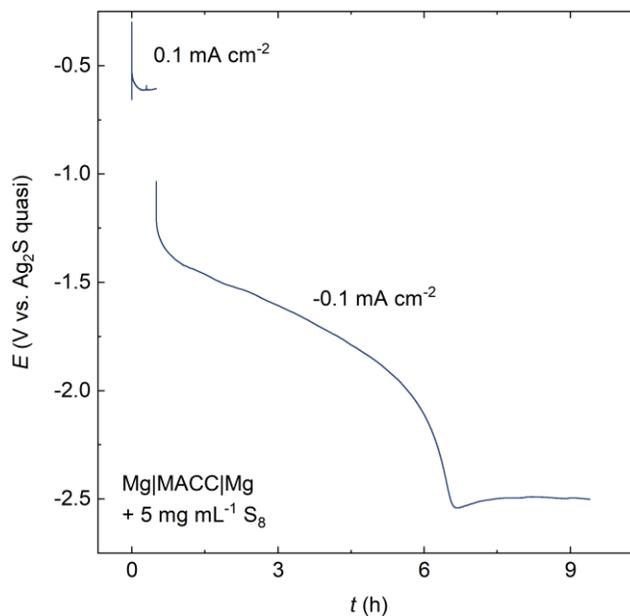


Figure S8. Extended cathodic plating in MACC with 5 mg mL⁻¹ S₈. Results show that the overpotential continuously grows until the cathodic plateau is reached. We note here that the WE area is larger (1.046 cm²) than those used in the main text figure (0.2-0.5 cm²), while the amount of electrolyte was the same (1.5 mL). The increased absolute current results in the cathodic plateau occurring at an earlier timepoint.

Plating current densities were examined at various overpotentials for the studied Mg|MACC|Mg cells (Figure S9). After S₈ addition, the absolute current decreases significantly at overpotentials of 500 mV and more. After the cathodic plateau is reached the current densities decrease to $\sim 0 \text{ mA cm}^{-2}$, indicating sluggish plating kinetics.

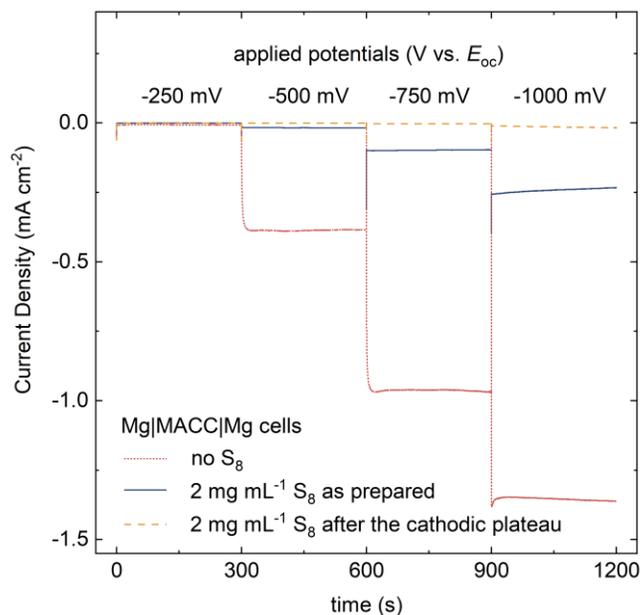


Figure S9. Current densities at various applied potentials for Mg in MACC, MACC immediately after 2 mg mL⁻¹ S₈ is dissolved and MACC after the cathodic plateau is reached. The results illustrate that S₈ presence decreases the plating kinetics. Once the cathodic plateau is reached, the plating kinetics become even more sluggish.

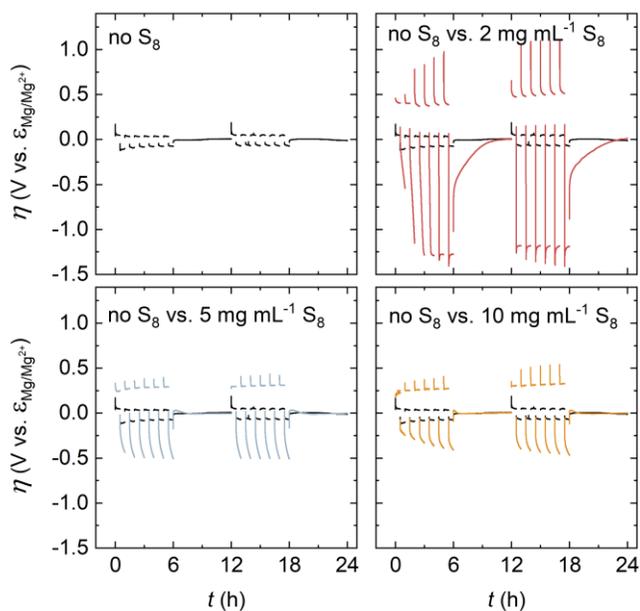


Figure S10. Data from Figure 3 replotted to show comparisons with the no-S₈ control. The data is centered around 0 V vs. Mg/Mg²⁺ by considering the final hour of the OCV hold to be ~ 0 V vs. Mg/Mg²⁺. In all cases, addition of S₈ results in larger overpotentials for plating/stripping.

Section 5. Electrochemical Impedance Spectroscopy

Prior to the EIS experiment shown in Figure 5, spectra were collected on the Mg|MACC|Mg cells before S_8 dissolution (Figure S11). The results show a small high-frequency semicircle and an extended low-frequency feature. The small high-frequency feature is attributed to the solution resistance because its shape/magnitude is independent of the applied potential. The extended low-frequency feature would likely form a second semicircle if lower frequency data were to be collected (<0.1 Hz). However, given the 100 mV sinusoidal potential, the plating/stripping kinetics are sluggish relative to solution resistance.

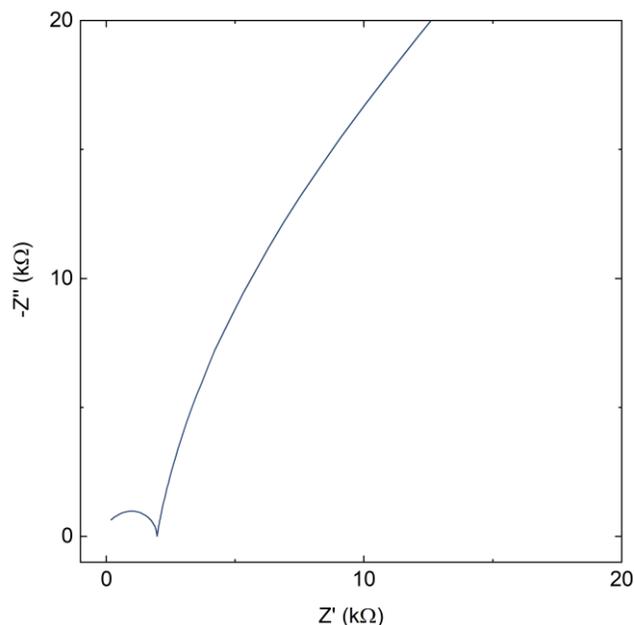


Figure S11. The electrochemical impedance spectra of an Mg|MACC|Mg cell before dissolving S_8 into the electrolyte. The low frequency feature exhibits some curvature.

The post-OCV curves in Figure 5 of the main text exhibit a low-frequency blocking feature. To rationalize the observed blocking feature, we have compared the J-V character of Mg|MACC|Mg cells before and after S_8 addition (Figure S12). The data show more sluggish kinetics for the system once S_8 is introduced. This observation is especially true in the 100 mV amplitude range centered at 0 V vs. $E_{Mg/Mg^{2+}}$. Thus, we expect the low-frequency feature to be more blocking after S_8 is introduced.

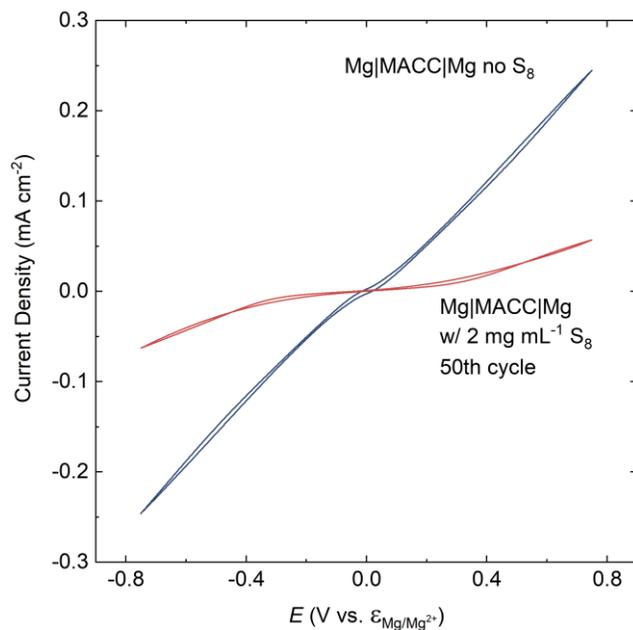


Figure S12. The J-V behavior of Mg|MACC|Mg cells before and after addition of 2 mg mL⁻¹ S₈. The data illustrate that 2 mg mL⁻¹ S₈ presence diminishes the achievable current density at any given potential.

REFERENCES

- (1) Bieker, G.; Wellmann, J.; Kolek, M.; Jalkanen, K.; Winter, M.; Bieker, P. Influence of Cations in Lithium and Magnesium Polysulphide Solutions: Dependence of the Solvent Chemistry. *Physical Chemistry Chemical Physics* **2017**, *19*, 11152–11162. <https://doi.org/10.1039/C7CP01238A>.