The critical role of the interphase at magnesium electrodes in chloride-free, simple salt electrolytes

Supporting Information

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Materials and methods

Electrolyte preparation. Tetraglyme (4G) (Sigma-Aldrich, ≥99%) was distilled under vacuum over sodium (Sigma-Aldrich, 99.9%) and benzophenone (Sigma-Aldrich, 99%). The distilled solvent was introduced to a N_2 glovebox (H_2O <0.1ppm, O_2 <0.1 ppm) and was dried using freshly activated 4 Å molecular sieves (Sigma-Aldrich) for 72 hours (h). Magnesium bis(trifluoromethanesulfonyl)imide ($Mg(TFSI)_2$) (Solvionic, 99.5%) was dried in a Buchi oven at 120 °C for 72 h and transferred into the N_2 glove-box. The electrolyte was prepared by dissolving 0.5 M $Mg(TFSI)_2$ in tetraglyme at room temperature. The solution was left stirring overnight until a colourless solution was obtained. The water content measured by Karl Fischer titration was found to be <15 ppm. 2 M butyl magnesium chloride (BuMgCl) in tetrahydrofuran (THF, Sigma Aldrich) was used as received.

Electrochemical Experiments. All electrochemical experiments and any required preparation were performed inside an N_2 glove box. Cyclic voltammetry was performed using a Biologic SP-300 potentiostat at a scan rate of 100 mV s^{-1} in a three-electrode cell, consisting of 3 Mg ribbons (Sigma-Aldrich). The dried Mg ribbons, acting as the working, counter and reference electrodes, were scraped thoroughly to remove the oxidized layer and reveal a fresh Mg surface. Then the 3 ribbons were arranged in a glass cell with 0.5 ml of electrolyte solution being added. Prior to use, the glass cell was dried in a vacuum oven at 80 °C overnight to minimize the water content on the glass surface. Copper foil was cut into ribbons, dried in a Buchi oven at 120 °C overnight and inserted in the glovebox ready to be used.

Chemical characterisation. Cycled Mg electrodes were washed with 1,2-dimethoxyethane (dried using 4 Å molecular sieves) and allowed to dry before characterisation. Scanning electron microscopy (SEM) and Energy-dispersive X-ray (EDX) spectroscopy were performed using a FEI Quanta 200 3D Dual Beam FIB-SEM, at an accelerating voltage of 10 kV. The samples were transferred from the glove box to the SEM chamber via an air-tight transfer device. Fourier-transform infrared (FTIR) spectroscopy was performed within an Ar glovebox using a Bruker-Alpha II spectrometer in attenuated total reflection mode. 200 scans were acquired per FTIR spectrum. Table S1 shows the peak assignments.

Table S1. IR peak assignment in Figure 4. [1-2]

Peak frequency (cm^{-1})	Group bonding
1350	S=O stretching
1320	S=O stretching
1180	C-F stretching
1135	C-O stretching
1088	C-O stretching
1058	C-O stretching
<700	MgO and $Mg(OH)_2$ species

Supplementary Data

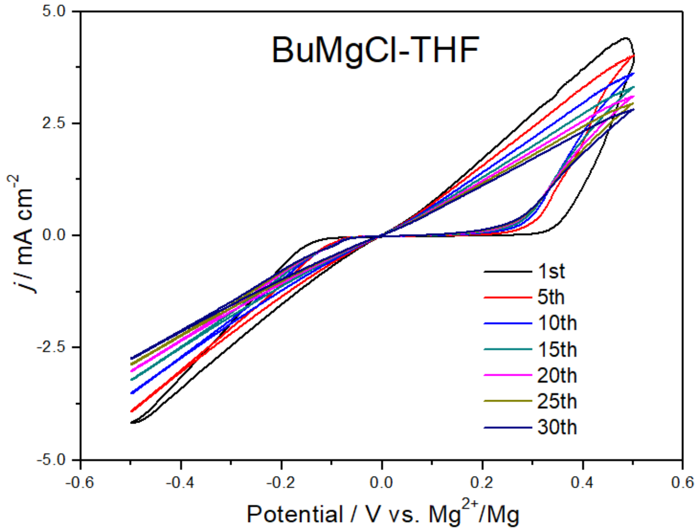

Figure S1. Cyclic voltammograms at a Cu electrode in 2 M BuMgCl-THF, recorded using a Mg reference and counter electrodes at a scan rate of 100 mV s^{-1}.

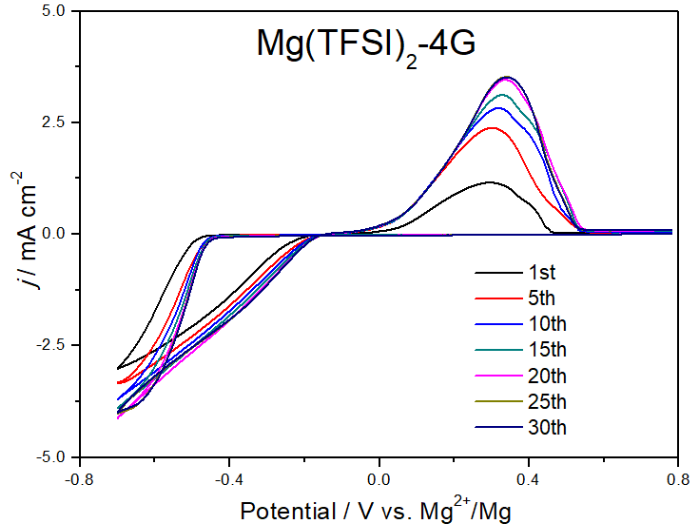

Figure S2. Cyclic voltammograms at a Cu electrode in 0.5 M $Mg(TFSI)_2$-4G, recorded using a Mg reference and counter electrodes at a scan rate of 100 mV s^{-1}.

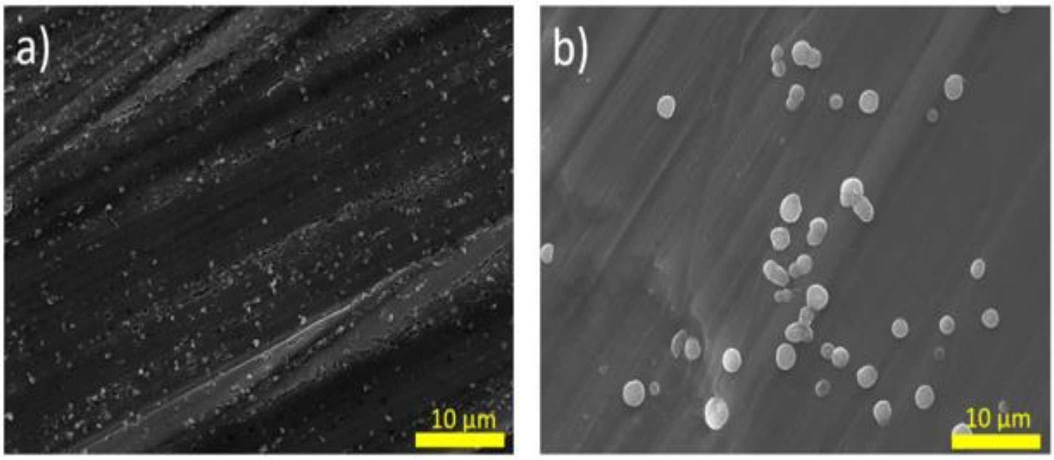

Figure S3. SEM images of Mg electrodes after 1 cycle in a) 2 M BuMgCl-THF, and c) 0.5 M MgTFSI-4G. Cycling conditions were the same as those described in Figure 1.

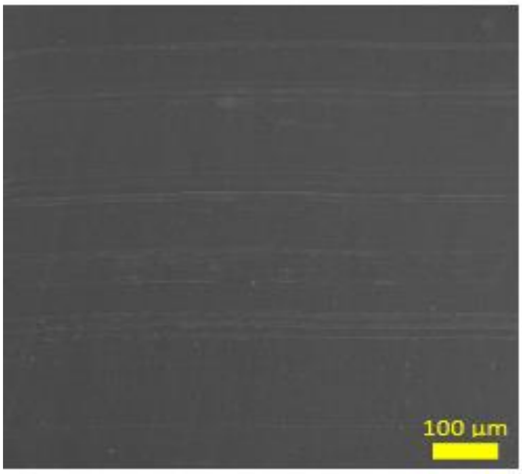

Figure S4. SEM image of an uncycled pristine Mg electrode.

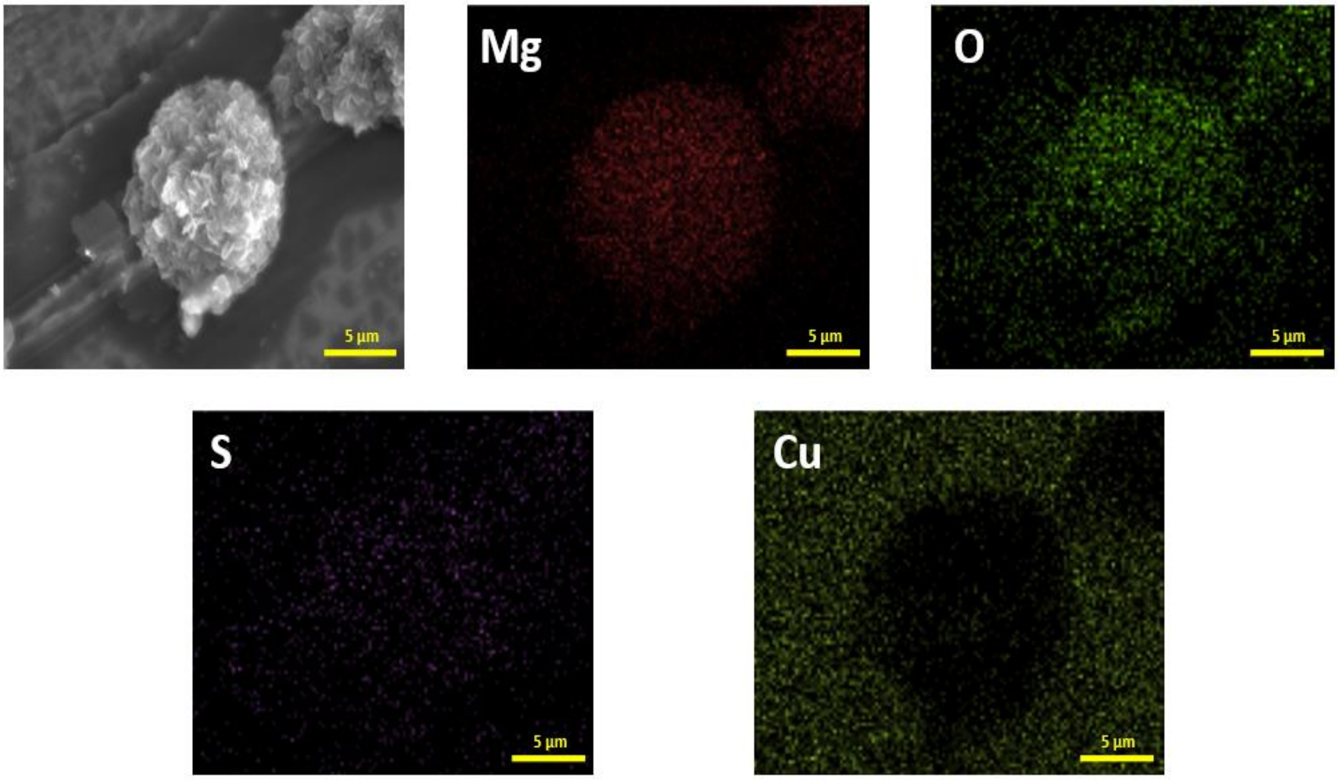

Figure S5. SEM image of a Mg deposit on a Cu electrode after conditioning in 0.5 M MgTFSI-4G, coupled with EDX elemental mapping showing the composition of the deposit.

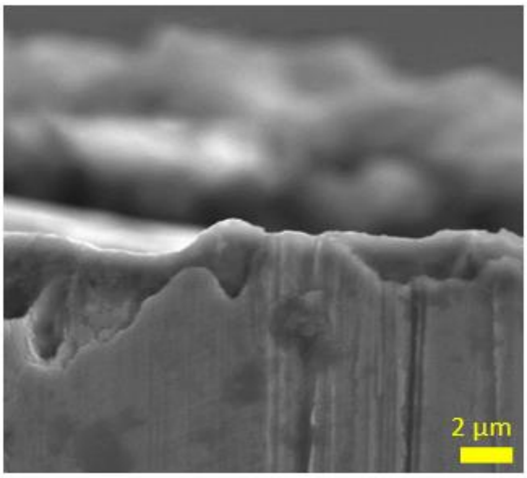

Figure S6. SEM image of a cleaved cross section of a Mg electrode after conditioning in 0.5 M MgTFSI-4G. Cycling conditions were the same as those described in Figure 1.

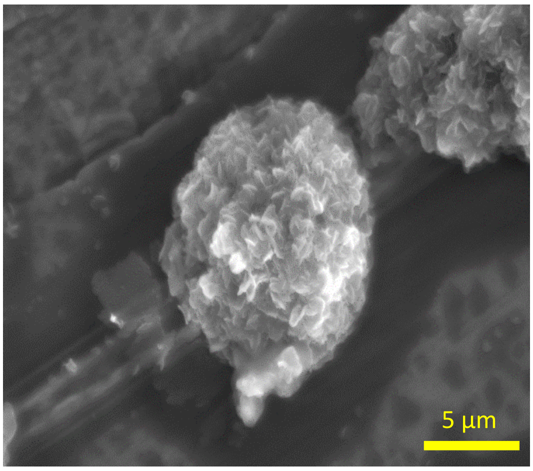

Figure S7. SEM image of Cu electrode after conditioning in 0.5 M MgTFSI-4G. Cycling conditions were the same as those described in Figure 1.

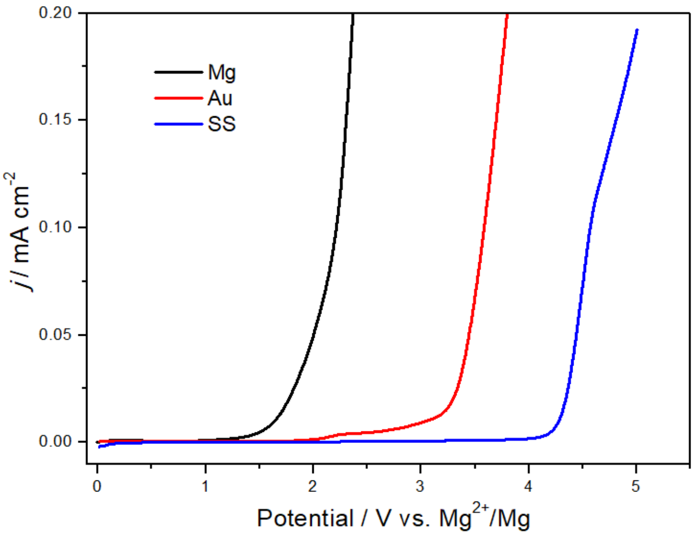

Figure S8. Linear sweep voltammograms in 0.5 M MgTFSI-4G at Mg, Au and stainless steel (SS) electrodes, recorded using a Mg reference electrode and a Mg counter electrode at a scan rate of 100 mV s^{-1}.

References

(1) Ha, S.-Y.; Lee, Y.-W.; Woo, S. W.; Koo, B.; Kim, J.-S.; Cho, J.; Lee, K. T.; Choi, N.-S. Magnesium(II) Bis(Trifluoromethane Sulfonyl) Imide-Based Electrolytes with Wide Electrochemical Windows for Rechargeable Magnesium Batteries. *ACS Appl. Mater. Interfaces* **2014**, *6*, 4063–4073.

(2) Jay, R.; Tomich, A. W.; Zhang, J.; Zhao, Y.; De Gorostiza, A.; Lavallo, V.; Guo, J. Comparative Study of $Mg(CB_{11}H_{12})_2$ and $Mg(TFSI)_2$ at the Magnesium/Electrolyte Interface. *ACS Appl. Mater. Interfaces* **2019**, *11*, 11414–11420.