

Electronic Supplementary information

Unveiling the Electronic Properties of Native Solid Electrolyte Interphase Layers on Mg Metal Electrodes Using Local Electrochemistry

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S1. Experimental section

S1.1 Electrolytes preparation

All chemicals and electrolyte solutions were prepared and stored in an argon-filled glovebox (H_2O , $\text{O}_2 < 0.1$ ppm). Tetrahydrofuran (THF, anhydrous, > 99.9%, Sigma Aldrich), monoglyme (anhydrous, > 99.5%, inhibitor-free, Sigma Aldrich) and diglyme (anhydrous, > 99.5%, Sigma Aldrich) solvents were used for the electrolyte syntheses after being dried over molecular sieve (4 Å) for 72 h. 0.4 M all phenyl complex electrolyte was prepared by mixing phenylmagnesium chloride (2 M PhMgCl in THF, Sigma-Aldrich) and aluminium chloride (AlCl_3 , anhydrous, 99.99%, Sigma-Aldrich) in a proportion of 1:2 AlCl_3 :PhMgCl in THF. From now on, this electrolyte solution will be referred to as “APC”.¹

Prior to the preparation of the 0.3 M TFSI-based electrolyte, magnesium bis(trifluoromethanesulfonyl)imide ($\text{Mg}(\text{TFSI})_2$, 99.5%, Solvionic) was dried under vacuum at 170°C overnight. After drying, the electrolyte was prepared by mixing the appropriate amount of $\text{Mg}(\text{TFSI})_2$ in monoglyme:diglyme mixture (1:1 wt%) overnight (magnetic stirring).² This solution will be named as “TFSI” throughout the work.

Magnesium tetrakis(hexafluoroisopropoxy)borate salt ($\text{Mg}[\text{B}(\text{hfp})_4]_2$) was prepared by following the protocol reported by Zhao-Karger *et al.*,³ using tetraglyme (> 99%, Sigma Aldrich) and 1,1,1,3,3,3-Hexafluoro-2-propanol (> 99%, Sigma Aldrich) as the precursors. Successively, the electrolyte “BOR” (0.3 M $\text{Mg}[\text{B}(\text{hfp})_4]_2$ in monoglyme) was prepared by dissolving the as-prepared salt in monoglyme solvent. The electrolyte used with the reference electrode for the SECM control experiments was prepared with 1 M lithium perchlorate (LiClO_4 , 99.99% dry, Sigma Aldrich) in a mixture of ethylene carbonate (EC, anhydrous, Sigma Aldrich) and propylene carbonate (PC, anhydrous, Sigma Aldrich) in a proportion of 1:1 %wt. Feedback (FB) SECM experiments were performed with the addition of 10 mM ferrocene in the electrolyte (Fc, 98%, Sigma Aldrich). The 1 M LiClO_4 in EC:PC will be referred to as the “LIB electrolyte” throughout the text.

S1.2 Native SEI Mg discs preparation

Before being used, the Mg discs were polished with fine polishing paper (Sia Abrasives Industries AG) to remove the native oxide layers from their surfaces. The polished discs were soaked in the APC, TFSI and BOR electrolytes for 12 h. Afterwards, each Mg disc was washed with THF, when APC was used as the electrolyte, or monoglyme, when TFSI and BOR electrolytes were selected, to rinse the remaining salts from the sample surface. *In-situ* SECM measurements and *ex-situ* morphological and spectroscopic analyses were performed after the rinsing and drying steps.

S1.3 Mo_6S_8 reference electrode preparation

$\text{Cu}_2\text{Mo}_6\text{S}_8$ powder was synthesised by solid-state route, adapting the procedure reported by Saha *et al.*⁴ Stoichiometric amounts of Mo (powder, 1-5 μm , $\geq 99.9\%$ trace metals basis, Sigma Aldrich), MoS_2 (99%, metal

basis, 325 mesh powder, Alfa Aesar) and CuS (powder, ≥ 99.9 trace metals basis, 100 mesh, Sigma Aldrich) were ball milled for 3 h at 300 rpm under ambient atmosphere using a zirconia bowl and balls (powder:ball mass ratio of 1:10). Successively, the mixture was calcined at 1000°C for 5 h in a high purity (5.0) Ar atmosphere. $\text{Cu}_2\text{Mo}_6\text{S}_8$ powder was then dissolved in a solution of 6 M HCl (ACS reagent, 37%w/w, Sigma Aldrich) and 1 mL HNO_3 (65%, Merck) to leach out the Cu ions and obtain the final Mo_6S_8 (CP) electrode active material powder. The acidic dispersion was stirred for 20 h using a magnetic bar. The CP powder was then filtered after centrifugation and washed with de-ionised water and, as the last step, ethanol (99%, VWR) was used to remove residual traces of the acid solution. Prior to the electrode preparation, the CP powder was dried under vacuum at 60°C overnight. Reference electrodes were obtained by a wet-slurry process. The slurries were prepared by mixing 80 wt.% CP active material, 10 wt.% carbon black (Super C 65, TIMCAL) and 10 wt.% polyvinylidene fluoride (PVDF, SOLEF® 5130/1001) binder (6 wt% solution of PVDF in 1-methyl-2-pyrrolidinone (NMP, anhydrous, 99.5%, Sigma Aldrich). The slurries were homogenised by magnetic stirring for *ca.* 12 h and were casted on stainless steel foil (12 μm , MTI) using a blade gap of 120 μm . After coating, the casted electrode sheets were dried at 80 °C overnight. Successively, the electrodes were punched as discs (15 mm diameter) and dried under vacuum at 120 °C for 12 h using a Büchi® glass oven before being introduced into an Ar-filled glove box. Approximately 4 mg of active material were loaded on each electrode. The electrochemical Mg intercalation of the CP electrodes was carried out using a BioLogic MPG-2 potentiostat. After being discharged to 0.4 V vs. $\text{Mg}^{2+}|\text{Mg}$ at 10 mA g^{-1} , the CP electrodes were charged up to 1.2 vs. $\text{Mg}^{2+}|\text{Mg}$ using the same current rate. Successively, the cells were transported and disassembled in an Ar-filled glove box to collect the magnesiated CP electrodes (MCP). Prior to the implementation into the FB-SECM setup, the electrodes were rinsed with anhydrous THF to dissolve residual trace of electrolyte salt.

S1.4 Local electrochemical measurements

A custom-made scanning electrochemical microscope was assembled inside an Ar-filled glovebox (H_2O , $\text{O}_2 < 0.1$ ppm). Feedback mode SECM measurements were performed in an open electrochemical cell where a ultramicroelectrode (SECM tip, platinum disc with 12 μm radius) was employed as the working electrode (WE). MCP electrodes were used as a quasi-reference counter electrode (QRCE) for the n-SEI evaluation. The compartment was filled with 10 mM ferrocene (Fc) dissolved in the referred electrolyte (LIB electrolyte or APC). Cyclic voltammograms were recorded by scanning the potential to convert Fc to Fc^+ (oxidation reaction) at 10 or 50 mV s^{-1} . The FB-SECM approach curves were registered by polarising the SECM tip at 3.5 V vs. $\text{Li}^+|\text{Li}$ or 0.8 V vs. MCP. The tip was moved towards the sample surface at each increment of 1 μm and an approach speed of 1 $\mu\text{m s}^{-1}$.

As control FB-SECM experiments, a lithium-ion battery-based reference electrode (RE) was used, which consisted of a lithium ribbon inserted in a glass pipette filled with LIB electrolyte. In the case of FB-SECM experiments where the SECM electrochemical cell was filled with APC electrolyte, a double junction RE (filled with the SECM compartment electrolyte) was employed to avoid cross-contamination of electrolytes and ensure RE stability. Note the Li-reference was not immersed directly to the SECM electrochemical cell.

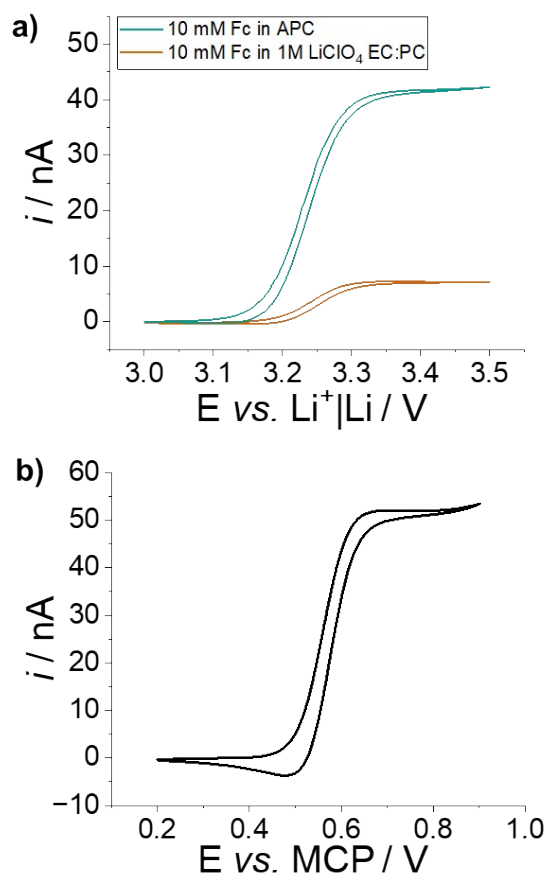
S1.5 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) spectra were acquired in symmetric cell configuration. CR2032 coin cells were assembled using polished Mg discs as the working (WE) and reference (RE) electrodes, a glass fiber separator (GF/C) and 200 μL of each electrolyte: APC, TFSI or BOR. EIS spectra were recorded in potentiostatic mode in the frequency range of 1 MHz to 10 mHz after 6 hours at the open-circuit potential (OCP) and amplitude of 10 mV.

S1.6 Chemical composition and morphological analysis

Pristine polished Mg discs and n-SEI samples were analysed by X-ray photoelectron and Raman spectroscopies to investigate their surface composition. X-ray photoelectron spectroscopy (XPS) analyses (Nexsa, Thermofisher) were performed using an Al $K\alpha$ radiation at 72 W and a pass energy of 200 eV. A spot size of 400 μm , "Standard Lens Mode", CAE Analyser Mode and integrated flood gun were used. Data analysis was performed with CASA XPS software, employing Shirley/Tougaard backgrounds. Deconvolution of spectra was carried out using Gaussian-Lorentzian peaks (GL(30)). No charge correction was applied (C1s signal is around 284.82 eV). The Mg discs were stored and transported under an inert atmosphere prior to the XPS measurements, before being briefly exposed to air for inserting into the ultra-high vacuum system. Raman spectra were recorded at room temperature using a Xplora Plus (Jobin-Yvon-Horiba) Raman spectrometer equipped with a highly sensitive CCD-detector with thermoelectric cooling down to -60°C for signal detection. A Nd:YAG laser (532 nm) was used as the excitation source. The laser was focused onto the sample using a 50 \times magnifying objective. Spectra were recorded under inert atmosphere with a 1200 gr mm^{-1} grating, using an acquisition time of 30 s and an accumulation number of 5. The polished Mg discs were placed between two glass slides inside the Ar-filled glove box and then transferred to the Raman spectrometer to acquire the spectra.

The morphologies of the surfaces of the pristine polished Mg discs and n-SEI samples were investigated by scanning electron microscopy (SEM) using a Carl Zeiss Supra 40 scanning electron microscope with Everhart-Thornley (ETD) and Through-Lens (TLD) detectors with a primary electron-beam energy of 5 keV. The samples were fixed onto a SEM sample holder in an Ar-filled glovebox, transferred to the instrument in an air-tight vessel and inserted in the SEM chamber (air contact of maximum 5 s).



S2. Cyclic voltammograms using the Pt-SECM tip.

Figure S1. a) Cyclic voltammograms registered at the Pt-SECM tip (radius of 12 μm) at a scan rate of 10 mV s^{-1} in solution of 10 mM Fc in lithium-ion battery electrolyte (orange data) and 10 mM Fc in APC electrolyte (green data). Note: The Li reference was not immersed in the electrochemical cell filled with APC. A double junction RE was used for avoiding contamination of different electrolytes (see in the S1.4). b) Cyclic voltammogram (scan rate of 50 mV s^{-1}) recorded at the SECM tip using the MCP electrode as QRCE in APC electrolyte containing 10 mM Fc.

S3. Insertion of Mg ion in the Chevrel Phase electrode.

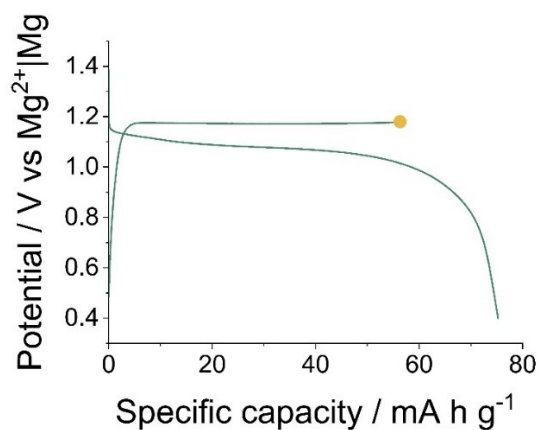


Figure S2. Galvanostatic discharging and charging profile for the first cycle of a coin cell consisting of CP working electrode, a metal Mg anode and an APC electrolyte. The electrochemical de-magnesiumation was

performed until 1.2 V vs $\text{Mg}^{2+}|\text{Mg}$ (yellow dot).

S4. Sequences of SECM approach curves

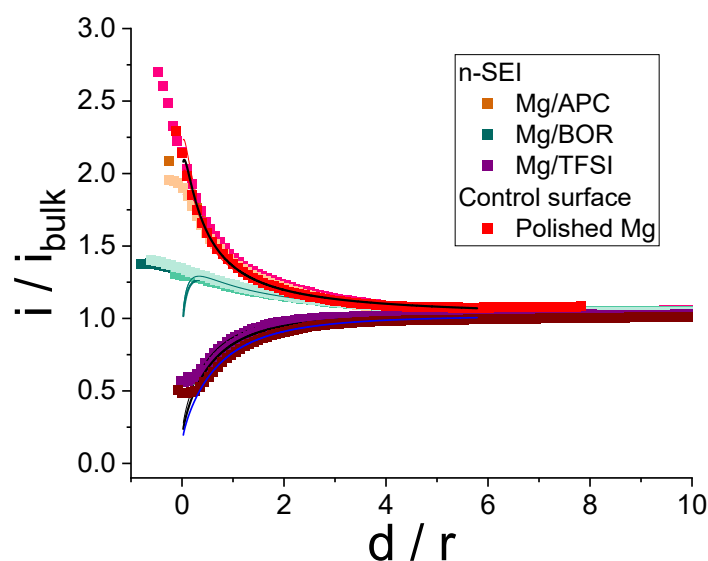


Figure S3. The sequence of approach curves registered towards the n-SEI formed spontaneously on Mg discs when immersed in APC (orange data), BOR (green data) and TFSI (purple data) electrolytes. The approach curve was performed towards the fresh polished Mg (red data). Solid lines: mathematical fit of the approach curves where the calculated k values are plotted in **Table 1** (main manuscript). E_{tip} : 0.8 V vs. MCP.

S5. XPS spectra of n-SEI formed after soaking in APC, TFSI and BOR electrolytes

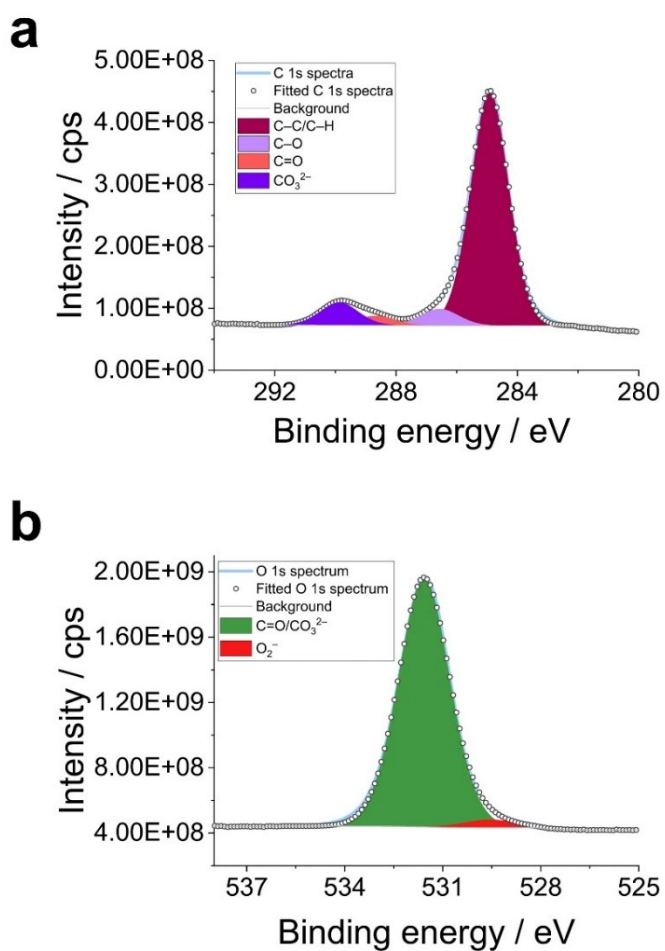


Figure S4. Deconvoluted a) C 1s, b) O 1s and c) Mg 1s XPS spectra of Mg/APC sample.

The deconvoluted C1s core XPS spectrum (**Figure S4 a**) shows two major components related to carbon aliphatic chains (C–C and C–H) and MgCO₃ at 284.9 and 289.9 eV, respectively. Two weak peaks are also identified and assigned to C–O (286.6 eV) and C=O (288.7 eV) species. The etheral C–O moiety corresponds to the decomposition of THF used as solvent, whereas the carbonyl group can be related to CO₂.⁵ The existence of inorganic (MgCO₃) and organic (C–O and C=O) compounds is further confirmed by the O1s spectrum in **Figure S4b**. In addition, a weak peak related to oxide species (MgO, Al₂O₃)^{6,7} was detected at 529.6 eV and carbonate species at 531.6 eV. The Mg 1s core-level spectrum (**Figure S4c**) confirms the presence of inorganic Mg-based species showing a peak at 1304.7 eV. The traces of electrolyte species (C–Mg–Cl) produce a strong feature at 1303.7 eV.⁸

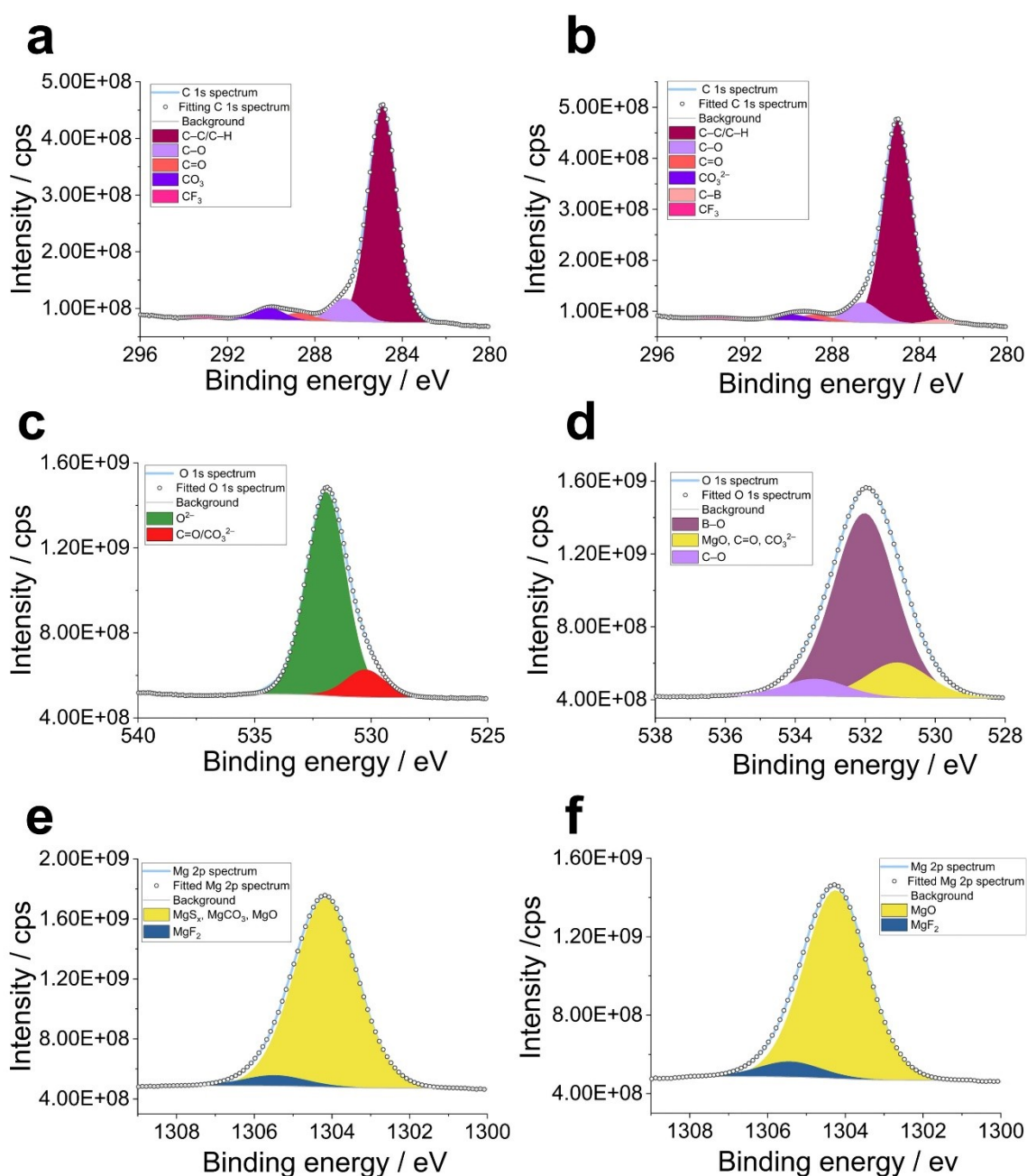


Figure S5. Deconvoluted C 1s (a, b), O 1s (c, d) and Mg 1s (e, f) XPS spectra of (a, c and e) Mg/TFSI and (b, d and f) Mg/BOR samples.

C1s XPS spectra (**Figure S5 a,b**) show two components at 293.0 and 293.2 eV for the Mg/TFSI and Mg/BOR samples, respectively. As already observed for cycled electrodes, both spectra are characterised by C–C/C–H, C–O and C=O components, which are probably related to environmental contamination and/or solvent instability.^{9,10} Peaks assigned to CO₃²⁻ moieties are also detected and tentatively assigned to decomposition species of the electrolyte solutions, as already described for the APC case. Considering the Mg/BOR sample, an additional peak of the C–B was observed at 283.2 eV revealing the existence of remaining salt Mg[B(hfp)₄]₂.⁹ The presence of these carbon-based species as well as MgO moieties is confirmed by the O1s spectra in **Figure 5 c,d**. The peak at 532.0 eV is assigned to B–O containing species, as suggested by Tang *et al.*^{6,11} The Mg 1s core spectra are characterised by one broad peak for both chemistries (**Figure S5 e,f**). The deconvolution of these peaks shows the presence of inorganic moieties (e.g. MgO) at binding energies, while evidence of MgF₂ formation is observed at around 1305.4 eV in both cases confirming what was observed in the F1s spectra.^{6,9,11} For the TFSI-electrolyte sample the signal at around 1305.4 eV can result from the reduction of the TFSI⁻ anion, which further leads to MgS_x species.^{9,10,12}

S6. Raman spectra of pristine polished Mg discs and n-SEIs formed on Mg metal with APC, TFSI and BOR electrolytes

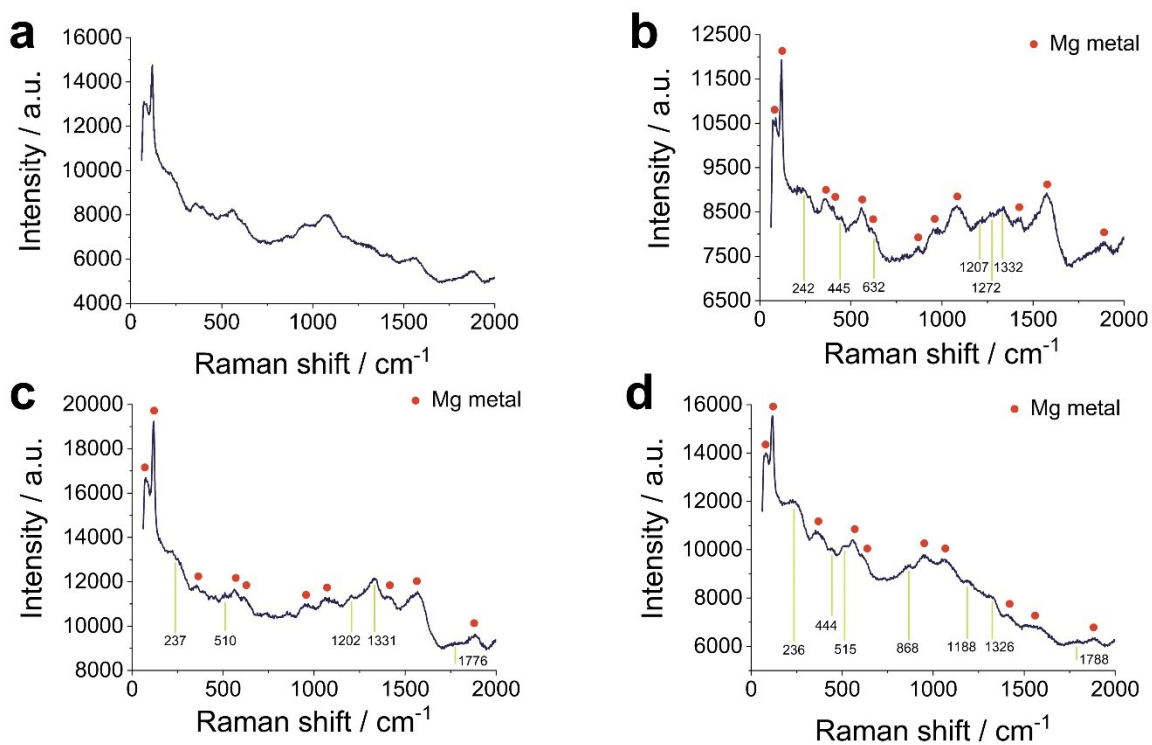


Figure S6. Raman spectra of a) pristine polished Mg disc and n-SEI layers deposited on Mg metal discs after soaking in b) APC, c) TFSI and d) BOR electrolytes.

S7. Fitting parameters for the EIS results of Mg symmetric cells with APC, TFSI and BOR electrolytes at the OCP condition

Table S1. Fitting parameters for the EIS results of Mg symmetric cells with APC, TFSI and BOR electrolytes at the OCP condition

	Q_{SEI} (s^α/Ω)	α_{SEI}	Q_{dl} (s^α/Ω)	α_{dl}	R_e	R_{SEI}	R_{ct}	χ^2
APC	1.35E-05	0.860894	1.61E-05	0.917567	5.3769	1.52E+04	4.22E+04	0.095233
TFSI	8.57E-06	0.950424	1.02E-04	0.702622	2.34504	1.41E+05	7.42E+01	0.049117
BOR	9.28E-06	0.85227	2.73E-05	1	4.34172	1.85E+05	1.27E+04	0.024045

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