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Supporting Information for:

Oxygen – A Fatal Impurity for Reversible Magnesium Deposition/Dissolution

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Experimental detail

Materials: Materials: Di-n-butylmagnesium [$Mg(Bu)_2$; 0.5 mol dm^{-3} heptane solution] was purchased from Thermo Fisher Scientific Inc., USA, and used as received without further purification. 1,1,1,3,3,3-hexafluoro-iso-propanol (HFIP-H) and ethylmagnesium chloride (C_2H_5MgCl; ca. 2 mol dm^{-3} in anhydrous THF; a precursor of air-stable ethoxymagnesium chloride C_2H_5OMgCl) were obtained from Tokyo Chemical Industries, Co., Ltd., Japan. In addition, borane–tetrahydrofuran (BH_3–THF), anhydrous ethanol, and silver nitrate were purchased from FUJIFILM Wako Chemicals, Japan. The HFIP-H was distilled over calcium oxide and stored in an Ar-filled glovebox with 3 Å molecular sieves. Anhydrous diglyme (G2), triglyme (G3), and tetraglyme were obtained from Kanto Chemical Co., Inc., Japan, and used without further purification. Battery-grade magnesium bis(trifluoromethanesulfonyl)amide ($Mg[TFSA]_2$) was purchased from Kishida Chemical Co., Ltd., Japan, dried under vacuum at 120 °C for several days, and then stored in an Ar-filled glovebox. The C_2H_5OMgCl and $Mg[B(HFIP)_4]_2$ salts were synthesized according to procedures reported elsewhere.[1–3] The optimal ternary electrolyte consisting of C_2H_5OMgCl, $Mg[TFSA]_2$, and G3 in the molar ratio of 2:1:15 was prepared according to the reported procedure. The electrolyte solution of 0.3 mol dm^{-3} $Mg[B(HFIP)_4]_2$/G2 was prepared by dissolving predetermined amounts of the salts in G2. The water content of the prepared electrolytes was measured to be <50 ppm using Karl Fischer titration unless otherwise noted.

Surface treatment: A series of treatment solutions, that is, $Al(CH_3)_3$, $Bi(Ph)_3$ (Ph: phenyl), $BiCl_3$, $Ca(BH_4)_2$, $Ge(C_2H_5)_4$, *n*-BuLi (Bu: butyl), $LiBH_4$, Mg(*n*-Bu)$_2$, C_2H_5MgCl, $Mn(Cp)_2$ (Cp: cyclopentadienyl), $NiCl_2$, $Sn(CH_3)_4$, $SnCl_2$, $Zn(C_2H_5)_2$, $ZnCl_2$, $Zn(Ph)_2$, and $Zn[TFSA]_2$, were prepared by dissolving prefixed amounts of the compounds in anhydrous G1 or THF in an Ar-filled glovebox. Excepting $NiCl_2$, the concentration of the treatment solutions was fixed at 0.1 mol dm^{-3}. Due to the limited solubility of the $NiCl_2(G1)_2$ complex in ethers, a saturated solution of $NiCl_2$/G1 was prepared. A mechanically polished magnesium disk (φ = 16 mm, t = 40 μm) was soaked in the above-mentioned solutions for 1 h at 25 °C, washed with anhydrous THF to remove any residual solution, dried under high vacuum, and finally used as modified magnesium metal.

Measurements: Typical electrochemical cycling tests were conducted using cyclic voltammetry (CV) with a three-electrode beaker cell. A Pt disk (φ3 mm, BAS) or modified/unmodified magnesium ribbon (FUJIFILM Wako Chemicals, Japan) was used as the working electrode. An additional modified/unmodified magnesium ribbon and Ag^+/Ag reference electrode served as counter and reference electrodes, respectively. The Ag^+/Ag reference electrode was fabricated according to a previously described procedure.[1] The potential of the reference electrode was calibrated as −2.49 V vs. the reference for 0 V vs. Mg^{2+}/Mg^0.[2,3] CV measurements were conducted using an electrochemical analyzer (HSV-110, Hokuto–Denko Corporation, Japan) in an Ar-filled glovebox or dry chamber with dew points below −76 °C. The O_2 content of the electrolyte solution was measured at 30 ± 0.5 °C using a fiber optic oxygen meter (FireSting-O_2) equipped with a temperature controller. The measured values were first calibrated using a calibration solution for 0% O_2, and then with O_2-saturated tetraglyme and dimethylacetamide based on their Henry constants for O_2.[4] A galvanostatic magnesium deposition/dissolution cycling test was performed on the Swagelok-type two-electrode cells. Cu (t = 20 μm) and modified/unmodified magnesium (t = 40 μm)[5] foils were employed as working and counter electrodes, respectively, and GF/A (t = 0.26 mm, Whatman, UK) was used as a separator. A galvanostatic cycling test was performed using an automatic charge/discharge instrument (HJ0610SD8Y, Hokuto–Denko Corporation, Japan) operating at 1.0 mA cm^{-2} for 1 h at 30 °C for each dissolution and deposition (1.0 mAh cm^{-2}). A magnesium full cell was also assembled using a Zn-modified magnesium metal as a negative electrode and Mo_6S_8 or α-MnO_2 composite as a positive electrode under a dry-air atmosphere. Mo_6S_8 was prepared from $CuMo_6S_8$ (Kojundo Chemical Laboratory CO., Ltd.) according to the reported procedure.[1] All electrochemical cells were assembled in a glove box.

Raman spectra of the magnesium salts were obtained using a Nicolet iS50R Fourier Transform–Raman spectrometer (Themo Fisher Scientific Inc.) and a 1064 nm laser at a resolution of 1 cm^{-1}. The samples were sealed in a glass tube under an Ar or dry-air atmosphere to avoid the exposure to ambient air. All spectra were calibrated with a polypropylene standard and a Si single crystal. The surfaces and cross-sectional views of the modified/unmodified magnesium metals were observed using scanning electron microscopy (SEM; JSM-7800F, JEOL, Japan) and were subsequently characterized by energy dispersive X-ray (EDX) spectroscopy. X-ray photoelectron spectroscopy (XPS; VersaProbe II, ULVAC-PHI, Japan) was performed on polished magnesium metals that were exposed to dry air and soaked in O_2-containing electrolytes. XPS measurements were also conducted on the modified magnesium metals. All samples were washed with anhydrous THF to remove any residual electrolyte, dried under high vacuum at ambient temperature, placed in an airtight chamber, and transferred for SEM–EDX or XPS analyses without exposure to air. XPS measurements were performed with an Al Kα X-ray source under a base pressure of 6.7×10^{-8} Pa. The binding energy of the obtained spectra was calibrated using the C 1s peak from sp2-hybridized carbon at 284.5 eV as a reference.

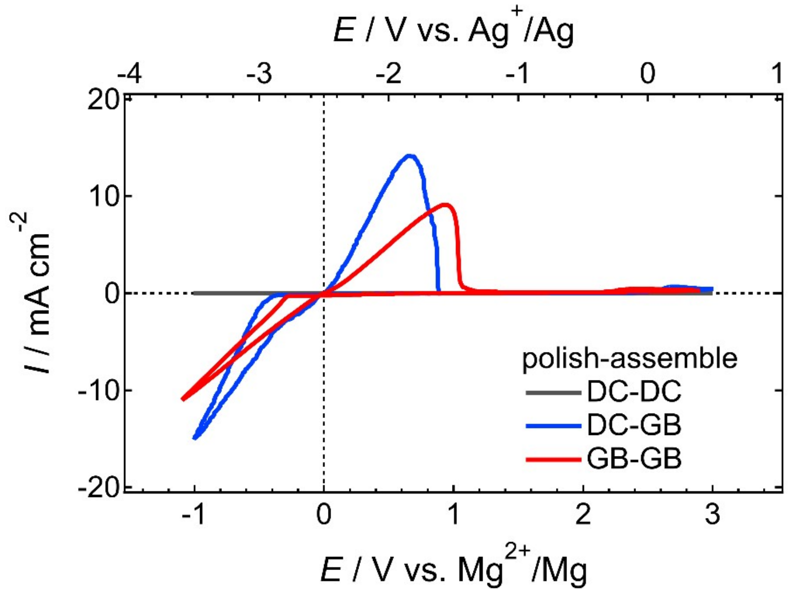


Figure S1. CV profiles of Pt electrodes recorded in 0.3 mol dm^{-3} Mg[B(HFIP)$_4$]$_2$/G2 using magnesium negative electrodes polished in a dry chamber (DC; dew point < −76 °C) and an Ar-filled glove box (GB; H_2O and O_2 contents <1 ppm). The presence of O_2 during pretreatment has a minor effect on the electrochemical magnesium deposition–dissolution activity, whereas it is critical during electrochemical measurements. It should be noted that the observed current density for the DC-GB measurement is larger than that for the GB-GB. This can be caused by some uncontrollable experimental factors, such as physical/chemical conditions of electrodes, electrolytes, glassware, and geometry of each electrode in voltammetry cells, even if the identical cell compartments and the same cleansing protocol are adopted for each measurement.

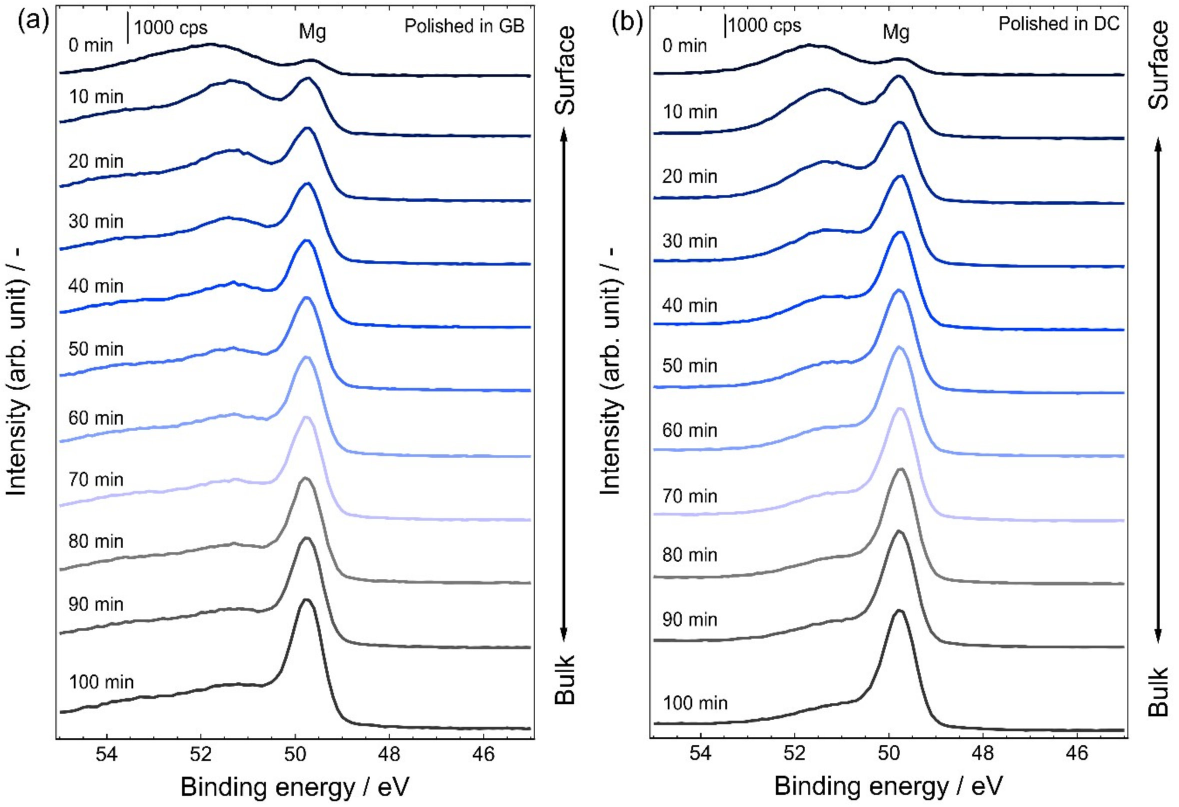


Figure S2. Depth profiles of Mg 2p spectra of magnesium metals polished in (a) GB and (b) DC.

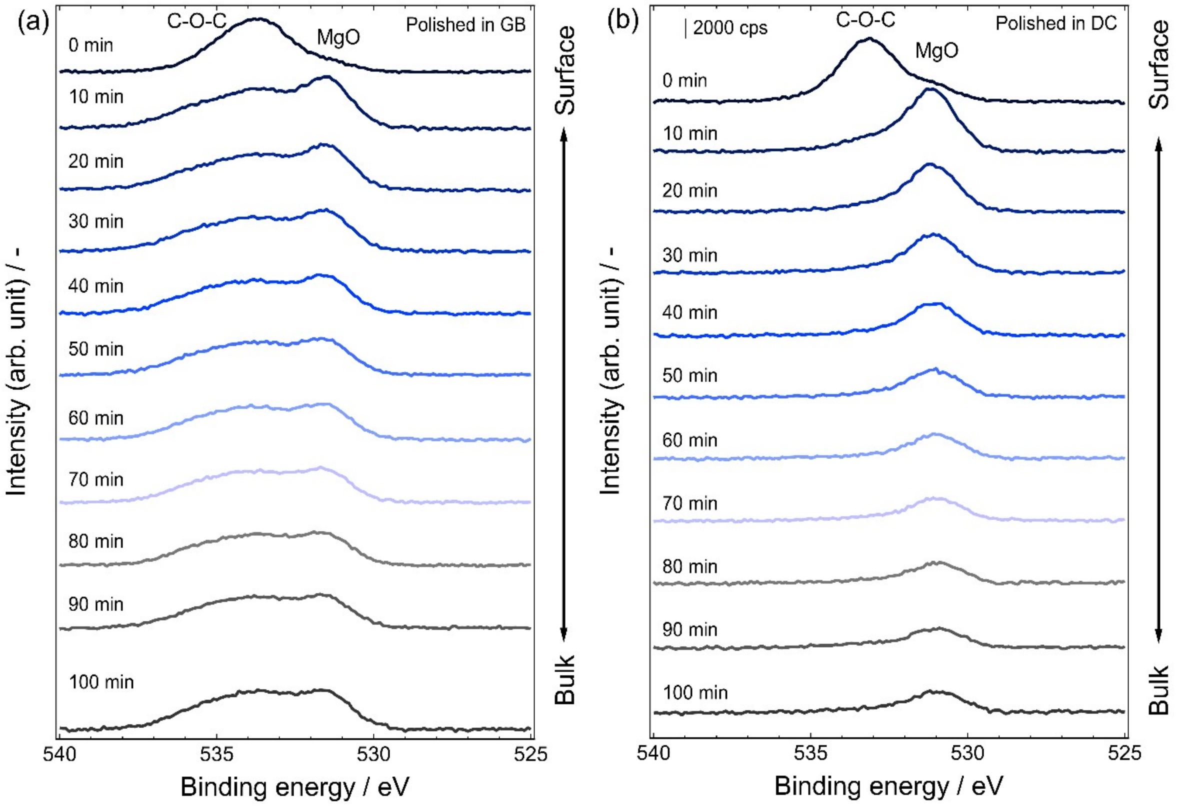


Figure S3. Depth profiles of O 1s spectra of magnesium metals polished in (a) GB and (b) DC.

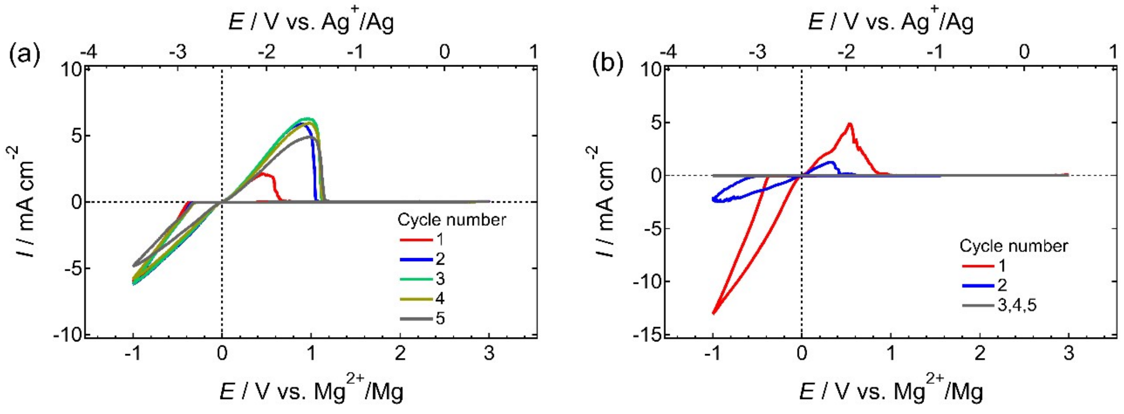


Figure S4. CV profiles of Pt electrodes recorded in 0.3 mol dm^{-3} Mg[B(HFIP)$_4$]$_2$/G2 at 10 mV s^{-1} and 30 °C immediately after (a) 1 and (b) 5 min of steady flow of O_2 gases at 10 mL min^{-1}. The O_2 gas flow was stopped during CV measurements.

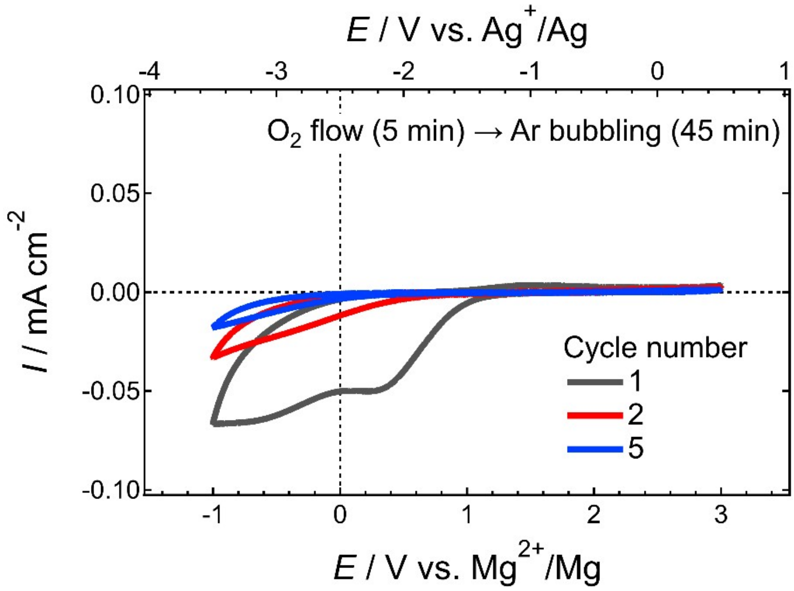


Figure S5. CV profiles of Pt electrodes recorded in 0.3 mol dm^{-3} Mg[B(HFIP)$_4$]$_2$/G2 at 10 mV s^{-1} at 30 °C after 5 min of O_2 gas flow, followed by 45 min of Ar bubbling at a rate of 10 mL min^{-1}. The O_2 content after Ar bubbling is < 1 ppm.

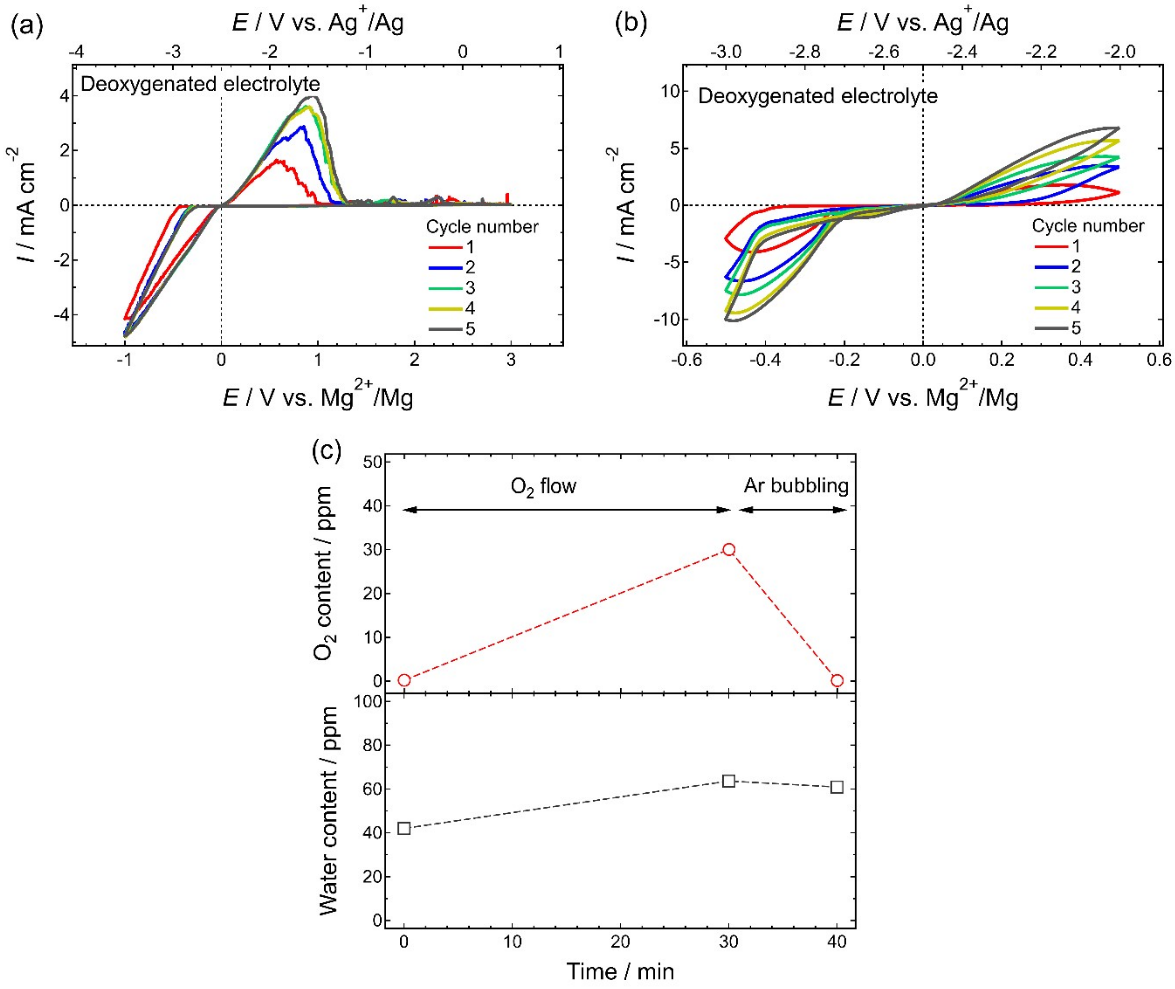


Figure S6. CV profiles of (a) Pt and (b) Mg electrodes recorded in deoxygenated 0.3 mol dm^{-3} Mg[B(HFIP)$_4$]$_2$/G2 at 10 mV s^{-1} at 30 °C. The electrolyte was placed alone in the gas-tight chamber, then O_2 gas was introduced for 30 min, followed by 10 min of Ar bubbling at a rate of 10 mL min^{-1}. (c) The water and O_2 contents in the electrolyte solution measured at each experimental condition.

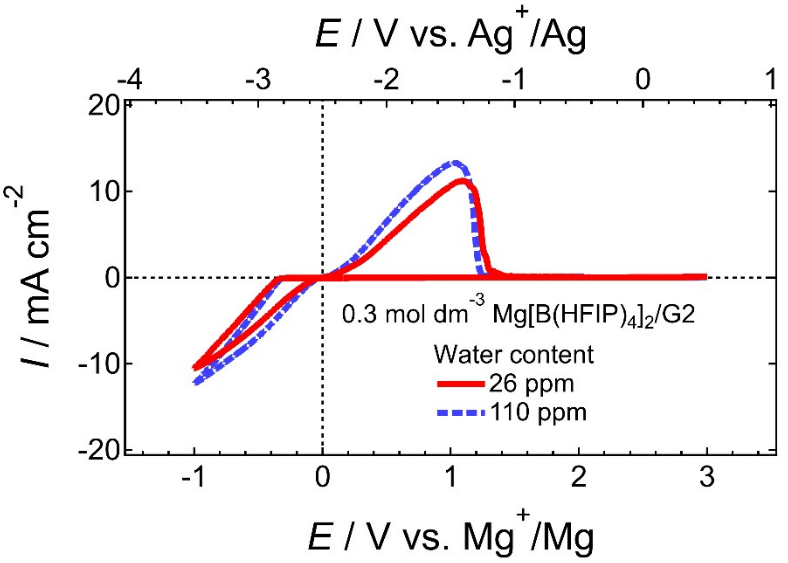


Figure S7. CV profiles of Pt electrodes recorded in 0.3 mol dm^{-3} Mg[B(HFIP)$_4$]$_2$/G2 containing an amount of water impurity measured at 10 mV s^{-1} at 30 °C.

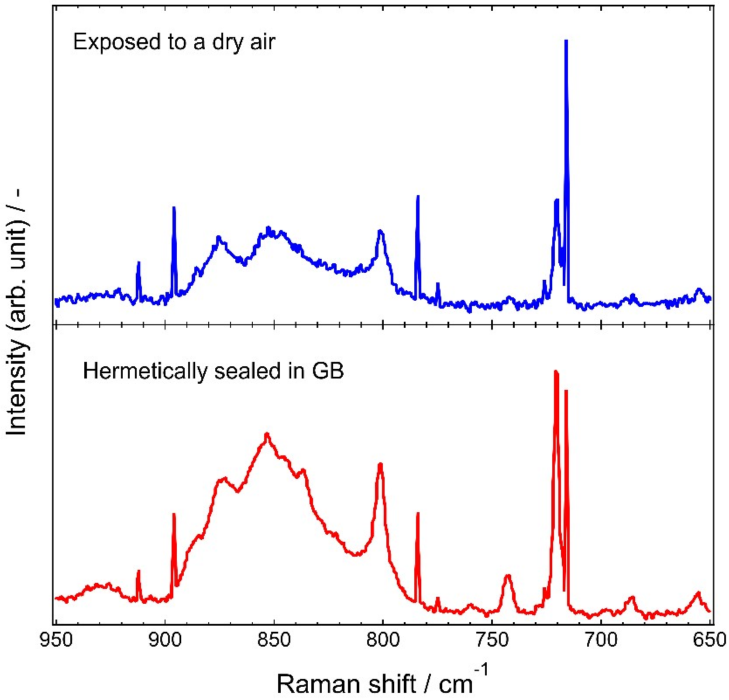


Figure S8. Raman spectrum of the electrolyte solutions after exposure to O_2 for 30 min. The spectrum of the electrolyte sealed in GB is included as a reference system.

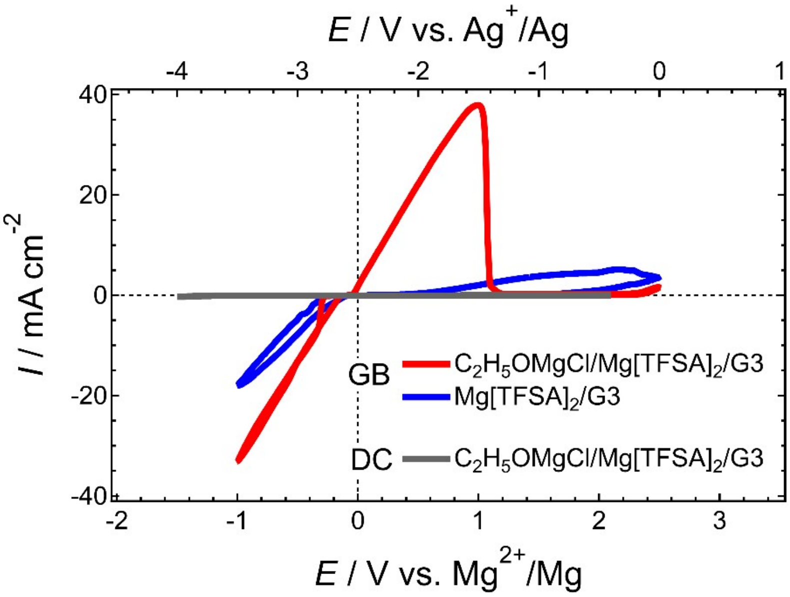


Figure S9. CV profiles of Pt electrodes recorded in binary Mg[TFSA]$_2$/G3 and ternary C_2H_5OMgCl/Mg[TFSA]$_2$/G3 electrolytes measured under an Ar (GB) and a dry air (DC) atmosphere. The concentration of Mg was fixed at *ca*. 0.9 mol dm^{-3} in each electrolyte solution.

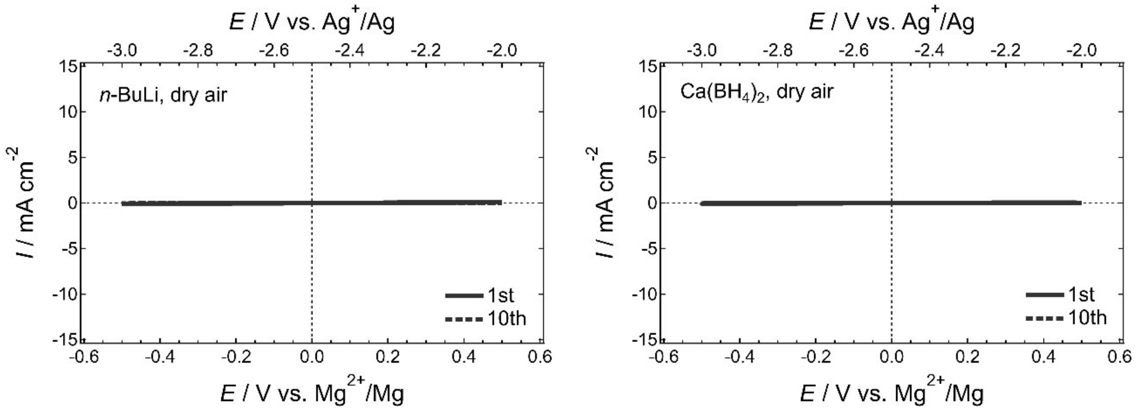


Figure S10. CV profiles of *n*-butyllithium and Ca(BH$_4$)$_2$-treated magnesium electrodes recorded in 0.3 mol dm^{-3} Mg[B(HFIP)$_4$]$_2$/G2 electrolytes.

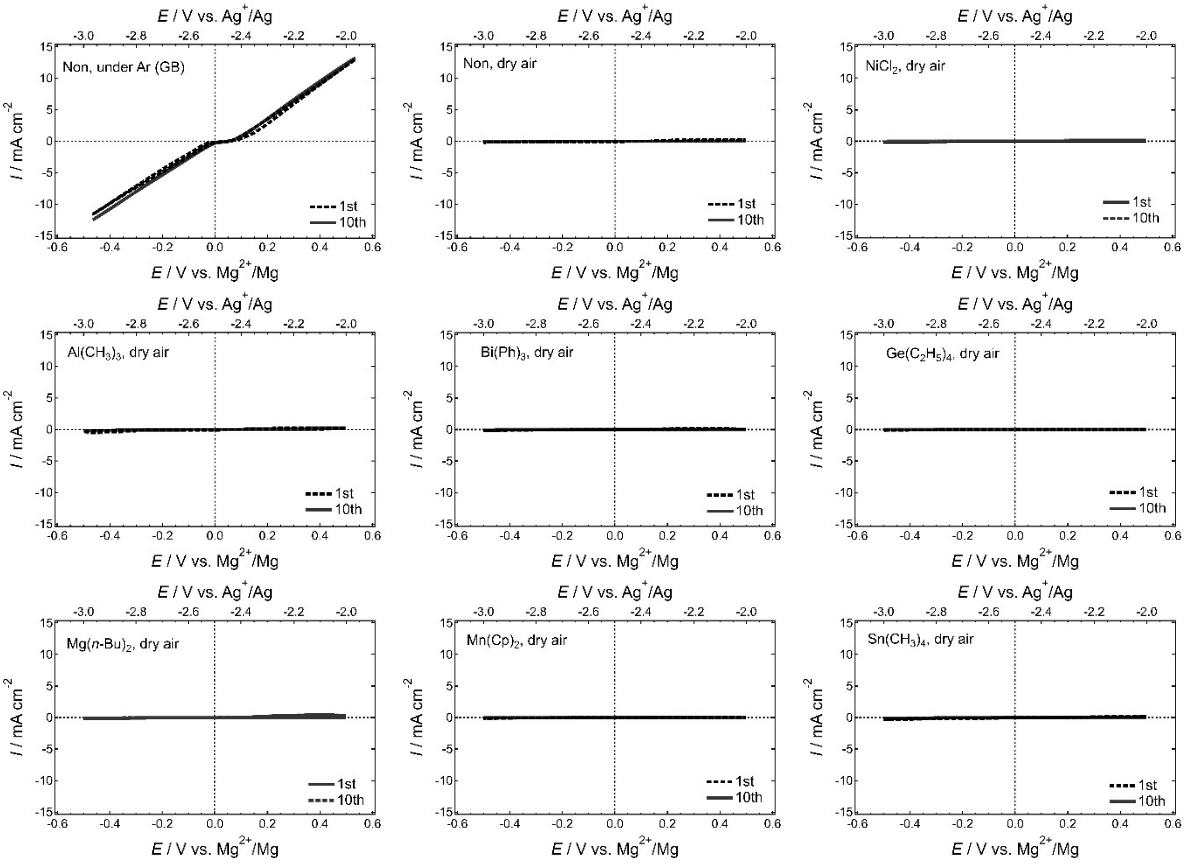


Figure S11. CV profiles of treated magnesium electrodes recorded in 0.3 mol dm^{-3} Mg[B(HFIP)$_4$]$_2$/G2 electrolytes. The profiles using non-treated magnesium electrodes are included as reference systems.

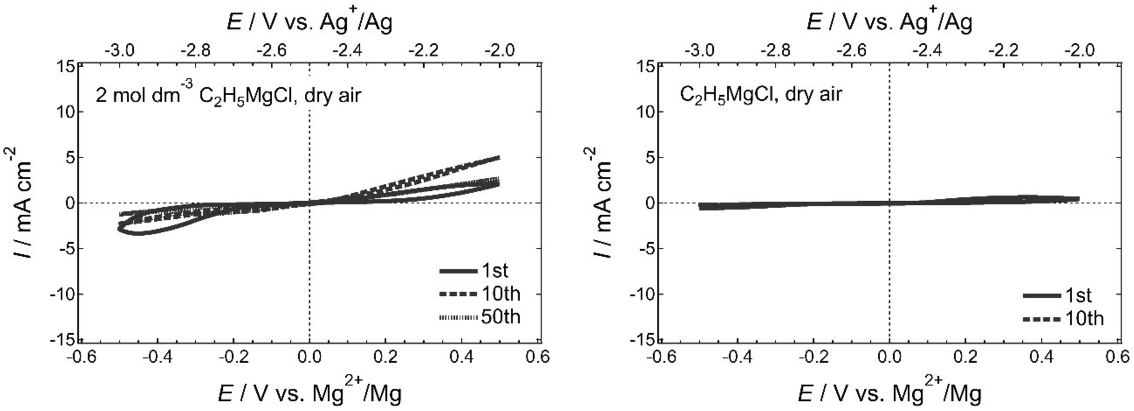


Figure S12. CV profiles of (left) *ca*. 2 and (right) *ca*. 0.1 mol dm^{-3} C_2H_5MgCl/THF-treated magnesium electrodes recorded in 0.3 mol dm^{-3} Mg[B(HFIP)$_4$]$_2$/G2 electrolytes.

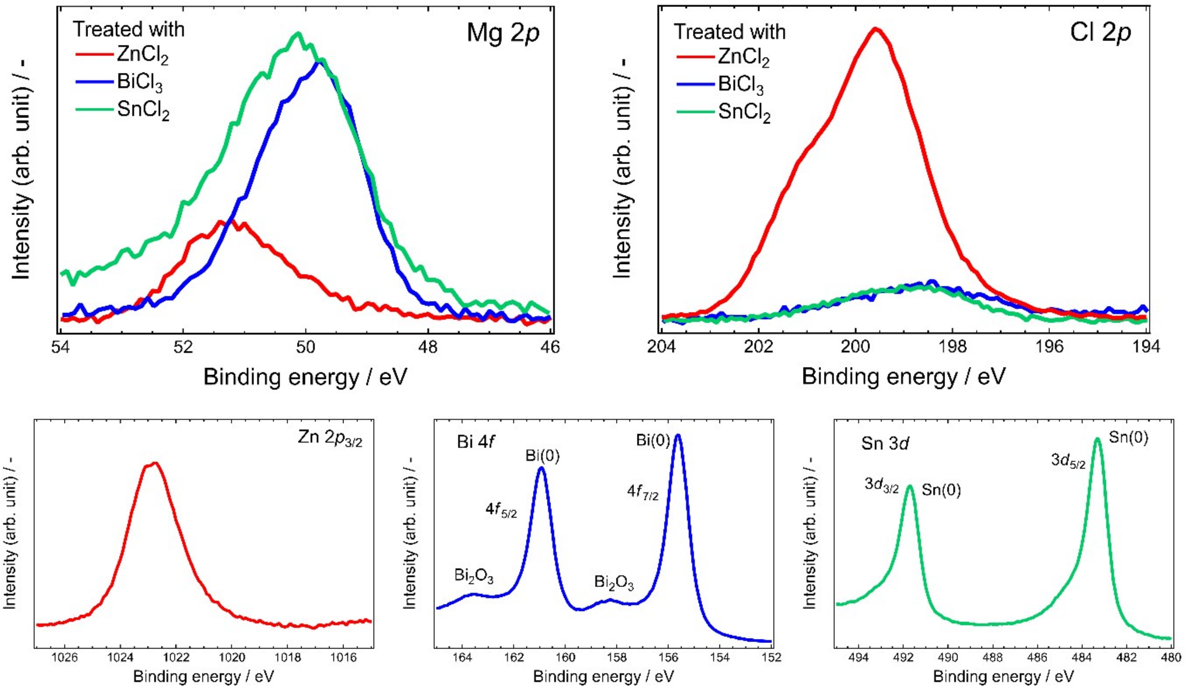


Figure S13. Mg 2*p*, Cl 2*p*, and each corresponding XPS spectra of $ZnCl_2$, $BiCl_3$, and $SnCl_2$-treated magnesium electrodes. Peak intensity of Mg 2*p* and Cl 2*p* spectra are normalized.

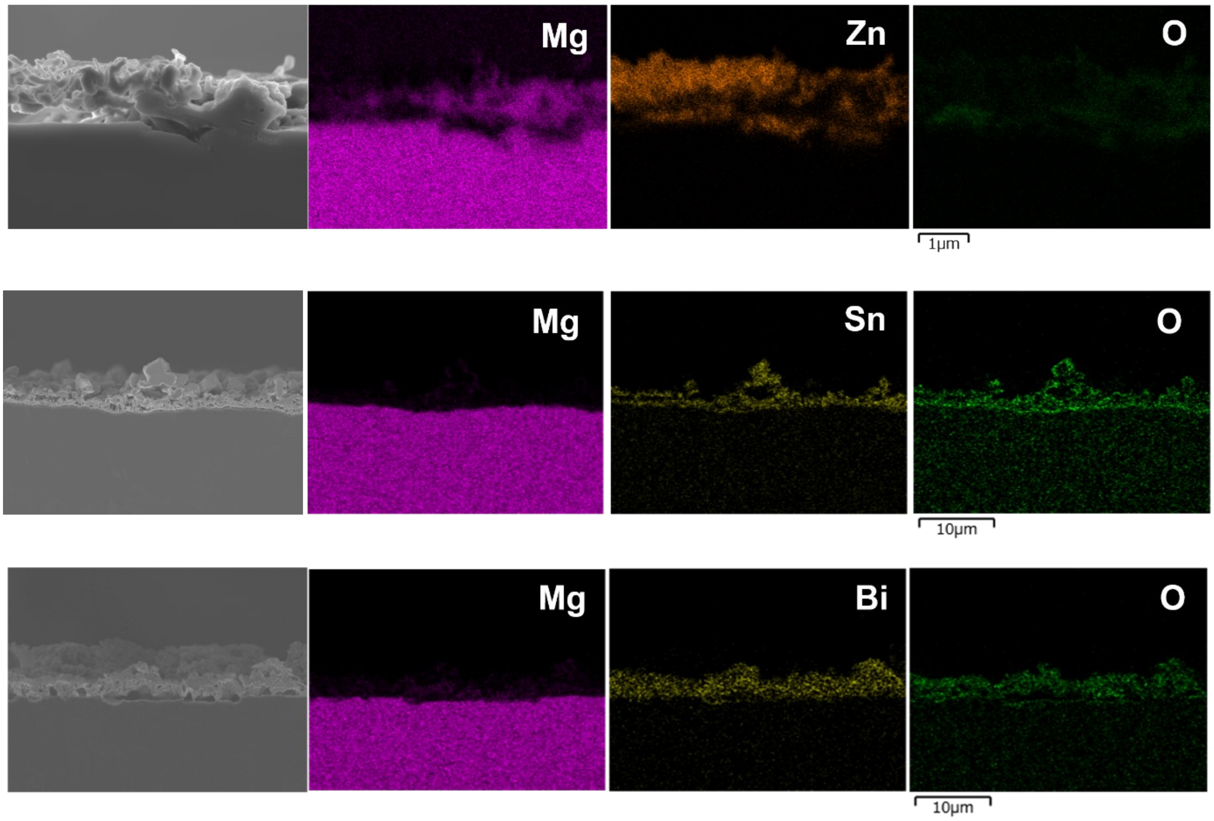
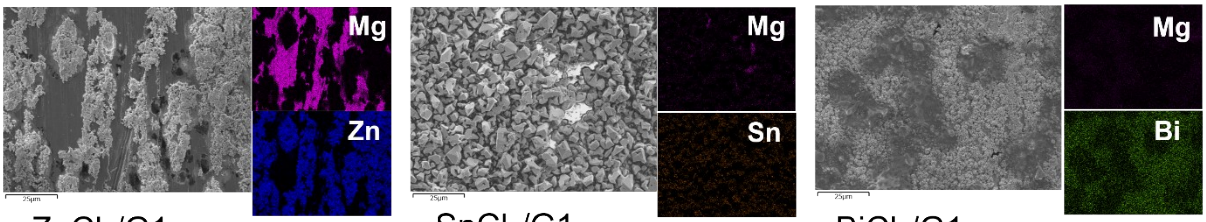


Figure S14. Cross-sectional and surface views of SEM images and corresponding EDX profiles of $ZnCl_2$, $SnCl_2$, and $BiCl_3$-treated magnesium electrodes before cycling.



$ZnCl_2$/G1

$SnCl_2$/G1

$BiCl_3$/G1

Figure S15. SEM images of $ZnCl_2$, $SnCl_2$, and $BiCl_3$-treated magnesium electrodes after CV cycling.

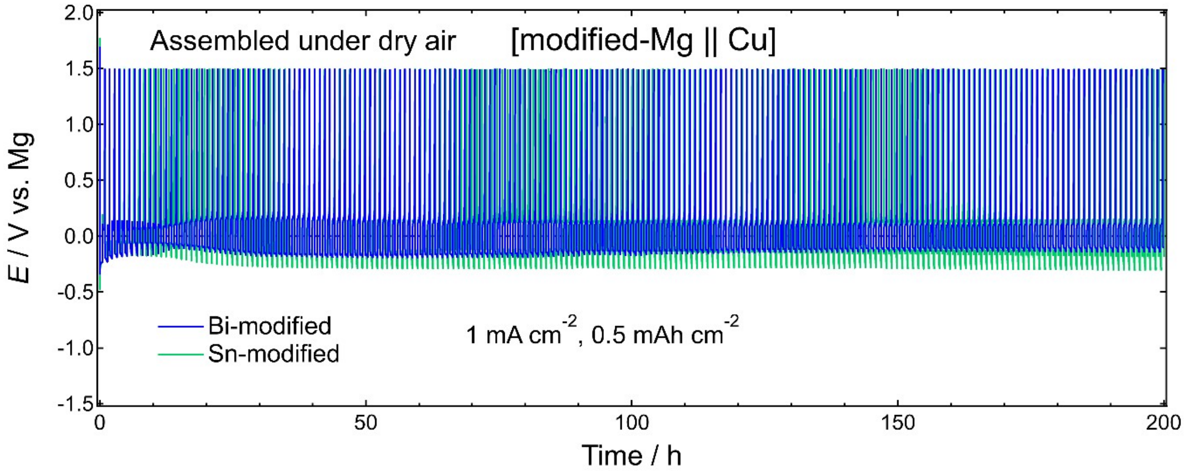


Figure S16. Galvanostatic magnesium dissolution-deposition cycling profiles of [modified-Mg || Cu] cells assembled under a dry air atmosphere.

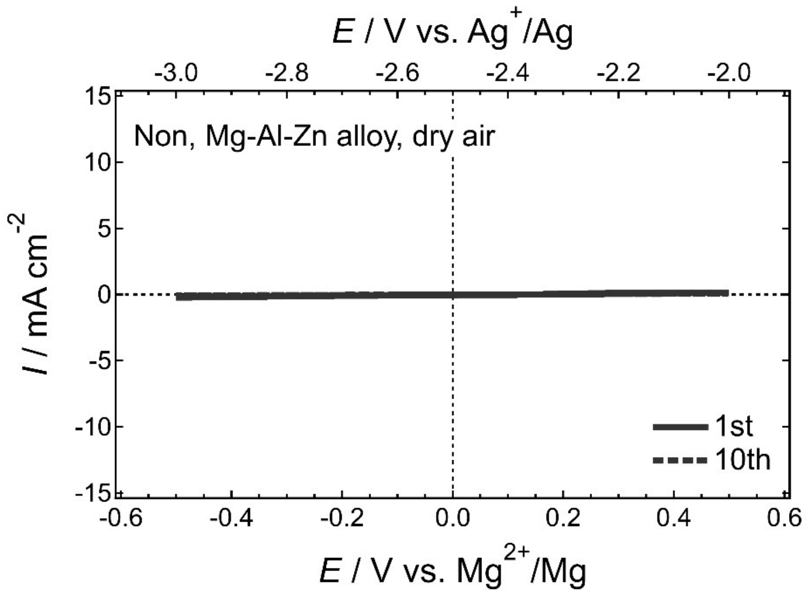


Figure S17. CV profiles of non-modified magnesium-aluminum-zinc solid solution (AZ31) electrode recorded in 0.3 mol dm^{-3} $Mg[B(HFIP)_4]_2$/G2 electrolytes under a dry air atmosphere.

Table S1. Ionic conductivities of 0.3 mol dm^{-3} Mg[B(HFIP)$_4$]$_2$/G2 before and after exposure to O_2 gas for 30 min at 30 °C.

	σ / mS cm^{-1}
Before (under Ar)	5.7
After	5.9

References

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