

*Supporting Information for:*

***A key concept of utilization of both non-Grignard  
magnesium chloride and imide salts for rechargeable  
Mg battery electrolytes***

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## Experimental

### *Materials and electrolyte preparation*

Ethylmagnesium chloride (EtMgCl; *ca.* 18% in tetrahydrofuran, *ca.* 2 mol dm<sup>-3</sup>), anhydrous ethanol, 1-propanol, ethylene glycol monomethyl ether, ethylene glycol, 2-(dimethylamino)ethanol, diethylamine, bis(2-methoxyethyl)amine, diphenylamine, *N*-(2-methoxyethyl)methylamine, and silver nitrate (AgNO<sub>3</sub>) were all purchased from Tokyo Chemical Industry Co., Ltd. Anhydrous tetrahydrofuran (THF) and triglyme (G3; for electrochemistry) were obtained from Wako Pure Chemical Industries, Ltd., and Kanto Chemical Co., Inc., respectively. Battery grade magnesium bis(trifluoromethanesulfonyl)imide (Mg(TFSI)<sub>2</sub>) was purchased from Kishida Chemical Co., Ltd. All purchased chemicals were used without further purification.

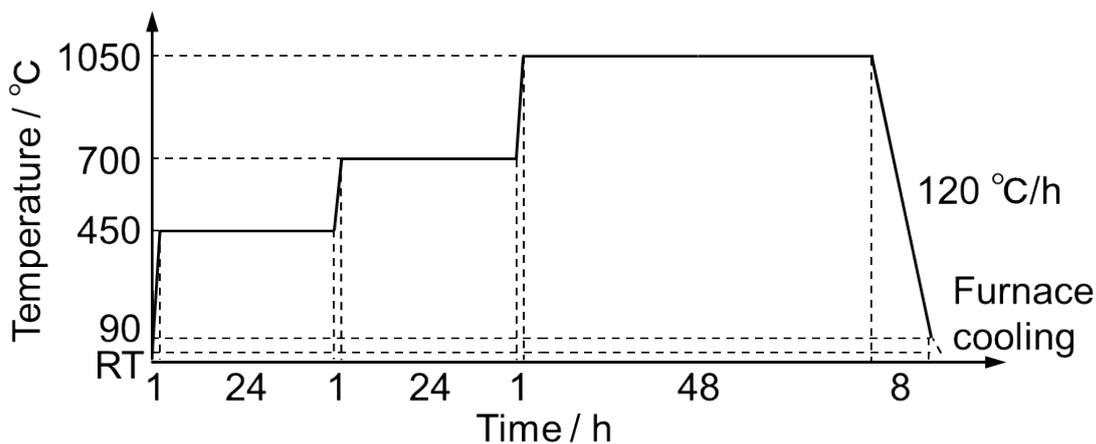
The studied magnesium chloride salts were all synthesized by slowly adding the appropriate amount of alcohols or amines dropwise into EtMgCl/THF in an open beaker and stirring for 30 minutes inside an Ar-filled glovebox (< 1 ppm H<sub>2</sub>O, < 1 ppm O<sub>2</sub>). The reaction proceeds immediately after mixing as confirmed by the rapid evolution of ethane gas via a hydrogen metal exchange reaction. Complete removal of the THF solvent and starting materials by slow evaporation at 60 °C overnight and subsequent vacuum drying at 80 °C for several days yielded the desired salts as light-grey powders. The ternary electrolyte solutions were prepared by mixing stoichiometric amounts of each component and vigorously stirring at 100 °C inside the glovebox to obtain a desired homogeneous clear liquid.

## Measurements

The transport properties of the selected electrolyte solutions were characterized with respect to their ionic conductivity and density (concentration). The ionic conductivities ( $\sigma$ ) of O1/Mg(TFSI)<sub>2</sub>/G3 and EtMgCl/Mg(TFSI)<sub>2</sub>/G3 were determined by the complex impedance method using an electrochemical analyzer (ALS 760B, HCH Instrument) in the frequency range of 1 to 100 kHz with a sinusoidal alternating voltage amplitude of 10 mV root-mean-square (rms). A homemade cell equipped with two platinum black electrodes, whose cell constant was predetermined by a standard 0.1 M KCl aqueous solution, was used for the impedance measurements. The  $\sigma$  values of O1/Mg(TFSI)<sub>2</sub>/G3 and EtMgCl/Mg(TFSI)<sub>2</sub>/G3 were determined to be 0.55 and 0.21 mS cm<sup>-1</sup>, respectively, at 100 °C. The liquid densities of the ternary electrolytes were measured using an oscillating U-tube densitometer (DMA4100M, Anton Paar) at 80 °C. The measured density was used to calculate the concentration of the magnesium in the solution.

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were performed on the ternary electrolytes using a typical three-electrode cell by an electrochemical analyzer (HSV-110, Hokuto). A Pt disk (3 mm diameter) and a coiled Mg wire (0.3 mm diameter) were employed as the working and counter electrodes, respectively. A reference electrode was fabricated by soaking a Ag wire in a (0.01 M AgNO<sub>3</sub> + 0.1 M Mg(TFSI)<sub>2</sub>)/G3 solution, confined in a glass tube with a liquid junction of porous Vycor glass. The electrode potential of the reference electrode was calibrated using the (0.5 M PhMgCl + 0.25 M AlCl<sub>3</sub>)/THF solution where magnesium stripping takes place at almost the ideal electrode potential.<sup>1</sup> Electrochemical magnesium plating/stripping cycles in the selected electrolyte were

evaluated using a coin cell with TOSCAT 3100 (Toyo system). Symmetric cells in which the AZ31 alloy foil (Mg, 96%; Al, 3%; Zn, 1%. Fujisougyou Co., Ltd.) served as both the working and counter electrodes were assembled inside the glovebox. The cells with Cu and AZ31 foils that served as the working and counter electrodes, respectively, were also prepared. For the cycling measurements, a constant cathodic/anodic current of  $500 \text{ mA cm}^{-2}$  was applied for 30 minutes in each cycle at 30 and 100 °C. A galvanostatic charge-discharge test was performed on the  $\text{Mo}_6\text{S}_8$ -AZ31 cells incorporating the O1/Mg(TFSI)<sub>2</sub>/G3 electrolyte using a 2032-type coin cell. The Chevrel phase  $\text{Mo}_6\text{S}_8$  was synthesized by the following process based on the procedure reported by Aurbach et al.<sup>2,3</sup> The stoichiometric mixture of 99.7% Cu powder (dendritic, <45  $\mu\text{m}$ , Aldrich), 99.9% Mo powder (<150  $\mu\text{m}$ , Aldrich), and reagent-grade S powder (100 mesh, Sigma-Aldrich) was pelletized at about 20 MPa for 5 min. The pellet was sealed in an evacuated quartz tube, and was heat-treated according to the temperature-time profile shown in Scheme S1. After the heat treatment,  $\text{Cu}^{2+}$  ions were extracted from the product  $\text{Cu}_2\text{Mo}_6\text{S}_8$  in the mixed solution of 12 M HCl aqueous solution and deionized water (1:3 by volume) for 144 h at room temperature using dissolved oxygen as the oxidizing agent, which was continuously supplied from air. The obtained  $\text{Mo}_6\text{S}_8$  powder was subjected to centrifugal washing at 5,000 rpm using water and ethanol both more than 2 times each, followed by drying in vacuum at room temperature.



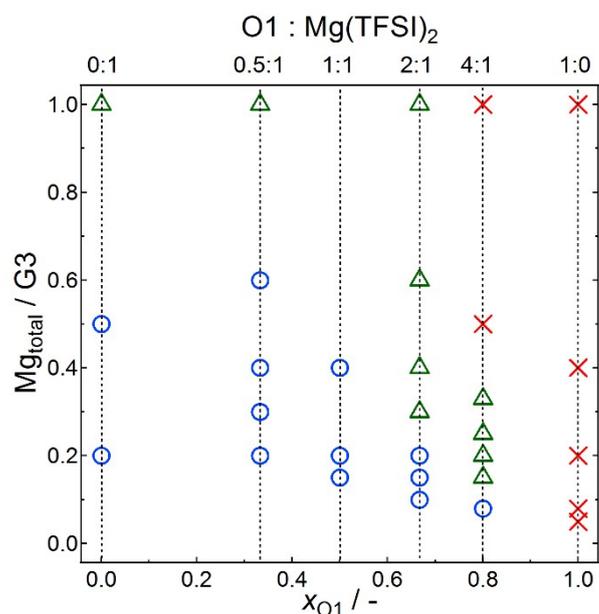
**Scheme S1.** Temperature-time profile of the heat treatment for the synthesis of  $\text{Cu}_2\text{Mo}_6\text{S}_8$ .

The composite cathode was fabricated by thoroughly mixing  $\text{Mo}_6\text{S}_8$  as the active material, acetylene black (Denka) as an electrically conductive support, and poly(vinylidene fluoride) (Kureha) as a binder in the weight ratio of 80:10:10. The mixture was homogenized in a solvent of *N*-methylpyrrolidone (Wako) to obtain a slurry, then spread onto a Pt foil current collector (Nilaco) and dried at 80 °C for several days. The as-obtained composite sheet was compressed at 0.2 kN  $\text{cm}^{-1}$  to improve the electrical conductivity. A coin cell consisting of the  $\text{Mo}_6\text{S}_8$  composite cathode, AZ31 anode, and glass fiber separator (GA200, ADVANTEC) was assembled in the glovebox. The cycling test was carried out in the voltage range of 0.3–1.8 V at 30 and 100 °C with a current density of 12.2  $\text{mA g}^{-1}$  (at C/10-rate based on the mass of  $\text{Mo}_6\text{S}_8$ ).

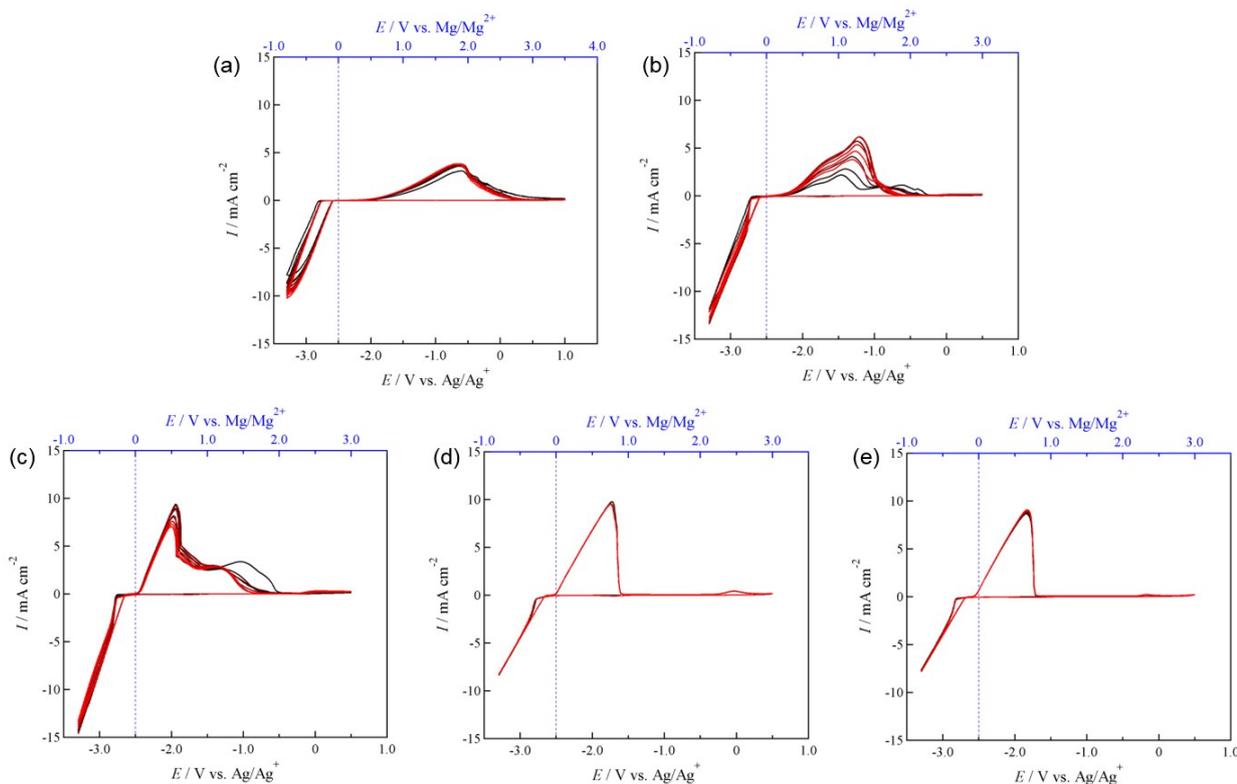
Single crystals suitable for X-ray crystallography were isolated from the  $\text{O1/Mg}(\text{TFSI})_2/\text{THF} = 2/1/30$  (molar ratio) solution. A single crystal of  $[\text{Mg}_3\text{Cl}_3(\text{C}_2\text{H}_5\text{O})_2(\text{THF})_6][\text{TFSI}] \cdot (\text{THF})$  ( $0.290 \times 0.160 \times 0.120$ ) coated with Parabar 10312 (Hampton Research) to avoid absorbing moisture was mounted on a glass pin with CryoLoop (Hampton Research), and cooled to  $-100$  °C by the steady flow

of a nitrogen gas stream. All the diffraction measurements were performed by a Rigaku XtaLAB P200 diffractometer using multilayer mirror monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). An empirical absorption correction was applied by the multiscan averaging of symmetry equivalent data in the SADABS program.<sup>4</sup> The structures were solved by the direct method using SIR92,<sup>5</sup> and refined full-matrix least-squares in the anisotropic approximation for non-hydrogen atoms using SHELXL2014/7.<sup>6</sup> The relatively large residual density, *ca.*  $\pm 1.0 \text{ e \AA}^{-3}$ , is located close to the THF molecule co-crystallized with ionic entities. All the hydrogen atoms were placed in geometrically ideal positions and refined using the riding model. All calculations, except for the refinement, were performed using the CrystalStructure crystallographic software package.<sup>7</sup> Crystal data for  $[\text{Mg}_3\text{Cl}_3(\text{C}_2\text{H}_5\text{O})_2(\text{THF})_6][\text{TFSI}] \cdot (\text{THF})$ :  $\text{C}_{34}\text{H}_{66}\text{Cl}_3\text{F}_6\text{Mg}_3\text{NO}_{13}\text{S}_2$ ,  $M_w = 1054.28$ , monoclinic crystal system, space group  $C2/c$  (no. 15),  $a = 27.799(3)$ ,  $b = 19.3811(19)$ ,  $c = 19.2402(2) \text{ \AA}$ ,  $\beta = 103.381(2)^\circ$ ,  $V = 10084.6(18) \text{ \AA}^3$ ,  $Z = 8$ ,  $D_{\text{calc}} = 1.389 \text{ g cm}^{-3}$ ,  $\mu = 3.785 \text{ mm}^{-1}$ ,  $T = 173 \text{ K}$ , 47863 total reflections, 11570 unique reflections,  $R_{\text{int}} = 0.0343$ ,  $R_1 (I > 2\sigma(I)) = 0.0793$ ,  $R_1$  (all data) = 0.1012,  $wR_2$  (all data) = 0.2786, GooF = 1.088, residual minimum and maximum electron densities  $-1.03$  and  $1.78 \text{ e \AA}^{-3}$ , respectively. CCDC deposited number: 1510823.

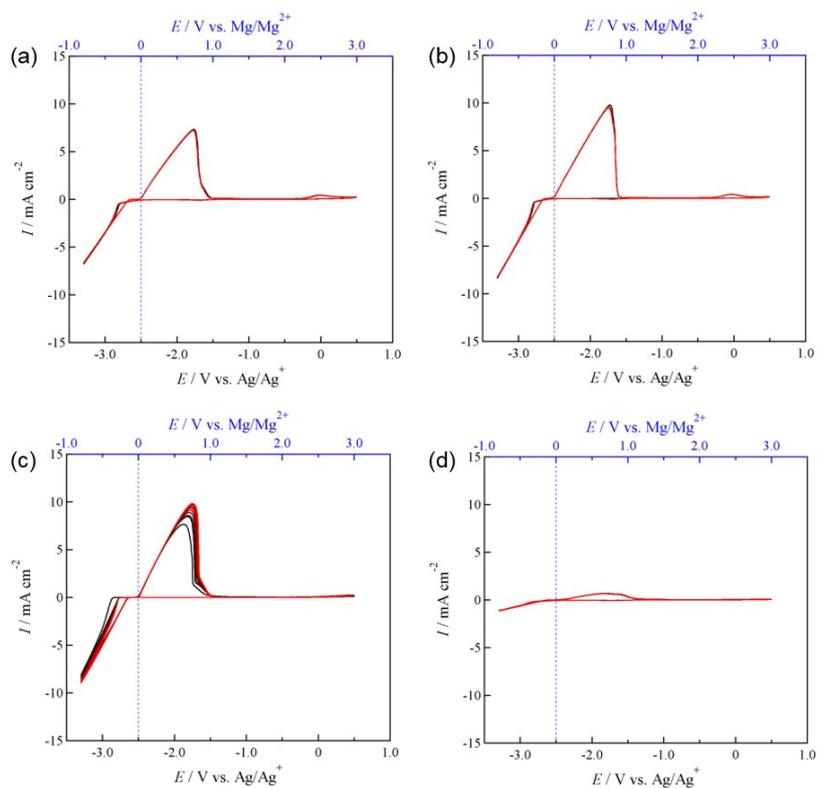
The Raman spectra were collected using a 532 nm laser Raman spectrophotometer (NRS1000, JASCO) at ambient temperature. The samples were enclosed in a glass capillary inside the glovebox and transferred to the instrument without exposure to air. A spectral resolution of  $4 \text{ cm}^{-1}$  and 30 scans with each accumulation time of 30 seconds were employed for all the measurements.



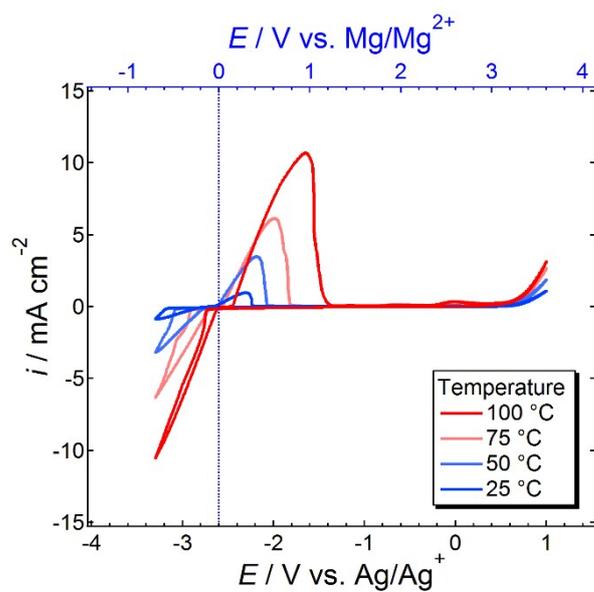
**Figure S1.** Solubility mapping of one selected ternary electrolyte of O1/Mg(TFSI)<sub>2</sub>/G3 as a function of the mole fraction  $x_{O1}$  and molar ratio Mg<sub>total</sub>/G3. Circle, totally soluble at 25 °C; triangle, soluble at 100 °C while precipitates found at 25 °C; cross, insoluble even at 100 °C.



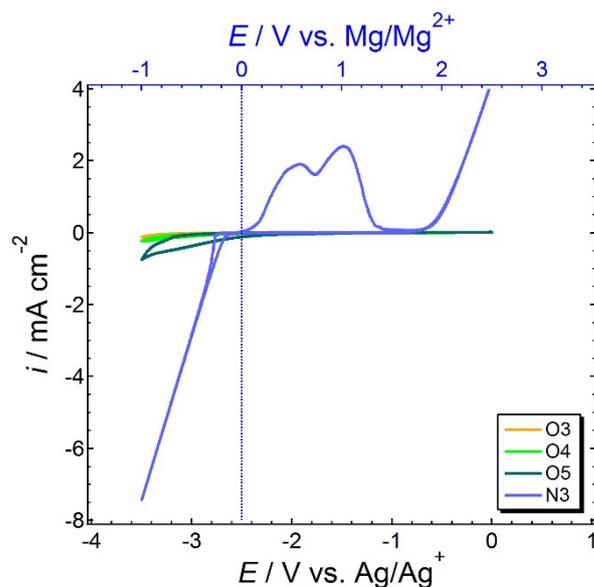
**Figure S2.** CVs of the ternary electrolytes of O1/Mg(TFSI)<sub>2</sub>/G3 at the fixed molar ratio of Mg<sub>total</sub>/G3 = 0.2.  $x_{O1} = 0$ (a), 0.33(b), 0.5(c), 0.67(d), and 0.8(e).



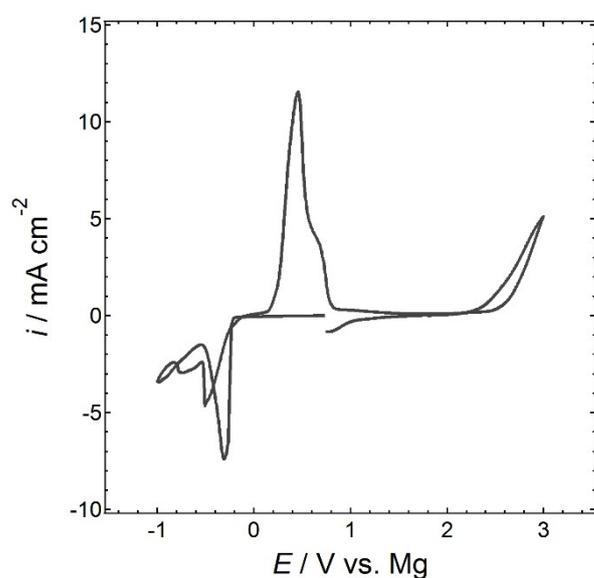
**Figure S3.** CVs of the ternary electrolytes of O1/Mg(TFSI)<sub>2</sub>/G3 at the fixed mole fraction of  $x_{O1} = 0.67$ .  $Mg_{total}/G3 = 0.1$ (a),  $0.2$ (b),  $0.5$ (c), and  $0.67$ (d).



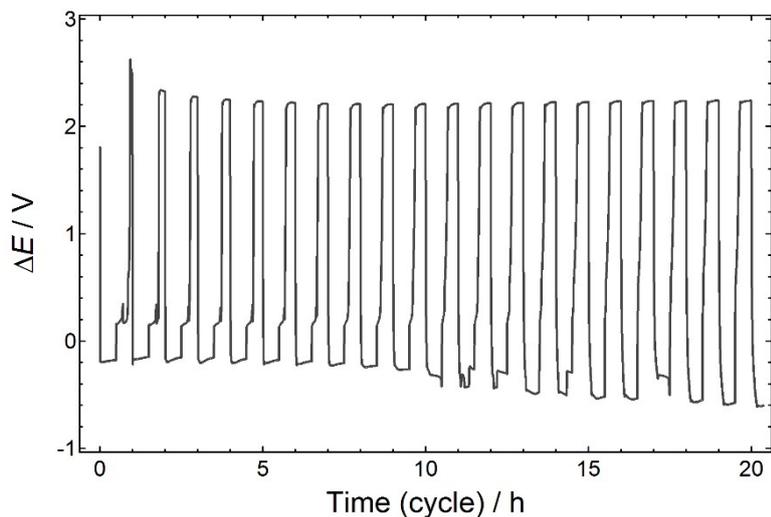
**Figure S4.** CVs of the ternary electrolyte of O1/Mg(TFSI)<sub>2</sub>/G3 = 2/1/15 recorded on the Pt electrode at a scan rate of  $50 \text{ mV s}^{-1}$  at four different temperatures.



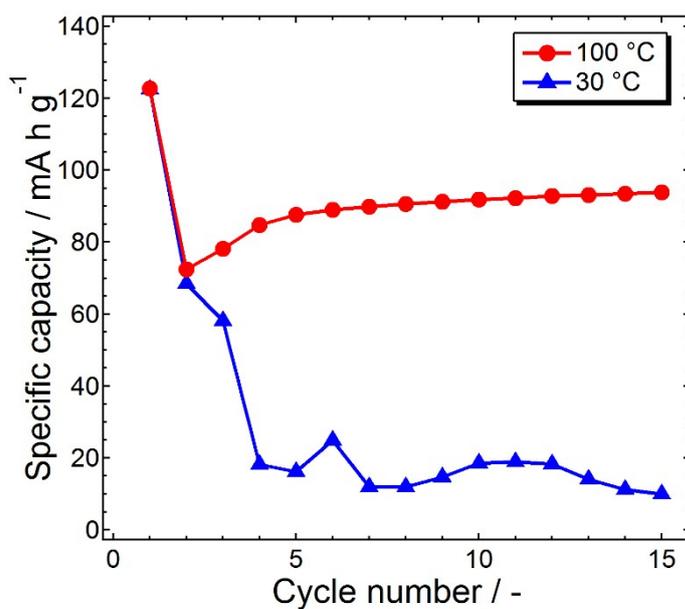
**Figure S5.** CVs of the selected ternary electrolytes recorded on the Pt electrode at a scan rate of 50  $\text{mV s}^{-1}$  at 100  $^{\circ}\text{C}$ . Molar ratio of (ROMgCl or RR'NMgCl)/Mg(TFSI)<sub>2</sub>/G3 was fixed at 2/1/15 ( $\text{Mg}_{\text{total}}/\text{G3} = 1/5$ ). This figure magnifies in scale the current density (vertical axis) from Figure 1a in the manuscript.



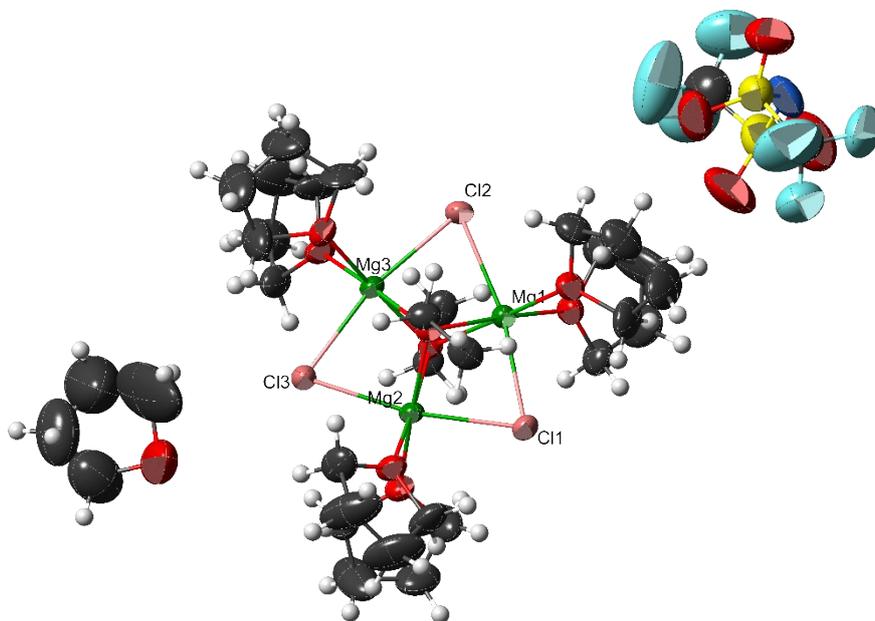
**Figure S6.** CV of the ternary electrolyte of O1/Mg(TFSI)<sub>2</sub>/G3 = 2/1/15 recorded on a stainless steel electrode at a scan rate of 50  $\text{mV s}^{-1}$  at 100  $^{\circ}\text{C}$ .



**Figure S7.** Electroplating/stripping cycling in the O1/Mg(TFSI)<sub>2</sub>/G3 electrolyte carried out on the stainless steel electrode at the current density of 0.5 mA cm<sup>-2</sup> at 100 °C.

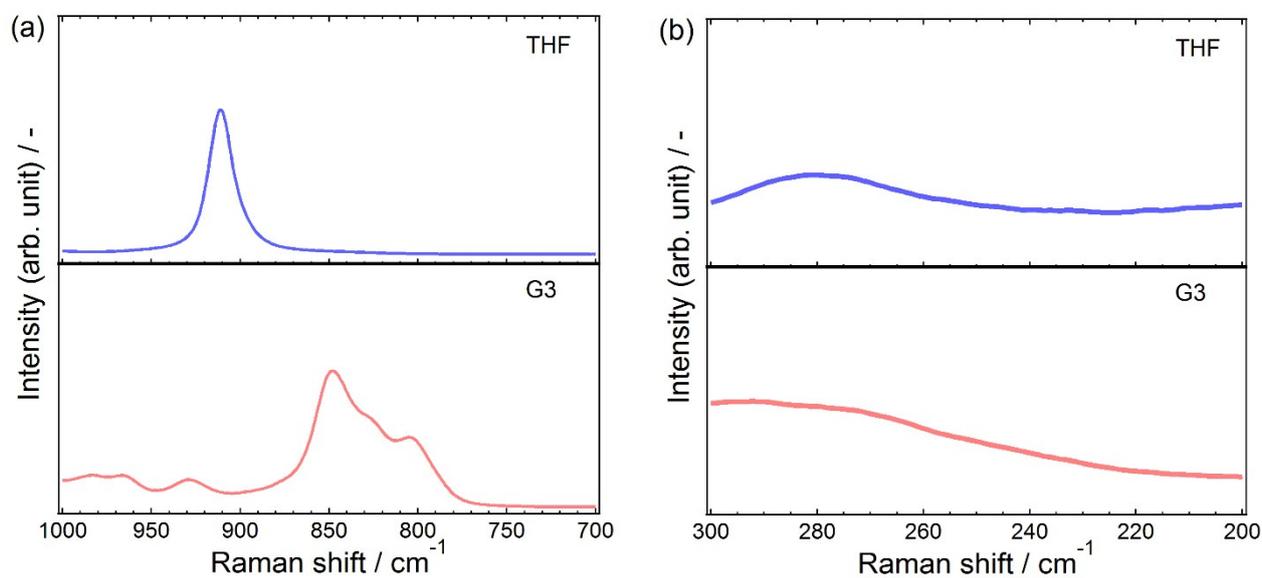


**Figure S8.** Discharge capacities of the Mo<sub>6</sub>S<sub>8</sub>-AZ31 cells with the O1/Mg(TFSI)<sub>2</sub>/G3 electrolyte cycled at the current density of 12.2 mA g<sup>-1</sup> at 30 and 100 °C.



**Figure S9.** Thermal ellipsoid model of the single crystal of  $[\text{Mg}_3\text{Cl}_3(\text{C}_2\text{H}_5\text{O})_2(\text{THF})_6][\text{TFSI}] \cdot (\text{THF})$ .

Thermal ellipsoids are drawn at 50% probability level. Labels on the atoms other than Mg and Cl are omitted for clarity. Green, Mg; pink, Cl; gray, C; red, O; light blue, F; blue, N; yellow, S.



**Figure S10.** Raman spectra of neat THF and G3 in the range of (a) 1000–700 and (b) 300–200  $\text{cm}^{-1}$  measured at ambient temperature.

## References

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