Supporting information for

Dissociation of protic ethyl mercaptan cosolvent enables better magnesium electrochemistry reversibility

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This profile contains *Experimental section*, *Fig. S1 to S12*.

1. Experimental Section

Materials: All chemical reagents, including magnesium(II) bis(trifluoromethanesulfonyl)imide ($Mg(TFSI)_2$, 99.5%, Prmat(Shanghai)Technology Co. Ltd), diglyme (G2, 99.5%, Sigma-Aldrich), ethyl mercaptan (EM, 98%, Macklin), and Mg foil (Beijing Juguang Technology Co, LTD.), were used as received without further treatment.

Electrolyte preparation: All electrolytes were prepared in an argon-filled glovebox (Mikrouna). 0.2M $Mg(TFSI)_2$/G2 (MG) electrolyte was prepared by introducing 0.234 g $Mg(TFSI)_2$ into 2.0 mL G2 solvent with magnetically stirring until $Mg(TFSI)_2$ was completely dissolved to obtain the desired electrolyte solution. 0.2M $Mg(TFSI)_2$/(EM+G2) (MEG) electrolyte was prepared by introducing 0.234 g $Mg(TFSI)_2$ into a mixed solvent solution containing 1.4 mL G2 and 0.6 mL EM.

Cell assembly: The oxide layer and impurities on the surface of Mg foil was scraped off using a scalpel. The polished Mg foil was cut into discs with a diameter of 12 mm (area: 1.13 cm^2) using a manual cutter to serve as the anode. Stainless steel (SS), Cu and Ti foils were also cut into the same size to serve as the current collector. Glass fiber and polyimide (PI) were cut into discs with a diameter of 16 mm as separator. For asymmetric Mg//Cu cell assembly, the Mg foil anode, Cu current collectors, and separators were assembled into a coin-type CR2032 cell using 160 μL electrolytes. The coin cells were pressed at 1.0 T of pressure using a compact hydraulic press (MSK-160E, Hefei Kejing Materials Technology Co., Ltd.). Other Mg//SS and Mg//Ti cells were assembled by the same procedure by using SS and Ti current collectors. Symmetric SS//SS cells using SS as both anode and cathode were assembled to evaluate the ionic conductivity of the electrolytes. A PI interlayer was used to collect the Mg electrodeposits, which can avoid the sample contamination from GF separator. After discharging the Mg//Cu cells at 1.0 mA cm^{-2} for 4.0 hours, the cells were disassembled and the Mg electrodeposits on PI interlayer were washed with G2 prior to test.

Electrochemical performance investigation: All galvanostatic charge-discharge tests were performed on a LAND battery testing system (CT3002A). The asymmetric cells were discharged at a constant current density of 0.1 mA cm^{-2} for 1.0 hour and recharged to a cutoff voltage of 1.5 V. Electrochemical impedance spectroscopy (EIS) tests of the SS/SS cells were conducted on an electrochemical workstation (Autolab PGSTAT302N) within a frequency range from 0Hz to 10000Hz at a disturbance voltage of 5 mV. EIS tests of Mg//Cu cells were also conducted to investigate the charge transfer resistances during Mg plating/stripping in varied electrolytes. Linear sweep voltammetry (LSV) tests were performed using the same electrochemical workstation with a voltage scan rate of 5mV s^{-1} from the open circuit potential to 5.0 V or current response overload.

Raman characterization was conducted using a HORIBA Lab RAM HR Evolution spectrometer. An excitation wavelength of 532 nm was used to collect the Raman spectroscopy data. Fourier transform infrared (FTIR) tests of electrolyte solutions and G2 solvent were conducted on a Thermo Scientific Nicolet Apex FT-IR spectrometer.

Molecular dynamics (MD) simulations: The microscopic solvation structures of MEG electrolyte with(out) EM dissociation were simulated by the MD simulations via Material Studio. Prior to MD calculations, the steepest descent method was applied to minimize the initial energy of each system, with a force tolerance of 1 kJ mol^{-1} nm^{-1} and a maximum step size of 0.002 ps. Periodic boundary conditions were imposed in all three directions. The leapfrog algorithm was used to

integrate the Newtonian equations of motion. For the MEG electrolyte without EM dissociation, the AC module was used to build a solution box which contains 20 Mg^{2+} molecules, 40 $TFSI^-$ molecules, 404 EM molecules and 490 G2 molecules. As for the MEG electrolyte with EM dissociation, partial EM (~25%) were hypothesized to transform into EM^- and H^+. Therefore, an AC module was used to build a solution box which contains 20 Mg^{2+} molecules, 40 $TFSI^-$ molecules, 304 EM molecules, 100 EM^-, 100 H^+, and 490 G2 molecules. MD simulations were carried out in the NPT ensemble for a total simulation time of 20 ns. In the NPT simulations, the Berendsen barostat was used to maintain the pressure at 1 bar in an isotropic manner, and the velocity-rescaling thermostat was employed to keep the temperature at 298.15 K. The Particle Mesh Ewald (PME) method with fourth-order interpolation was used to evaluate electrostatic interactions, and a cutoff distance of 1.0 nm was adopted for calculating short-range van der Waals interactions.

Structure investigation on Mg electrodeposits: Scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) characterizations of electrodeposits from different electrolytes were conducted. Typical SEM and the X-ray energy-dispersive spectroscopy (EDS) tests were conducted on a TESCAN MIRA LMS instrument. A small piece of PI with the electrodeposited layer was directly attached to a conductive adhesive for SEM testing. Platinum sputtering was performed for 60 seconds using an Oxford Quorum SC7620 sputter coater. XPS characterization was performed using a PHI5000 Versaprobe III spectrometer with monochromatic Al K_α radiation (1486.6 eV, 15 kV, 4.5 mA, CAE mode).
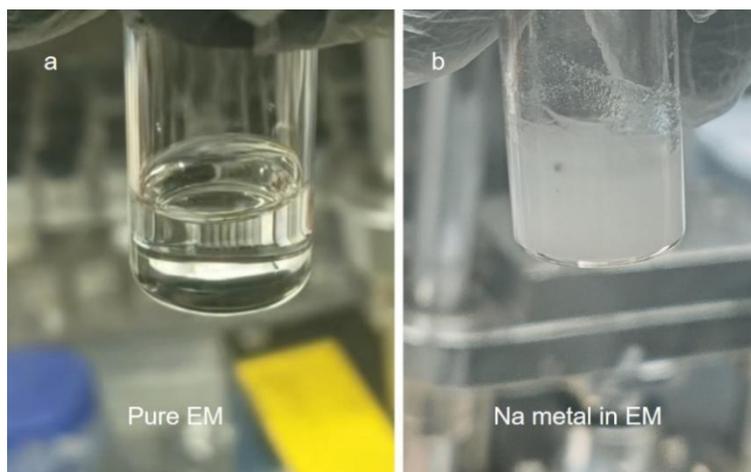
Fig. S1 Digital photo of 0.2M Mg(TFSI)$_2$ in varied solvents (left: G2; middle: EM+G2; right: EM).
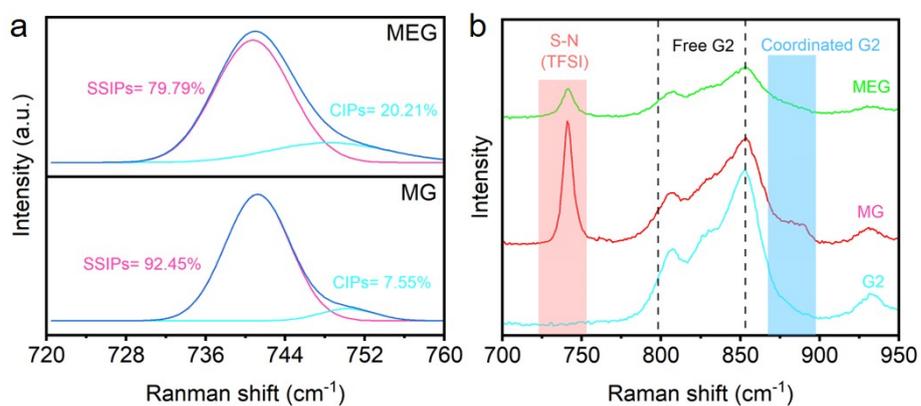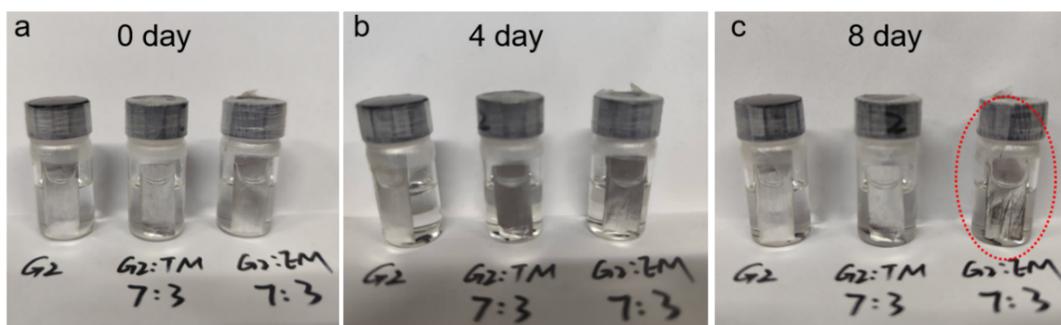

Fig. S2 (a) Raman spectra within a Raman shift of 720~760 cm^{-1} of both electrolyte solutions. (b) Raman spectra of vaired solutions within a Raman shift of 700~950 cm^{-1}.
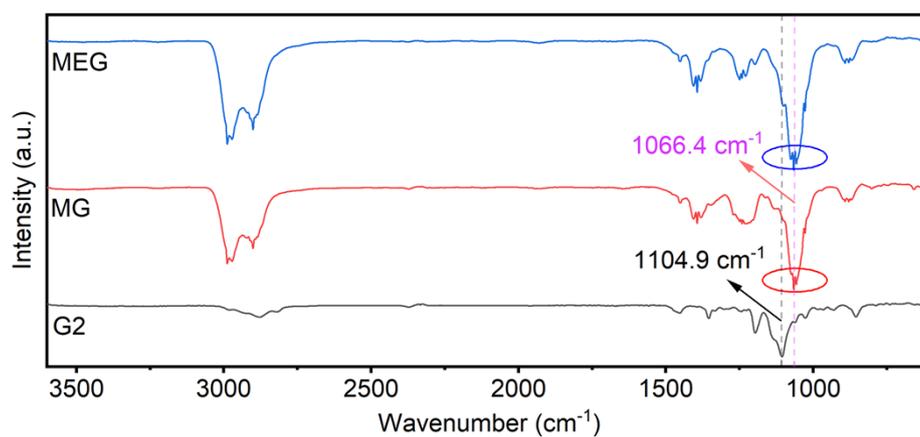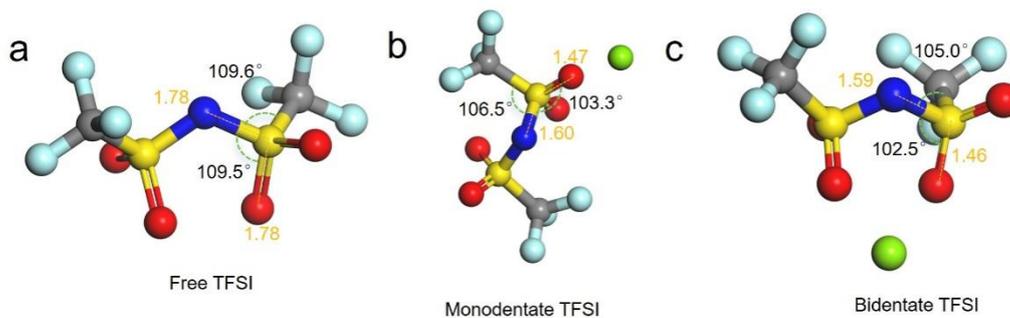

**Fig. S3** FTIR spectra of various electrolytes and G2.

**Fig. S4** Digital photo of pure EM solvent and the Na metal in EM solvent. This demonstrates the serious hydrogen evolution reaction between EM and Na-metal.

Fig. S5 Digital photo of Mg foils in varied electrolyte solutions after 0 day (a), 4 days (b) and 8 days (c).
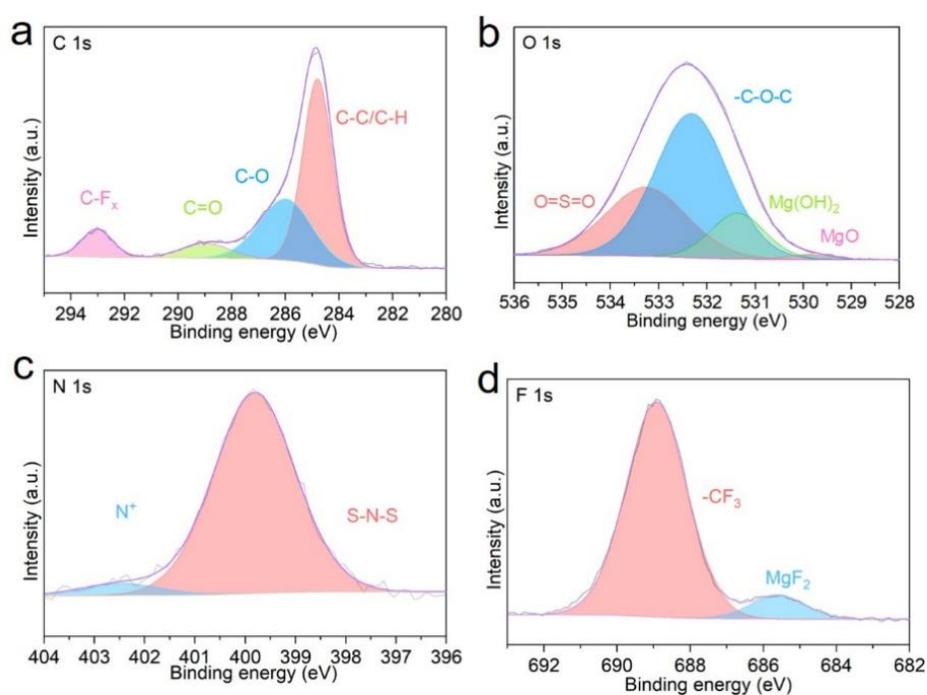

Fig. S6 Bond scheleton strains in bidentate TFSI$^-$ and monodentate TFSI$^-$ when they coordinate to Mg^{2+} (a: free TFSI. b: monodentate TFSI. c: bidentate TFSI).
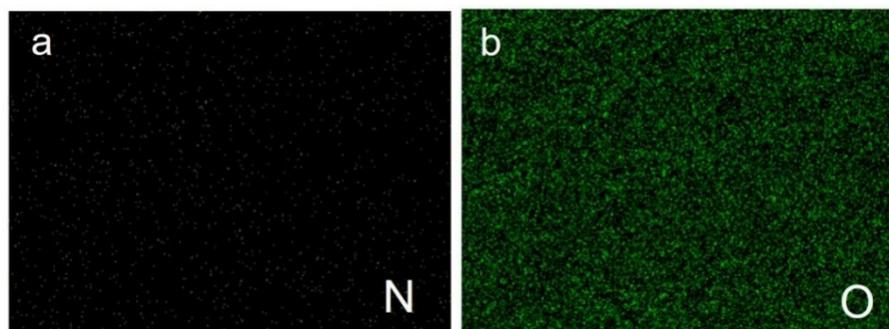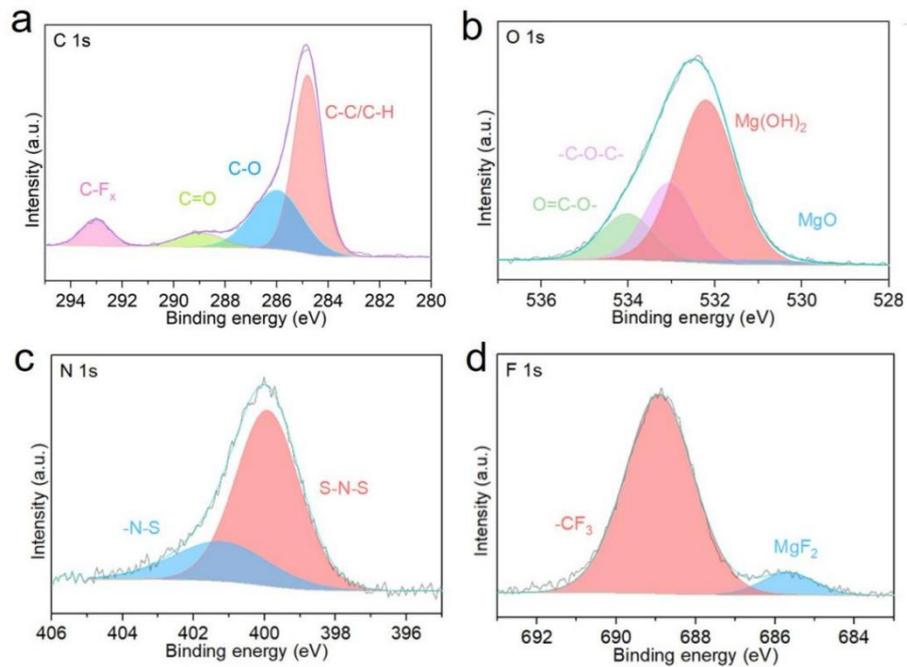
**Fig. S7** The EDS-mapping images of N and O elements in Mg electrodeposits from MEG electrolytes.
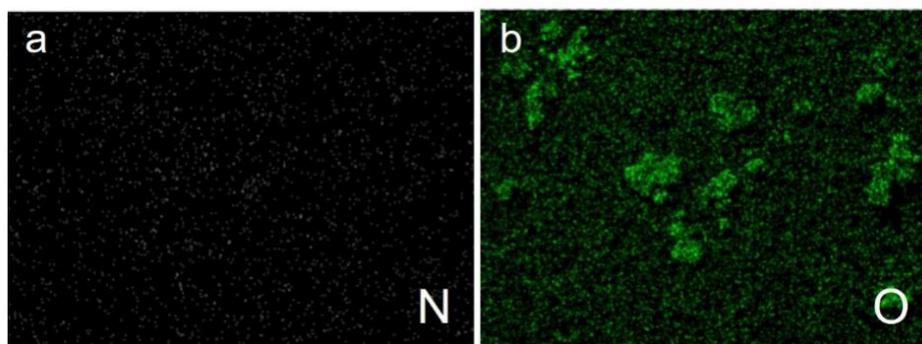
Fig. S8 The EDS-mapping images of N and O elements in Mg electrodeposits from MG electrolytes.
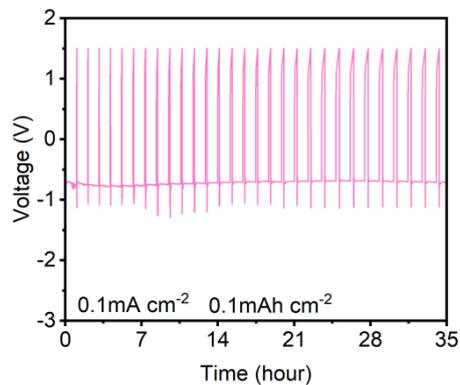

Fig. S9 The C 1s (a), O 1s (b), N 1s (c) and F 1s (d) XPS profiles of Mg electrodeposits from MEG electrolytes.
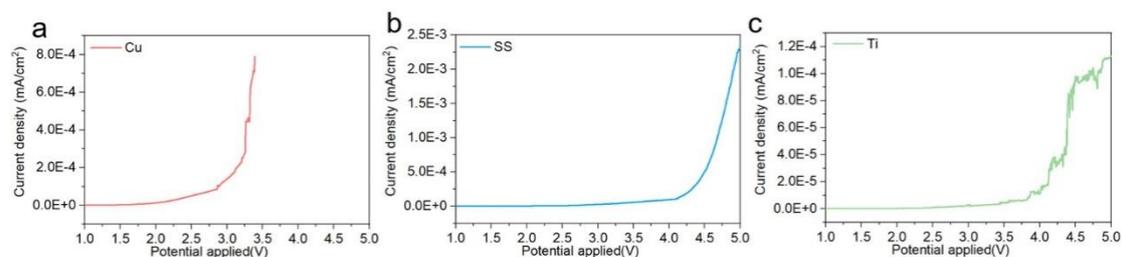
Fig. S10 The C 1s (a), O 1s (b), N 1s (c) and F 1s (d) XPS profiles of Mg electrodeposits from MG electrolytes.
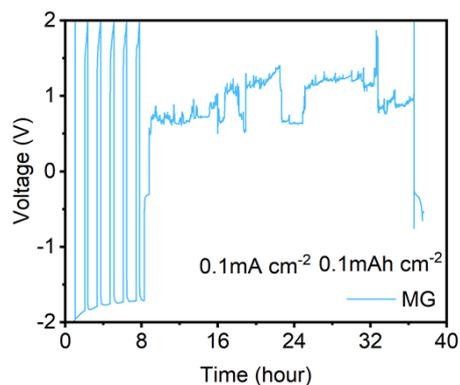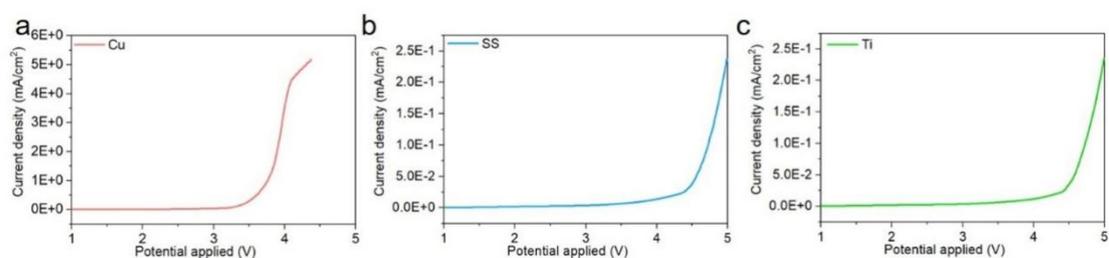

Fig. S11 The voltage-time profiles of Mg//Cu cell using MG electrolyte.

Fig. S12 The voltage-time profiles of Mg//Cu cell using MTG electrolyte.

Fig. S13 Linear sweep voltammetry curves of asymmetric cells using MEG electrolyte (a: Cu current collector. b: SS current collector. c: Ti current collector).

Fig. S14 Linear sweep voltammetry curves of asymmetric cells using MG electrolyte (a: Cu current collector. b: SS current collector; c: Ti current collector).

Table S1 Performance comparison with previous reports.

Electrolytes	Plating potential (V)	Coulombic efficiency	Cycle lifespan of asymmetric cells	Ref.
$Mg(TFSI)_2/(G2+DMAPA)$	–0.10	~94%	~100 cycles	11
$Mg(TFSI)_2/(DME+TEP+TFTMS)$	–0.21	~89.0%	750 cycles	12
$Mg(TFSI)_2/(DME-Mx)$	–0.15	~95%	~100 cycles	6
$Mg(TFSI)_2/(TEGDME+PDA)$	-1.5	-	70 cycles	29
$Mg(TFSI)_2/(DME+LiOTF+TMP)$	-0.58	~95.0%	~100 cycles	20
$Mg(TFSI)_2/(G2+IPA)$	-0.16	~90.0%	~20 cycles	26
$Mg(TFSI)_2/(G2+EM)$	-0.5	65.1%	280 cycles	Our work