Electronic Supplementary Information for

Al-compatible boron-based electrolytes for rechargeable magnesium batteries

Jung Hoon Ha,[a,1,] Boeun Lee,[a,1] Minseok Lee,[a] Taeeun Yim,[*b] and Si Hyoung Oh*[a,c]

[a] Centre for Energy Storage Research, Korea Institute of Science and Technology, 5, Hwarang-ro 14-gil, Seongbuk-gu, Seoul, 02792, Korea.

[b]Department of Chemistry, Incheon National University, 119, Academy-ro, Songdo-dong, Yeonsu-gu, Incheon, 22012, Republic of Korea.

[c] Division of Energy & Environment Technology, Korea University of Science and Technology, Seoul, 02792, Korea.

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Experimental Details and *Supplementary Figures S1 to S7*

[*]To whom correspondence should be addressed - S.H.O: sho74@kist.re.kr; T. Yim: yte0102@inu.ac.kr

[1]J.H. Ha and B. Lee contributed equally to the work.

Experimental details

Electrolyte preparation

Electrolyte A: In an argon-filled glove box, tris(2H-hexafluoroisopropyl)borate (THFPB, 0.5119 g) was dissolved in 1,2-dimethoxyethane (DME, 5 mL) in a glass bottle to obtain a clear solution. Next, $CrCl_3$ (0.0050 g) was dissolved in the solution, which caused the color of the solution to turn violet. Magnesium metal plate or powder (0.1500 g) was added and stirred for two days, during which the color of the magnesium plate turned black. Finally, the solution was filtered with a glass syringe to remove any unreacted magnesium metal and the filtrate was collected to serve as electrolyte **A**. For comparative study, another electrolyte solution was prepared by following the same procedure but without any additive.

BCM: In an argon-filled glove box, THFPB (2.5600 g) was first dissolved in DME (5 mL) solvent. Subsequently, MgF_2 (0.0150 g) was added into the solution, and the solution was stirred overnight.

APC: APC solution was prepared via the reaction of $AlCl_3$ and PhMgCl in a 1:2 molar ratio in tetrahydrofuran (THF). Briefly, in an argon-filled glove box, $AlCl_3$ powder (0.6667 g) was slowly added to 2.0 M PhMgCl/THF Grignard reagent (5.0 mL) to produce 0.2 M APC solution. All electrolyte preparation procedures were conducted in an argon-filled glove box with oxygen and moisture levels strictly controlled below 0.1 ppm.

Synthesis of Chevrel phase, Mo_6S_8

Chevrel phase $Cu_2Mo_6S_8$ was synthesized using a KCl molten salt method following the literature (D. Aurbach *et al.*, *J. Solid State Chem.* **179** (2006) 1879-1882). To remove copper from the crystal structure, the powder was stirred for three days in a 6.0 M HCl aqueous solution under O_2 flow. The solution was filtered and the resulting power was dried in an oven at 100 ^{o}C.

Synthesis of S_8@CMK-3 nanocomposite

CMK-3 was prepared from commercial SBA-15 by following conventional nano-casting method. Sulfur and CMK-3 was mixed thoroughly in 2:1 ratio (w/w) using mortar and pestle. Then, the mixture was pelletized, being put in the autoclave. After being heated at 140 ^{o}C for 6 h, the pellet was recovered and gently ground into powder.

Electrochemical characterization of the electrolytes

The Mg plating–stripping activity of the electrolyte **A** was examined by performing a cyclic voltammetry (CV) with a scan rate of 1 mV s^{-1} between -0.5 and 2.0 V vs. Mg/Mg^{2+} in asymmetrical cells consisting of a stainless steel (316L) working electrode and a Mg metal strip served as reference and counter electrodes. The Mg plating–stripping behavior of the electrolytes were investigated in the same cell configuration via galvanostatic discharge-charge cycles with a current rate of 15 μA cm^{-2}. The oxidative stability of the electrolytes towards Mo, Cu, and Al working electrodes was evaluated through linear sweep voltammetry (LSV) measurements performed from open circuit potential to 4.5 V vs. Mg/Mg^{2+} at a scan rate of 5 mV s^{-1}. VMP3 (Bio-Logic) potentiostat /galvanostat instrument was employed to carry out these measurements.

Ionic conductivity of the electrolytes

The electrochemical impedance spectra were obtained with a symmetrical cell consisting of two identical Mg electrodes and the prepared electrolyte in a frequency range of $10^4 \sim 10^{-1}$ Hz with a perturbation voltage of 10 mV. Then, the ionic conductivity (κ) of the electrolyte was calculated from the solution resistance (R_s) based on the equation, $\kappa = 1/(R_s \cdot A)$, where A represents the electrode area of Mg metal.

Electrode preparation and evaluation

Typically, Chevrel phase, Mo_6S_8 was mixed in N-methyl-2-pyrrolidone (NMP) for 30 min together with Super P carbon black as conducting agent, poly(vinylidene fluoride) (PVDF) binder in 8: 1: 1 (w/w) ratio using a ball mill (Mini-Mill PULVERISETTE 23, Fritsch) and cast onto the aluminum current collector with a loading of approximately 2.0 mg cm^{-2} of Mo_6S_8. In case of sulfur cathode, S_8@CMK-3, Super P, and PVDF was mixed in 8: 1: 1 ratio with a typical loading of 0.8 mg cm^{-2} of S_8. 2032-type coin cells were fabricated with the composite electrodes as cathodes, in the as-prepared electrolytes with magnesium metal anodes. Electrochemical cycling was carried out between 0.4 ~ 1.8 V at a C/10 or 1C rate (1C= 128 mA g^{-1} of Mo_6S_8) for 300 cycles at 25 ^{o}C. For sulfur cathode, electrochemical cycling was carried out between 0.4 ~ 2.4 V at a C/10 (1C= 1,675 mA g^{-1} of S_8) at 25 ^{o}C.

Chemical analysis of the electrolyte during the synthesis

Elemental (B, Cr, Mg) analysis of the electrolytes (5 mL volume) was carried out by standard inductively coupled plasma with optical emission spectrometry (ICP-OES).

^{1}H-NMR measurement

^{1}H-NMR experiments for the electrolytes were conducted using a Bruker Advance 300 MHz spectrometer at room temperature. ^{1}H spectra in $CDCl_3$ were referenced to the residual $CHCl_3$ peak at 7.26 ppm.

Material characterization

The surface morphological feature of reacted Mg plate was analyzed with a field emission scanning electron microscopy (FE-SEM, Inspect F, FEI Corp.) equipped with energy dispersive X-ray spectroscopy (EDS). Transmission electron microscopy (TEM) of the Cr deposit on Mg plate was obtained using a high-resolution TEM (HR-TEM, FEI, TALOS F200 X) at an accelerating voltage of 200 kV. EDS elemental map and line scan were acquired by a TALOS Super-X EDS. For TEM specimen, Pt was coated on the surface and the cross section milling to a thickness of 100 μm were carried out using a focused ion beam (FIB).

Supplementary Figures

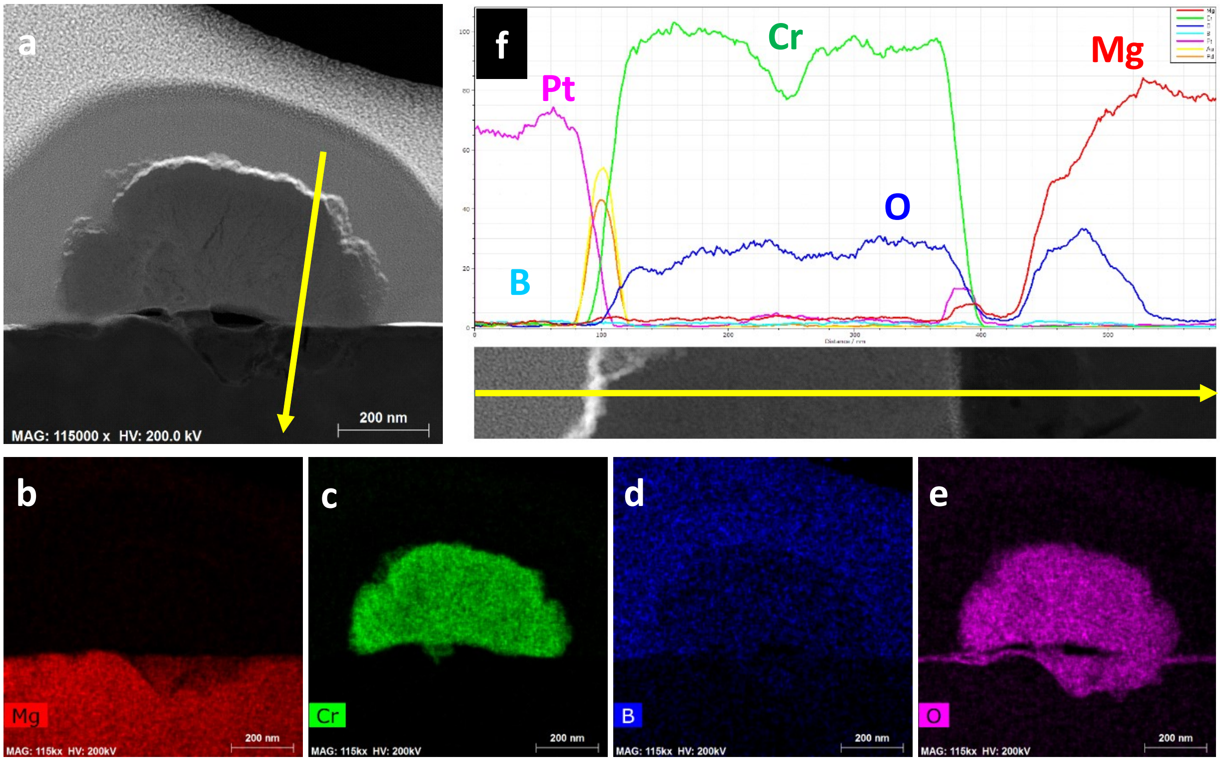

Fig. S1. (a) HAADF-TEM cross-sectional image of a Cr deposit on Mg plate, where Mg metal plate reacted in THFPB/$CrCl_3$/DME solution for 3 days, and EDS elemental mappings of (b) Mg, (c) Cr, (d) B, and (e) O. (f) EDS elemental line scan analysis across the Cr island on Mg metal plate for the region marked in (a).

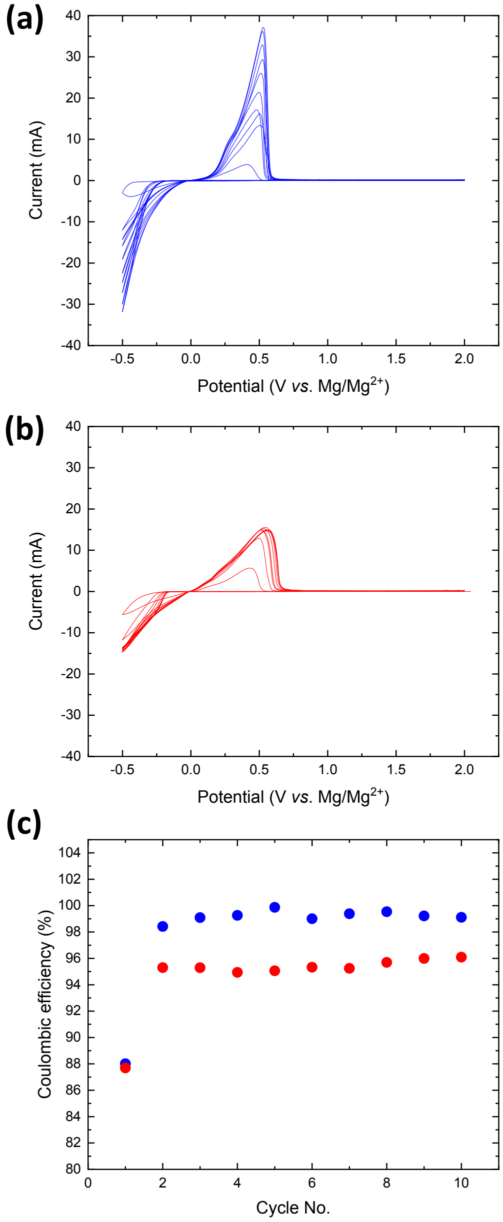

Fig. S2. Cyclic voltammograms (CVs) for evaluating the coulombic efficiency associated with Mg plating-stripping reactions in (a) electrolyte **A**, and (b) BCM. (c) Comparison of the coulombic efficiencies, where blue and red circles represent those in electrolyte **A** and BCM, respectively. CV data were obtained at a scan rate of 1 mV s^{-1}.

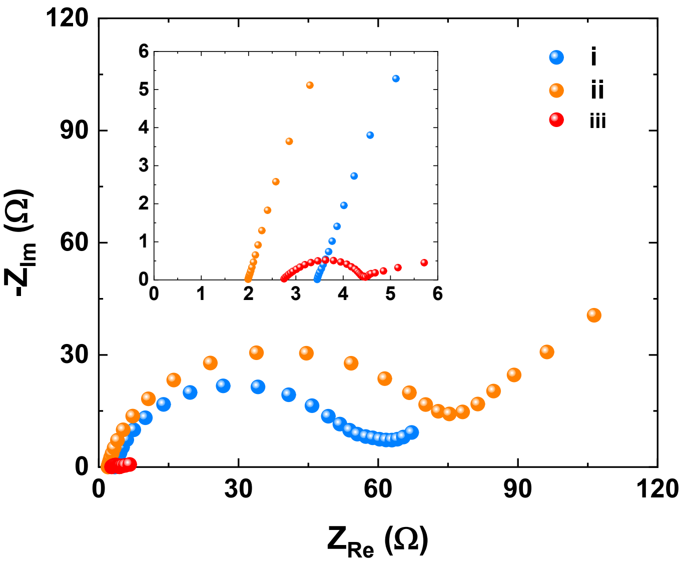

Fig. S3. Electrochemical impedance spectra for the symmetrical cells containing two identical Mg electrodes in a frequency range of 10^4 to 10^{-1} Hz in (i) electrolyte **A**, (ii) BCM, and (iii) APC solution to evaluate their ionic conductivity. The inset shows the enlarged spectra for the high frequency region to find the solution resistance, R_s, which was obtained from the resistance value at the *x*-intercept of the spectra at high frequency region. Then, the ionic conductivity (κ) of the electrolyte was calculated using R_s based on the equation, $\kappa = 1/(R_s \cdot A)$, where A represents the electrode area of Mg metal.

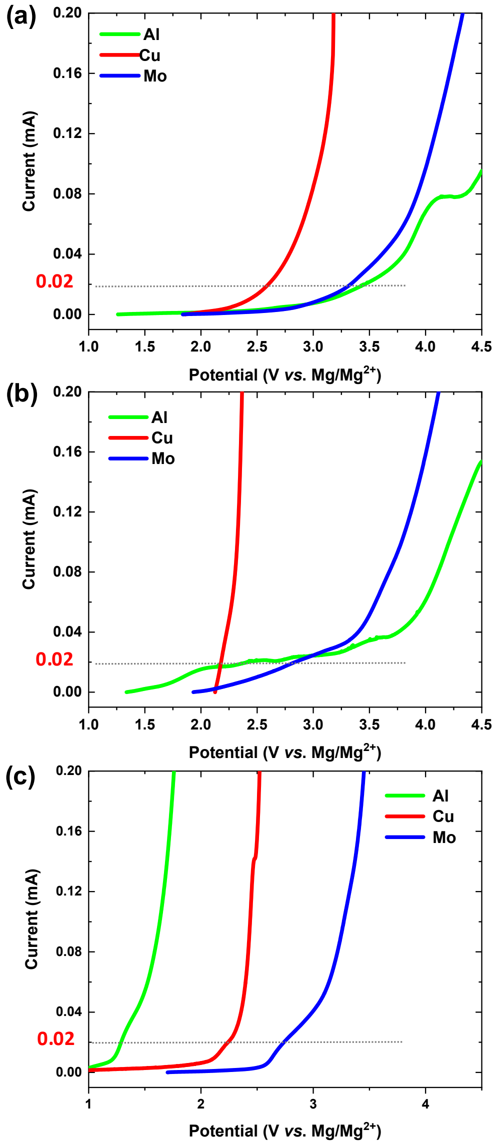

Fig. S4. The linear sweep voltammograms (LSVs) to evaluate the oxidative stability of (a) electrolyte **A**, (b) BCM, and (c) APC solution with Mo (blue), Cu (red) and Al (green) working electrodes. LSV data were obtained at a scan rate of 5 mV s^{-1}. Particularly, electrolyte A exhibited an excellent chemical stability with an Al electrode up to ~3.5 V vs. Mg/Mg^{2+}, while Al was unstable in the APC solution due to the presence of chloride ions.

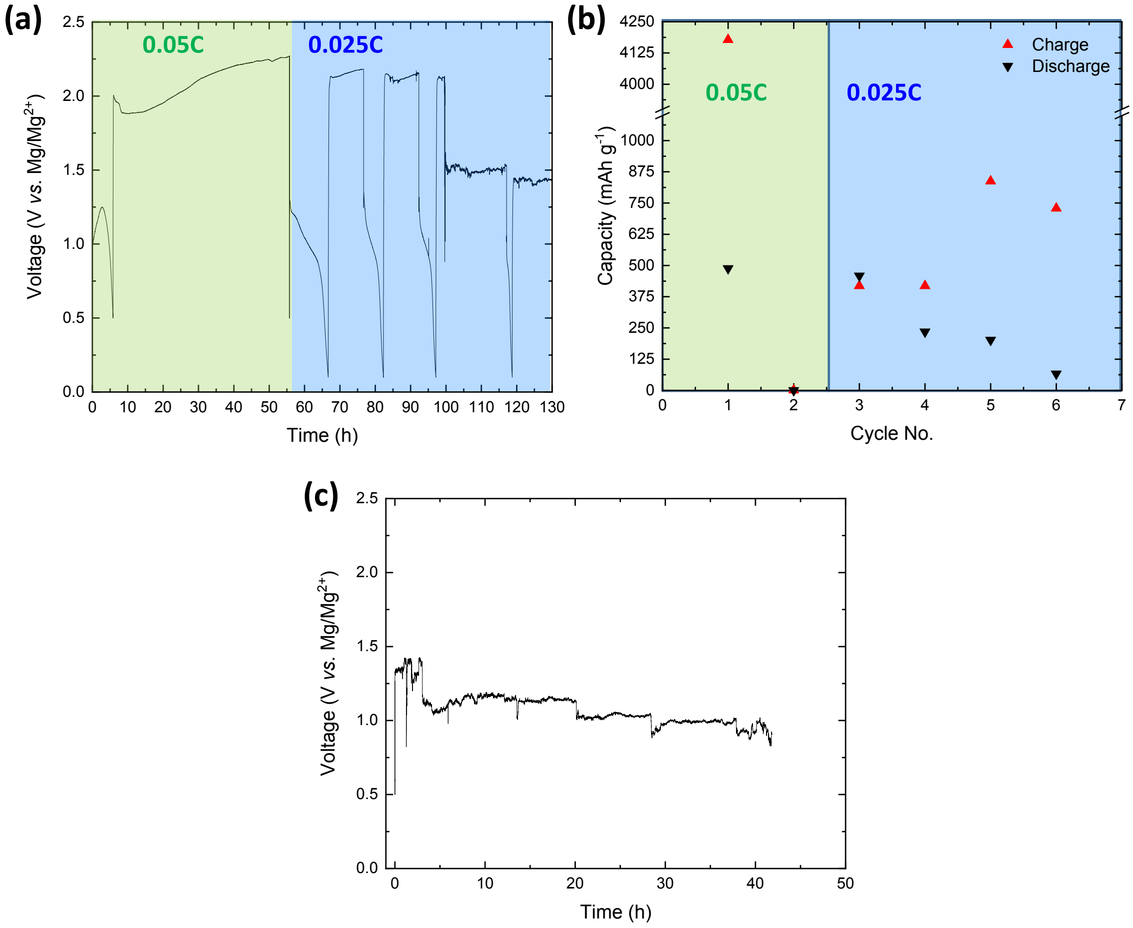

Fig. S5. (a) Discharge-charge profiles and (b) cycle performance for the rechargeable Mg cells composed of CMK-3/S_8 cathode on Al foil in BCM electrolyte. (c) Discharge-charge profile for the same electrode in APC solution. In BCM, the 1st discharge capacity was around 500 mAh g^{-1} at a slow current rate of C/20. After a large overcharge phenomenon (amounting to more than 4000 mAh g^{-1}) during the first charging process, virtually no discharge capacity was obtained at the 2nd discharging process due to the large overpotential developed. When even slower current rate (C/40) was applied, the cell was operated normally. However, repeated cycling with a large overpotential for the charging process likely induced electrolyte decomposition or corrosion of current collectors in the later cycles. In APC solution, the electrochemical cycling of CMK-3/S_8 cathode on Al foil was not possible, because sulfur likely reacted chemically with nucleophilic APC and corrosion of Al current collector occurred due to the large concentration of chloride species.

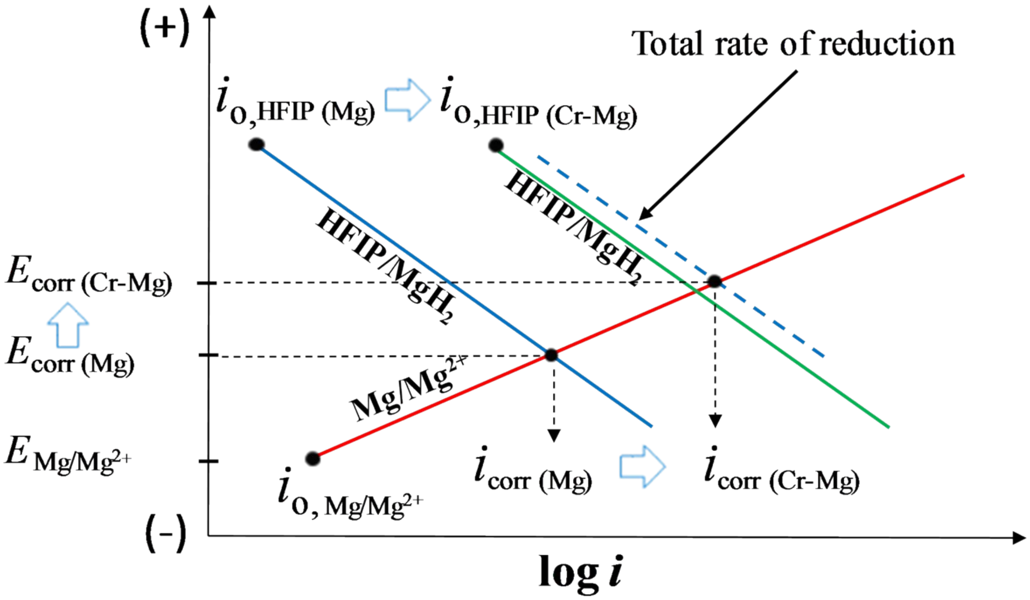

Fig. S6. A polarization diagram that describes a plausible mechanism for the enhanced corrosion rate of Mg metal when $CrCl_3$ is present during electrolyte preparation process. Cr deposit on Mg metal plate serves as a local cathodic center that leads to substantial increase in the exchange current rate for the cathodic reaction involving the reduction of THFPB. This causes the increase in the corrosion potential and the corrosion rate of Mg metal in the neighboring region.

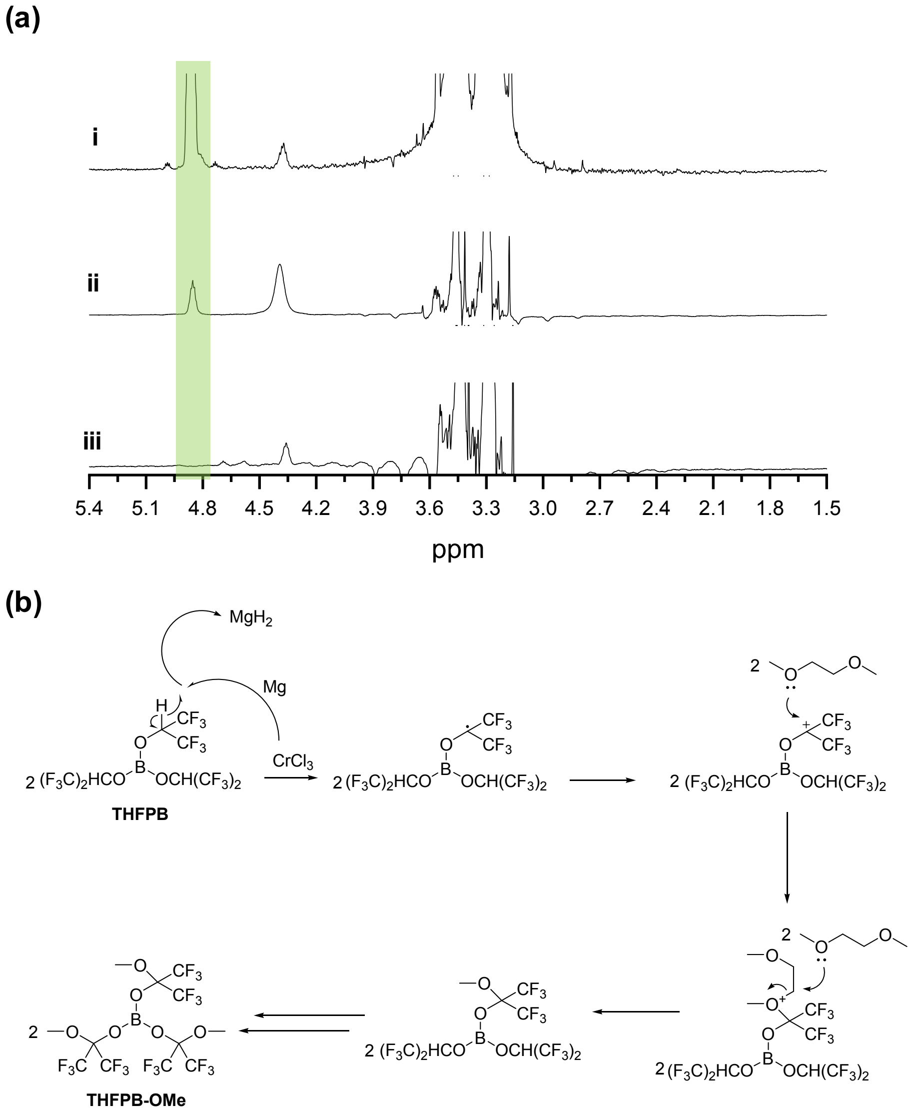

Fig. S7. (a) ^{1}H NMR spectra of (i) THFPB in DME, (ii) BCM, and (iii) electrolyte **A**. (b) The proposed mechanism for reaction between THFPB and Mg metal.