Electronic Supplementary Information for

Conditioning-Free Magnesium Chloride Complex Electrolyte for Rechargeable Magnesium Batteries

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Experimental Details

Preparation of Electrolyte Solutions

In an argon-filled glove box, $AlCl_3$ (0.1333 g, Sigma-Aldrich) was dissolved in THF (5 mL) in a glass bottle to obtain a clear solution. Next, $CrCl_3$ (0.0050 g, Sigma-Aldrich) was completely dissolved into the solution. Magnesium metal powder (0.1500 g, Sigma-Aldrich Product No. 13112) was added and stirred for 48 h, during which time the colour of the magnesium powder 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 solution **A**. For electrolyte solution **A'**, the same procedure was followed without the addition of $CrCl_3$.

Synthesis of the Chevrel phase, Mo₆S₈

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 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 °C.

NMR measurements

NMR experiments were conducted using a Bruker Advance 300 MHz spectrometer at room temperature. ¹H spectra in CDCl₃ were referenced to the residual CHCl₃ peak at 7.26 ppm. A sealed capillary with 50 mM AlCl₃ in H₂O was added as an internal standard for the ²⁷Al spectra in THF (Al(H₂O)₆Cl₃: 0 ppm).

Single-crystal X-ray crystallography

Data collection for the X-ray crystal structure of $[Mg_2Cl_3(THF)_6]^+/[AlCl_4]^-$ were carried out on a Smart Apex CCD (Bruker) at room temperature and at 230 K (under streaming nitrogen) utilizing Mo-K_a radiation. Crystals were formed by slow vapour diffusion of hexane into the THF-based electrolyte solution. Suitable crystals were coated in paratone and fixed to nylon loops for analysis.

Ionic conductivity

The conductivity of the electrolyte solution was measured with a conductivity meter (HI 8734 from Hanna Instruments Co. Ltd.).

Elemental analysis for electrolyte

Elemental (Al, Mg) analysis of the electrolytes (5 mL volume) was carried out by standard inductively coupled plasma (ICP).

Materials Characterization

The black material deposited on the Mg plates was investigated by powder X-ray diffraction (XRD) using Cu-K α 1 radiation ($\lambda = 1.5405$ Å, Rigaku D/MAX-2500/PC). Morphological features were observed by field-emission scanning electron microscopy (FE-SEM, Hitachi, S-4200) with an energy dispersive X-ray spectroscope (EDS) attachment. The samples for FE-SEM were sputter-coated with platinum prior to measurement.

Electrochemical studies

Magnesium deposition and stripping was monitored by cyclic voltammetry (CV) at a scan rate of 1 mV s^{-1} between -0.5 and 2.0 V vs. Mg/Mg²⁺, where a stainless steel plate (SS-316L) was used as a working electrode. The coulombic efficiency was calculated by the ratio of the electrical charge collected during the deposition *vs* the stripping processes. Linear sweep voltammetry (LSV) was carried out with a Pt plate as the working electrode and Mg metal plates as the reference and the counter electrodes, respectively. The scan rate was 25 mV s⁻¹. All electrochemical measurements were performed at room temperature using multichannel potentiostat/galvanostat (Bio-Logic, VMP3) with EC-Lab software.

Mg cell utilizing a Chevrel Mo₆S₈ cathode

Typically, the Chevrel phase, Mo_6S_8 (200 mg) was mixed in N-methyl-2-pyrrolidone for 30 min together with Super P carbon black conducting agent, polyvinylidene fluoride (PVdF) binder (25 mg) and cast onto the current collector (SS-316L) with a loading of approximately 2 mg cm⁻² of Mo_6S_8 . 2032-type coin cells were fabricated with the composite electrodes as cathodes, in the asprepared electrolytes with magnesium metal anodes. Electrochemical cycling was carried out between $0.3 \sim 1.9$ V at a C/8 rate for the initial 3 cycles and thereafter at 1C (= 128 mA g⁻¹ of Mo_6S_8) at 25 °C.

Supplementary Note

The determination of the anodic stability limit of the electrolyte system

In this work, the anodic stability limit of the electrolyte system was set to the point in the linear sweep voltammetric measurement (LSV) where the current density related to electrolyte decomposition reaches 0.02 mA cm⁻². This current density approximately corresponds to a C/100 current rate for common Li-ion batteries employing a layered oxide cathode and graphite anode, where the typical areal capacity for either electrode is optimized at around $2 \sim 3$ mAh cm⁻².

Supplementary Tables

Table S1. Mg and Al content expressed in molar concentrations in the electrolyte solution, as analyzed by ICP, with comparison to a standard APC solution.

Solution (5 mL THF)	Mg [M]	Al[M]	Cr [M]*
AlCl ₃ (0.1333g)	-	0.19	-
Electrolyte solution A	0.28	0.02	1.45 x 10 ⁻⁵
Electrolyte solution A'	6.8 x 10 ⁻³	0.19	-
0.2M APC solution	0.40	0.20	-

* The concentration of Cr is based on molar content in a 5mL solution

Table S2.	Coulombic	efficiency	for Mg	electro-de	position and	stripping	in electroly	te A
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Cycle No.	Coulombic efficiency [%]
1	100.0
2	100.0
3	100.0
4	100.0
5	99.9
6	99.9
7	99.8
8	100.0
9	99.8
10	99.9

Supplementary Figures



Figure SI. Photographs and SEM images for the original Mg plate and the those reacted in the electrolyte preparation solution. The photos and SEM images for (a), (d) original Mg plate, (b), (e) Mg plate reacted in THF solution containing only AlCl₃ for 12 h, and (c), (f) Mg plate reacted in THF solution containing both AlCl₃ and CrCl₃ for 12 h. It should be noted that for the preparation of electrolyte solution A and A', coarse Mg powder was used instead of Mg plate to speed up the process. Here, we used Mg plate for the visualization of the effect of CrCl₃ catalyst on Mg dissolution in THF.



Figure S2. **EDS analysis of the black deposit formed on the surface of the magnesium powder during electrolyte preparation**. (a) SEM image of the black deposit on the surface of the magnesium powder; (b) EDS mapping of elements on the surface, showing the deposit consists of many elements including Mg, Al, Cr, Cl, O which are evenly distributed on the entire surface.



Figure S3. SEM images, EDS analysis and XRD pattern of Mg metal deposited on a Ni substrate from electrolyte A at various cycles. FE-SEM images and EDS analysis, respectively, for Mg metal taken after (a), (d) the 1st, (b), (e) the 3rd, and (c), (f) the 5th deposition. The electode (Ni) area is 0.785 cm² and total charge for the deposition is around 1 C cm⁻². The entire SEM area was selected for EDS analysis, which shows only the presence of elemental Mg. The XRD pattern of (g) magnesium deposited on Ni substrate from electrolyte A (10 C cm⁻²)



Figure S4. Single crystal molecular structure of $[Mg_2Cl_3(THF)_6]^+$. $[AlCl_4]^-$ obtained in this work by structure solution at 230K.

Notes: (and see Table 1 below)

Colourless crystals (size: 0.020 x 0.316 x 0.340 mm) were mounted in a glass capillary owing to their air and moisture sensitivity. The data were collected using Bruker Kappa APEX II at 230K using omega and phi scan and utilizing Mo K_{α} (λ =0.71073 Å) radiation. After data reduction (correction for polarisation and Lorentz effect), the data were corrected for absoprtion using SADABS part of the BRUKER APEX II Suite. The structure solution was carried out using direct methods and the refinement was performed with the SHELXTL package part of the BRUKER APEX II Suite.

As the crystals were twinned and the data were weak, a structural model with an intermediate reliability factor was obtained due to disorder on the THF molecules which was not resolved.

Crystallographic data for [Mg2Cl3(THF)6]+.[AlCl4]-

Crystal System	Monoclinic
Space group	P 2 ₁ /c (No. 14)
Unit cell dimensions:	a = 13.2951(10) Å, $b = 12.1991(9)$ Å, $c = 24.0019(19)$,
	$\beta = 90.068(5)^{\circ}$, V = 3892.8(5) Å ³ , Z = 4
Collection temperature	230K

These data are the same as those previously reported given the difference in collection temperature, confirming the structure:

Unit cell from CCDC database (Refcode: KOCCAI):
Crystal SystemMonoclinicSpace group $P2_1/c$ (No. 14)
a = 12.909(1) Å, b = 12.252(1) Å, c = 23.790(2),
 $\beta = 90.38(1)^\circ$, V = 3762.573 Å³, Z = 4Collection temperature100 K
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Table S3. Refined atomic coordinates of the obtained model (large thermal displacement forTHF and for AlCl4 anion for unresolved disorder)

Coordina	ites and Eq	uivalent Is	sotropic Di	splacement Parameters	of the non-Hydrogen	atoms for:
[Mg ₂ Cl ₃ ($(THF)_{6}]^{+}.[A$	AlCl ₄] ⁻				
Atom	Х	у	Z	$U(eq) [Å^2]$		

Atom	V 701	L 13	7	U(aq) [
Cll	A 0 12412	y 0.87066	-0.04647	0.0944
Cl2	0.62357	0.13017	0.04618	0.0944
C12 C13	0.24988	0.13017	0.02211	0.0975
C14	0.25132	0.25854	0.33099	0.1236
Cl5	0.38134	0.23540	0.21039	0.1250
Cl6	0.12139	0 23442	0.21178	0.4193
C17	0.24356	0.03669	0.24725	0.4988
Mgl	0.74911	0.26700	0.07784	0.0740
Mg2	0.24985	0.88064	0.03013	0.0603
All	0.24938	0.20403	0.24862	0.0856
01	0.85809	0.38363	0.10002	0.1020
O2	0.64353	0.38417	0.09841	0.1011
O3	0.35790	0.87942	0.09040	0.0872
O4	0.14224	0.88338	0.09074	0.0895
O5	0.24956	1.05331	0.02971	0.0809
06	0.74549	0.20802	0.15790	0.0926
C1	0.44636	0.82933	0.17349	0.2055
C2	0.04544	0.82605	0.16991	0.1642
C3	0.35389	0.81172	0.14129	0.2711
C4	0.14074	0.80892	0.13626	0.3786
C5	0.51165	0.89951	0.14698	0.2080
C6	-0.00018	0.90677	0.14513	0.1824
C7	0.69371	0.08252	0.24059	0.2253
C8	0.79207	0.07375	0.23083	0.2545
C9	0.70306	0.09196	0.17063	0.4243
C10	0.49701	0.49455	0.09446	0.1983
C11	0.26334	1.24056	0.05225	0.2741
C12	1.01694	0.48416	0.09385	0.1933
C13	0.96396	0.39597	0.07781	0.2847
C14	0.81965	0.20521	0.19179	0.3157
C15	0.53714	0.37145	0.08294	0.2081
C16	0.99009	0.48523	0.14617	0.2831
C17	0.89202	0.38676	0.15438	0.2171
C18	0.31750	1.12491	0.07347	0.3966
C19	0.19462	1.22966	0.00873	0.2662
C20	0.17592	1.11457	-0.01215	0.3438
C21	0.41125	0.95339	0.10264	0.2893
C22	0.51846	0.48099	0.14677	0.2365
C23	0.03582	0.87671	0.08205	0.2531
C24	0.58553	0.37561	0.14951	0.2861



Figure S5. **EDS analysis of** (a) crystalline MgCl₂ (used as a reference) and dried electrolytes corresponding to (b) as-prepared MACC, and (c) electrolyte A (MaCC). The spectra and analytical data represent the data typical of that sampled.



Figure S6. Rate performance of the magnesium rechargeable battery with the Chevrel phase cathode in electrolytes A. The rate performance for magnesium rechargeable batteries at 25 °C with a Chevrel phase cathode and electrolyte A. Circle and square markers represent discharge and charge, respectively. The current density is 1C (128 mA g^{-1} of Mo₆S₈). At a low current rate (C/8), 90 % of the theoretical capacity was delivered, while at a high current rate (1C), 60 % capacity was obtained.



Figure S7. XRD patterns for the original Mo_6S_8 Chevrel phase powder and the electrode after 100 cycles of discharge-charge. The electrode containing the Mo_6S_8 Chevrel phase after 100 cycles of the discharge-charge in the electrolyte A shows no noticeable change in the positions and intensities of the reflections, as well as no sign of any other impurity phase.



Figure S8. Linear sweep voltammograms for electrolyte A on platinum and stainless steel electrodes. Mg metal plates were used as reference and counter electrodes, and platinum and stainless steel (316L) plates served as the working electrodes. The scan rate was 25 mV s⁻¹. For stainless steel, a corrosion current starts to appear around 2.5 V.



Figure S9. Discharge-charge profile of Chevrel Mo_6S_8 at C/8 before and after 50 cycles at 1C rate. The discharge-charge curve after 50 cycles shows two classical potential plateaus related to Mg insertion/deinsertion in site A and site B in the Chevrel phase