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Novel transmetalation reaction for electrolyte synthesis for rechargeable magnesium batteries

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Calculation details

All quantum mechanics calculations were performed with the Jaguar 8.0[1] program's implementation of the DFT-B3LYP functional, which utilizes the Becke three-parameter functional (B3)[2] combined with the correlation function developed by Lee, Yang, and Parr (LYP)[3], using the LACVP**++ basis set. Calculations with the LACVP*+ basis set were also carried out for the sake of making consistent comparisons with results from ref. [4] (see Tables S1 and S3). The influence of solvent was included using the Poisson–Boltzmann solver implemented in the Jaguar program (the parameters used within the solvent model to describe THF, diglyme and tetraglyme are given in Table S2). The solver was utilized for each step of the SCF energy convergence procedure, such that the solvation energy was included in the SCF energy at each of the SCF iterations and in calculating the forces at each of the geometry optimization steps. Thus, each of the LUMO and HOMO energy level values reported in Tables S3 and S4 corresponds to the geometry resulting from minimizing the anion's structure in the relevant solvent.

Table S1 Summary and comparison of calculation parameters

	Present work	[4]
Program	Jagaur 8.0	Gaussian 09
Method	DFT	DFT
Functional	B3LYP	B3LYP
Basis Set	LACVP**++ (= 6-31++G**)	6-31+G* (= LACVP*+)
Solvation Model	Poisson-Boltzmann Solver	IEFPCM

Table S2 Parameters used in solvation model

Solvent	Dielectric Constant	Probe Radius
THF	7.60[a]	2.52 Å[c]
Diglyme	7.65[b]	3.05 Å[c]
Tetraglyme	7.70[b]	3.52 Å[c]

a: Ref. [5]; b: Ref. [6]; c: Ref. [7]

Table S3 Comparison of calculated LUMO and HOMO energy levels with results from Ref. [1] (in THF)

Anion [Ph$_x$AlCl$_{4-x}$]$^-$	Source	Basis Set	HOMO (eV)	LUMO (eV)	Gap (eV)
AlCl$_4^-$	this work	LAVCP**++	-7.920	0.034	7.954
	this work	LAVCP*+	-7.920	0.034	7.954
	[4]	6-31+G*	-7.53	1.01	8.54
PhAlCl$_3^-$	this work	LAVCP**++	-6.638	-0.346	6.293
	this work	LAVCP*+	-6.627	-0.328	6.300
	[4]	6-31+G*	-6.20	0.23	6.43
Ph$_2$AlCl$_2^-$	this work	LAVCP**++	-6.383	-0.259	6.124
	this work	LAVCP*+	-6.368	-0.234	6.134
	[4]	6-31+G*	-5.98	0.34	6.32
Ph$_3$AlCl$^-$	this work	LAVCP**++	-6.126	-0.073	6.052
	this work	LAVCP*+	-6.115	0.044	6.159
	[4]	6-31+G*	-5.76	0.38	6.15
Ph$_4$Al$^-$	this work	LAVCP**++	-5.829	-0.096	5.733
	this work	LAVCP*+	-5.825	-0.073	5.752
	[4]	6-31+G*	-5.33	0.64	5.97

Table S4 Calculations of HOMO and LUMO energy levels for anions of interest in three different solvents

Anion [R$_x$AlCl$_{4-x}$]$^-$ x= 1, 2, 3	Solvent	HOMO (eV)	LUMO (eV)	Gap (eV)
[EtAlCl$_3$]$^-$	THF	-6.693	0.092	6.785
	Diglyme	-6.689	0.092	6.781
	Tetraglyme	-6.687	0.091	6.778
[Et$_2$AlCl$_2$]$^-$	THF	-5.865	0.089	5.954
	Diglyme	-5.859	0.089	5.948
	Tetraglyme	-5.859	0.088	5.948
[Et$_3$AlCl]$^-$	THF	-5.465	0.101	5.557
	Diglyme	-5.452	0.101	5.552
	Tetraglyme	-5.448	0.099	5.546
[MesAlCl$_3$]$^-$	THF	-6.116	-0.284	5.832
	Diglyme	-6.112	-0.279	5.832
	Tetraglyme	-6.108	-0.276	5.832
[Mes$_2$AlCl$_2$]$^-$	THF	-5.825	-0.057	5.768
	Diglyme	-5.804	-0.035	5.769
	Tetraglyme	-5.789	-0.043	5.755
[Mes$_3$AlCl]$^-$	THF	-5.571	0.096	5.667
	Diglyme	-5.559	0.103	5.662
	Tetraglyme	-5.547	0.111	5.658
[TMPAlCl$_3$]$^-$ *	THF	-5.023	0.084	5.107
	Diglyme	-5.011	0.084	5.095
	Tetraglyme	-5.011	0.084	5.095
[TMP$_2$AlCl$_2$]$^-$*	THF	-4.568	0.125	4.693
	Diglyme	-4.565	0.125	4.690
	Tetraglyme	-4.563	0.123	4.686
[TMP$_3$AlCl]$^-$ *	THF	-4.094	0.117	4.211
	Diglyme	-4.093	0.112	4.205
	Tetraglyme	-4.090	0.110	4.200
[PhAlCl$_3$]$^-$	THF	-6.638	-0.346	6.293
	Diglyme	-6.635	-0.342	6.293
	Tetraglyme	-6.623	-0.333	6.290
[Ph$_2$AlCl$_2$]$^-$	THF	-6.383	-0.259	6.124
	Diglyme	-6.386	-0.248	6.120
	Tetraglyme	-6.360	-0.242	6.118
[Ph$_3$AlCl]$^-$	THF	-6.126	-0.073	6.052
	Diglyme	-6.116	-0.064	6.051
	Tetraglyme	-6.110	-0.059	6.051
[HMDSAlCl$_3$]$^-$**	THF	-6.033	-0.007	6.026
	Diglyme	-6.030	-0.007	6.022
	Tetraglyme	-6.028	-0.008	6.019
[HMDS$_2$AlCl$_2$]$^-$ **	THF	-5.775	0.002	5.778
	Diglyme	-5.770	0.002	5.772
	Tetraglyme	-5.769	0.000	5.769
[HMDS$_3$AlCl]$^-$ **	THF	-5.470	0.116	5.486
	Diglyme	-5.472	0.009	5.481
	Tetraglyme	-5.471	0.010	5.480
[PhOAlCl$_3$]$^-$	THF	-5.882	-0.173	5.709
	Diglyme	-5.876	-0.170	5.707
	Tetraglyme	-5.861	-0.162	5.700
[(PhO)$_2$AlCl$_2$]$^-$	THF	-5.776	-0.140	5.637
	Diglyme	-5.760	-0.136	5.624
	Tetraglyme	-5.751	-0.133	5.618
[(PhO)$_3$AlCl]$^-$	THF	-5.619	-0.092	5.527
	Diglyme	-5.603	-0.087	5.516
	Tetraglyme	-5.586	-0.082	5.504

* TMP = 2,2,6,6-tetramethylpiperidide ; ** HMDS = hexamethyldisilazide

Experimental section

All the samples were handled in an argon-filled glove box with water and oxygen concentrations below 1 ppm. The chemical operations were either carried out on the bench under Ar (99.9999 %) using standard Schlenk techniques or in a glove box. The chemicals including anhydrous solvents, magnesium chloride (99%), ethylaluminum dichloride, diethylaluminum chloride, and triethylaluminum were purchased from Sigma-Aldrich. Dichloroaluminum phenolate was synthesized according to the procedure reported in the literature.[8]

Powder X-ray diffraction (XRD) patterns were recorded in the 2θ range 10-75° using a Philips X'pert diffractometer equipped with Cu Kα source. Scanning electron microscopy (SEM) was performed with a LEO 1530 at 15 keV using carbon tape as the substrate.^{1}H, ^{13}C and ^{27}Al NMR spectra were recorded with a Bruker Advance II 500 spectrometer. The ^{13}C NMR spectra were broadband ^{1}H decoupled. A 1 M solution of Al(NO)$_3$ in D$_2$O was used as the reference for the ^{27}Al NMR. THF-d_8 or C$_6$D$_6$ were used as solvents for NMR measurements and the chemical shifts were reported in ppm using the residual solvent peak as the reference.[3] X-ray single crystal diffraction was performed with a STOE IPDS II diffractometer using Mo-Kα (λ = 0.71073 Å) radiation. Structure solution and refinement against F2 were carried out using HELXS and SHELXL software.[9]

Representative synthesis of the electrolytes of MgCl$_2$-R$_x$AlCl$_{3-x}$ (x = 1, 2, 3)

In an argon-filled glove box, 0.35 ml (2.7 mmol) of Et$_2$AlCl was added to a vial charged with 4 ml of anhydrous THF and 384 mg (4.03 mmol) of MgCl$_2$ and stirred for 24 hours at room temperature. ^{1}H-NMR (d_8-THF, 500 MHz): δ = -0.17 (dd, CH$_2$), 0.96 (t, 0.96), 1.78 (m, THF), 3.64 (m, THF); ^{13}C{H}-NMR (d_8-THF, 126 MHz): δ 6.04 (s, CH$_2$), 8.70 (m, CH$_3$), 24.3 (m, THF), 66.7 (m, THF); ^{27}Al-NMR(C$_6$D$_6$, 130 MHz) 72.8 (s, [Et$_2$AlCl$_2$]$^-$), 163.0 (s, weak, Et$_2$AlCl).

The solutions of MgCl$_2$-EtAlCl$_2$ and MgCl$_2$-Et$_3$AlCl in diglyme or tetraglyme were prepared using the same procedures, the amount of aluminium compounds were determined by completely dissolving MgCl$_2$.

Preparation of [Mg$_2$(μ-Cl)$_3$(THF)$_6$][Et$_2$AlCl$_2$]

As-prepared THF solution of MgCl$_2$-Et$_2$AlCl was crystallized by slow diffusion of anhydrous hexane. The resulting crystals were washed with hexane and dried under vacuum. ^{1}H-NMR (d_8-THF, 500 MHz): δ - 0.16 (dd, CH$_2$), 0.98 (t, 0.96), 1.78 (m, THF), 3.64 (m, THF); ^{13}C{H}-NMR (d_8-THF, 126 MHz): δ 6.04 (s, CH$_2$), 8.80 (m, CH$_3$), 4.68 (s, CH$_3$), 24.3 (m, THF), 66.7 (m, THF); ^{27}Al-NMR(C$_6$D$_6$, 130 MHz) 72.4 (s, [Et$_2$AlCl$_2$]$^-$), 168.6 (s, weak, Et$_2$AlCl).

Synthesis of the electrolytes of Mg-TCP/DEG

In an argon-filled glove box, 207 mg (1.08 mmol) of PhOAlCl$_2$ was dissolved in 1.5 ml diglyme in a vial; subsequently, 87.4 mg (0.92 mmol) of MgCl$_2$ was added and stirred for 24 hours at room temperature. ^{1}H-NMR (d_8-THF, 500 MHz): δ 1.49 (s, OCH$_3$), 3.11−3.52 (m, (CH$_2$)$_4$O), 7.09 (m, 4H, Ph), 7.78 (s, 1H, Ph); ^{27}Al-NMR(C$_6$D$_6$, 130 MHz) 89.4 (s, [PhOAlCl$_3$]$^-$), 103.6 (s, Al$_2$Cl$_6$).

Crystallographic data for [Mg$_2$(μ-Cl)$_3$(THF)$_6$][Et$_2$AlCl$_2$] ‡ Mr = 743.59; space group P2_1/c; a = 12.905(3)Å; b = 24.536(5)Å; c = 12.310(3)Å; $α$ = 90°; $β$ = 90.12(3)°;$γ$ = 90°; V = 3897.8(14)Å^3; Z = 4; T = 180 K; colorless rod; crystal size: 0.28 x 0.25 x 0.24 mm; index ranges: -14≤h<15, -28≤k≤28, -14≤l≤14; $ρ_{calcd}$ = 1.267 g cm^{-3}; $μ$(Mo-K$α$) = 0.462mm^{-1}; R_1(I >2σ(I)) = 0.0878, wR_2(all data) = 0.2686.

Crystallographic data for [Mg$_2$(μ-Cl)$_2$(diglyme)$_2$]Cl$_2$ ‡ Mr = 458.76; space group P2_1/c; a = 10.3321(7) Å; b = 7.5712(7) Å; c = 14.2704(11) Å; $α$ = 90°; $β$ =110.807(5)°; $γ$ = 90°; V = 1043.52(14) Å^3; Z = 2; T = 150 K; colorless rod; crystal size: 0.15 × 0.04 × 0.03 mm; index ranges: -12 ≤ h ≤ 12, -9 ≤ k ≤ 5, -14 ≤ l ≤ 17; $ρ_{calcd}$ = 1.460 g cm^{-3}; $μ$(Mo-K$α$) = 0.650 mm^{-1}; R_1(I >2σ(I)) = 0.0306, wR_2(all data) = 0.0593.

Electrochemistry Electrochemical studies were performed in Swagelok type cells. The fabrication of all electrodes and the construction of the electrochemical cells were carried in an argon-filled glove box. Cyclic voltammograms were obtained using a Biologic VMP-3 potentiostat with a two-electrode cell comprising a Pt disc as working electrode, Mg foil as reference electrode at a scan rate of 25 mV s^{-1}. The conductivities were measured at 25 °C by a conductivity meter CDM 230, Meter Lab Radiometer analytical.

Cathodes were prepared by coating a Mo$_6$S$_8$–carbon composite slurry (75% Mo$_6$S$_8$, 15% carbon black, 10% polyvinylidene fluoride binder) on a stainless steel disc and dried at 120 °C for 12 h. Typically, each electrode contained about 1.5 mg of the active material. 100-μm-thick Mg foil (Goodfellow) was used as the negative electrode and a borosilicate glass fiber sheet as separator. The cells were placed in an incubator to maintain a constant temperature of 25 ± 0.1 °C. The electrochemical studies were carried out using an Arbin battery cycling unit.

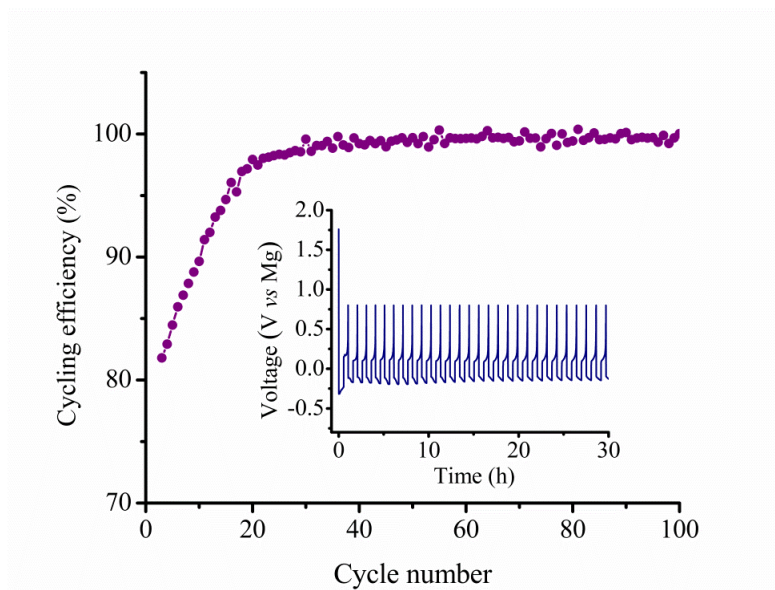**Fig. S1** Cycling efficiency and the first 30 chronopotentiograms (insert) of Mg deposition/dissolution on Pt in 1 M diglyme solution of MgCl$_2$-Et$_2$AlCl
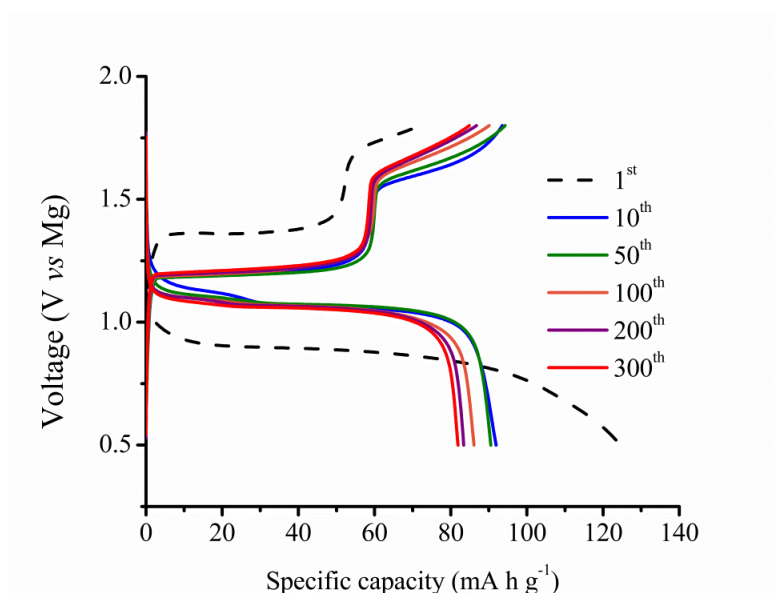
Fig. S2 Cycling behaviour of the rechargeable Mg/Mo$_6$S$_8$ cell using 1 M tetraglyme solution of MgCl$_2$-Et$_2$AlCl at a current rate of 20 mA g^{-1} at 25 °C.

Table S5 Conductivity of the electrolytes

Electrolyte (1M)	Conductivity (mS cm^{-1})
Et$_2$AlCl-MgCl$_2$-tetraglyme	0.9
Et$_2$AlCl-MgCl$_2$-diglyme	3.0
Et$_2$AlCl-MgCl$_2$-THF	3.2
EtAlCl$_2$-MgCl$_2$-tetraglyme	1.0
Et$_3$Al-MgCl$_2$-THF	1.8
Et$_3$Al-MgCl$_2$-tetraglyme	0.8

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