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S.1 General Experimental Details:

All reactions were carried out under a dry, oxygen free nitrogen or argon atmosphere using standard Schlenk and glovebox techniques in dry degassed solvents unless otherwise specified. All solvents were collected freshly distilled over sodium wire/benzophenone and stored over activated molecular sieves (THF and DME) and calcium hydride (DCM). Deuterated NMR solvents were dried over freshly pressed sodium wire (d_8 -THF). *Tert*-butanol (SigmaAldrich), hexafluoro-*iso*-propanol (Alfa Aesar), and perfluoro-*tert*-buranol (Fluorochem) were distilled and stored over activated molecular sieves. Phenol (Acros organics) was purified by sublimation and stored in a sealed flask in a glovebox. Pentafluorophenol (Fluorochem) was sublimed and stored in a vial over P₂O₅. Mg(AlH₄)₂ was prepared according to a literature procedure using NaAlH₄ (Acros organics) and anhydrous MgCl₂ (Alfa Aesar).¹

Solution-state NMR spectra were recorded at 298.0 K on a Bruker 400 MHz AVIII HD Smart Probe spectrometer (¹H at 400 MHz, ¹³C 101 MHz, ¹⁹F 376 MHz, and ²⁷Al 104 MHz). Solid-state NMR spectra were recorded on a Bruker 500 MHz Avance III spectrometer using a 1.3mm probe. ²³Na radiofrequency strength of 162 kHz and a CT-selective π /4-pulse were employed. All experiments employed a rotor-synchronised Hahn-echo pulse sequence. For the saturation-recovery experiment, a simple excitation-delay-acquisition pulse sequence was used. ²³Na shifts were referenced to NaCl powder (7.2 ppm). MAS spin rates and recycle delays are as shown in figure captions. Figure S28 shows a saturation-recovery experiment conducted on the Chevrel phase cathode extracted from the cell shown in Figure 7a at the end of discharge (Figure 8). Of the four resonances present in the spectrum, only one resonance (spanning 3 to -53 ppm; denoted -8.7 ppm in the main text) shows fast T₁-relaxation of 9.1 ms, thus confirming the paramagnetic nature of this resonance. The other resonances, despite not being fully recovered in the saturation-recovery experiment, clearly shows much slower relaxation (>150 ms) and are likely to be diamagnetic in nature. The exact nature of these resonances is not clear, apart from the narrow resonance at 7.2 ppm (NaCl); possible sources could be unrinsed Na-solvent complex or Na-electrolyte complex. Isotropic resonances were also extracted from two variable-spin rate spectra as shown in Figure S29. As expected from paramagnetic shifts following a Curie-Weiss type law ($\delta_{iso} \propto 1/(T-\Theta)$), where δ_{iso} is the isotropic shift, T is the sample temperature, and Θ is the Curie-Weiss constant of the system), larger frictional heating from faster MAS results in reduced paramagnetic shifts.

Single crystal X-ray diffraction was carried out at 180(2) K on a Bruker D8-Quest PHOTON-100 diffractometer equipped with an Incoatec IµS Cu microsource ($\lambda_{ave} = 1.5418$ Å). Structures were solved using SHELXT² and refined using full-matrix least squares on F^2 using SHELXL (ver.2018/1).³ Powder X-ray diffraction (XRD) data were collected using a PANalytical Empyrean X-ray diffractometer using non-monochromated CuKa radiation ($\lambda_{ave} = 1.5418$ Å).

Materials used for electrochemical measurements were prepared in an argon-filled glovebox. Mg ribbon electrodes (99.9%, Sigma Aldrich) were polished using a blade to remove surface oxides. Pt wire electrodes (99.95%, Alfa Aesar) were polished sequentially with 800 and 1200 grit Emory paper and finally washed with dry DME. Stainless steel (316 grade, Advent Research materials) and Al (Dexmet corp.) working electrodes were used as received and dried under vacuum. Gold wire electrodes were prepared in-house by plating gold onto titanium wire (99.99%, Alfa Aesar) according to a literature procedure.⁴ All linear sweep voltammetry and cyclic voltammetry experiments were performed in a glovebox under an atmosphere of dry argon using an IVIUM CompactStat. All solvents used for electrochemical measurements were distilled under dry argon. Coin cells were constructed using Mg ribbon anodes, gold-plated stainless steel disk electrodes (PI-KEM), stainless steel current collectors, and glass fibre or Celgard 3501 separators.

Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDX) spectra were obtained using a TESCAN MIRA3 FEG-SEM. SEM images were captured at a 5 or 15 kV accelerating voltage and EDX spectra were collected at 15 kV. Samples were transferred from an Ar-filled glovebox using a sealable transfer module.

High-resolution mass spectra (HRMS) were collected using a Waters Xevo G2-S QTOF mass spectrometer in negative mode using dry THF.

Elemental microanalytical data were obtained from the University of Cambridge, Department of Chemistry microanalytical service.

Electronic structure calculations on the $Mo_6S_8^{4-}$ cluster was performed with the Gaussian16 quantum chemistry package.⁵ The cluster was relaxed at B3LYP⁶ level of theory with Def2SVP basis functions⁷ and the MO energies and isosurface plots were generated from a final single point calculation.

S.2 General procedure for the synthesis of magnesium alkoxyaluminates 1-5:

In a N₂- or Ar-filled glovebox, a Schlenk tube was loaded with 50-100 mg of the light grey Mg(AlH₄)₂-containing solid (42.5 wt% Mg(AlH₄)₂) along with dry THF (ca. 5 mL). The alcohol (7.9 equiv.) was then added, resulting in vigorous bubbling and the release of H₂ gas. Once gas-release had subsided, the reaction vessel was sealed and removed from the glovebox to stir for 16-18 hours. The chloride-containing mixtures could be were isolated by filtering reaction mixture through glass fibre cannula filter. The clear colourless solution obtained was taken to dryness *in vacuo*, affording a white solid. The electrolyte salts could be further purified by suspending the dried crude reaction mixture in freshly distilled DCM and filtering through a glass fiber cannula filter to remove chloride-containing by-products.

$Mg[Al(O^{t}Bu)_{4}]_{2}(1):$

250 mg, 32% crystalline yield. ¹H NMR (400 MHz, 298.0 K, C_6D_6) δ 1.48 (s, 1H), 1.46 (s, 1H) ppm; ¹³C NMR (101 MHz, 298.0 K, C_6D_6) δ 71.82, 68.62, 34.20, 33.24 ppm; ²⁷Al NMR (104 MHz, 298.0 K, DME) δ 49.17 ppm. Anal. calc'd for $C_{32}H_{72}Al_2Cl_{0.2}MgNa_{0.2}O_8$ (**1** + 0.2 NaCl): C, 56.95; H, 10.75; N, 0.00; Cl, 1.05; found: C, 55.77; H, 10.63; N, 0.00; Cl, 0.24.

$Mg(THF)_{6}[Al(O^{t}Bu^{F})_{4}]_{2}(2):$

500 mg, 91%. ¹H NMR (400 MHz, 298.0 K, *d*₈-THF) δ 3.62 (m, THF), 1.79 (m, THF) ppm; ¹³C NMR (101 MHz, 298.0 K, *d*₈-THF) δ 122.75 (q, *J* = 293.5 Hz), 68.39, 26.54 ppm; ¹⁹F NMR (376 MHz, 298.0 k, C₆D₆) δ -75.77 ppm; ²⁷Al NMR (104 MHz, 298.0 K, DME) δ 52.40 ppm. HRMS *m*/*z* calc'd for C₁₆AlF₃₆O₄ [Al(O^{*t*}Bu^F)₄⁻]: 966.9037; found: 966.9148. Anal. calc'd for

C₆₄H₆₃Al₂Cl₂F₇₂MgNa₂O₁₆ (**2** + 2 NaCl + 2 THF): C, 28.99; H, 2.40; N, 0.00; Cl, 2.67; found: C, 28.84; H, 2.43; N, 0.00; Cl, 2.64.

$Mg(THF)_{6}[Al(O^{i}Pr^{F})_{4}]_{2}(3):$

330 mg, 74% with chloride. ¹H NMR (400 MHz, 298.0 K, *d*₈-THF) δ 4.53 (hept, *J* = 6.4 Hz), 3.62 (m, THF), 1.78 (m, THF) ppm; ¹³C NMR (126 MHz, 298.0 K, *d*₈-THF) δ 128.92-119.27 (m), 73.06-71.06 (m), 68.39, 26.54 ppm; ¹⁹F NMR (376 MHz, 298.0 K, *d*₈-THF) δ -77.73 (m) ppm; ²⁷Al NMR (104 MHz, 298.0 K, *d*₈-THF) δ 60.70 ppm. HRMS *m*/*z* calc'd for C₁₂H₄AlF₂₄O₄ [Al(O^{*i*}Pr^F)₄⁻]: 694.9542; found: 694.9530. Anal. calc'd for C₅₀H₆₀Al₂Cl₂F₄₈MgNa₂O₁₄ (**3** + 2 NaCl): C, 29.37; H, 2.82; N, 0.00; Cl, 3.61; found: C, 29.38; H, 2.92; N, 0.00; Cl, 3.20.

Mg(**THF**)₂[**Al**(**OPh**)₄]₂(4):

390 mg, 84% crystalline yield. ¹H NMR (400 MHz, 298.0 k, C_6D_6) δ 7.08-6.99 (m, 32H), 6.76 (t, J = 7.2 Hz, 8H), 3.64 (s, THF), 1.27 (s, THF) ppm; ¹³C NMR (101 MHz, 298.0 K, C_6D_6) δ 156.89, 129.99, 121.16, 120.44, 69.99, 25.11 ppm; ²⁷Al NMR (104 MHz, 298.0 K, DME) δ 54.46 ppm. HRMS *m*/*z* calc'd for C₂₄H₂₀AlO₄ [Al(OPh)₄⁻]: 399.1177; found: 399.1232. Anal. calc'd for C₅₆H₅₆Al₂Cl_{0.5}MgNa_{0.5}O₁₀ (**4** + 0.5 NaCl): C, 67.56; H, 5.70; N, 0.00; Cl, 1.78; found: C, 66.46; H, 5.42; N, 0.00; Cl, 1.68.

$Mg(THF)_{6}[Al(OPh^{F})_{4}]_{2}(5):$

370 mg, 78% with chloride. ¹H NMR (400 MHz, 298.0 K, d_8 -THF) δ 3.67-3.63 (m, THF), 1.84-1.78 (m, THF); ¹³C NMR (126 MHz, 298.0 K, d_8 -THF) δ 142.93-132.60 (m), 68.27, 26.43; ¹⁹F NMR (376 MHz, 298.0 K, d_8 -THF) δ –163.80 (d, J = 22.0 Hz), –169.85 (dd, J = 21.5, 19.6 Hz), –177.40 (tt, J = 22.5, 7.0 Hz); ²⁷Al NMR (104 MHz, 298.0K, d_8 -THF) δ 47.32. HRMS m/zcalc'd for C₂₄AlF₂₀O₄ [Al(OPh^F)₄⁻]: 758.9293; found: 758.9385. Anal. calc'd for C₇₂H₄₇Al₂Cl_{1.5}F₄₀MgNa_{1.5}O₁₄ (**5** + 1.5 NaCl): C, 41.94; H, 2.30; N, 0.00; Cl, 2.58; found: C, 42.08; H, 2.47; N, 0.00; Cl, 2.52.

S.3 Spectroscopic Analysis:



Figure S2¹³C NMR (101 MHz, 298.0 K, C₆D₆) of **1**.



Figure S5¹³C NMR (101 MHz, 298.0 K, *d*₈-THF) of **2**.



Figure S8 ¹H NMR (400 MHz, 298.0 K, d_8 -THF) of **3**.



Figure S11²⁷Al NMR (104 MHz, 298.0 K, *d*₈-THF) spectrum of **3**.



Figure S14²⁷Al NMR (104 MHz, 298.0 K, DME with DMSO- d_6 capillary) spectrum of 4.



Figure S17¹⁹F NMR (376 MHz, 298.0 K, *d*₈-THF) of **5**.



Figure S18²⁷Al NMR (104 MHz, 298.0 K, *d*₈-THF) spectrum of **5**.

S.4 Supporting Figures:



Figure S19 LSV measurements of a 0.25 M solutions of **5** in DME scanning at a rate of 10 mV·s⁻¹ on ss-316, Al, Cu, Au, and Pt working electrodes.



Figure S20 Galvanostatic cycling of 0.25 M solutions of a) chloride-containing 4 and b) chloride-free 4.



Figure S21 SEM and EDX analysis of Mg deposits removed onto a glass fibre separator from a chloridecontaining solution of 2 in DME (0.25 M) at a current density of 25 μ A·cm⁻².



Figure S22 Comparison of XRD patterns of Mg on Celgard (black) and of Celgard alone (red), verifying that peaks observed below 30° result from Celguard alone.



Figure S23 SEM and EDX analysis of Mg electrodeposited on a Au current collector from a chloridecontaining solution of 4 in DME (0.25 M) at a current density of 25 μ A·cm⁻².



Figure S24 SEM and EDX analysis of Mg electrodeposited on a Au current collector from a chloridecontaining solution of 4 in DME (0.25 M) at a current density of 25 μ A·cm⁻².



Figure S25 Charge-discharge behaviour of a Mg cell containing a Chevrel phase cathode, a Mg anode, and a 0.25 M solution of aluminate **5** in DME at room temperature (rate: C/25).



Figure S26 First discharge of a Na cell containing a Chevrel phase cathode, a Na anode, and a 1 M solution of NaBPh₄ in 2-methyltetrahydrofuran at room temperature (rate: C/25).



Figure S27 Fitted centreband region of the ²³Na NMR spectrum of Mo₆S₈ discharged against Mg metal (Figure 7a, main text; spectrum reproduced from Figure 8, red line) Spectrum was measured at 50 kHz MAS with a recycle delay of 1 s. Fitted parameters are displayed in Table S1.

Tuble 51 Three parameters of speed and shown in Figure 527.							
	Site 1	Site 2	Site 3	Site 4	Site 5		
δ _{iso} [ppm]	344.8	-10.8	7.2	84.2	22.8		
C _Q [MHz]	-	-	-	3.7	-		
η	-	-	-	0	-		
Lorentzian broadening [Hz]	4785	3961	300	503	1848		
Assignment	Chevrel Na2	Chevrel Na1	NaCl	Unknown	Unknown		

Table S1 Fitted parameters of spectrum shown in Figure S27.



Figure S28 ²³Na saturation-recovery data of Mo_6S_8 discharged against Mg metal (Figures 7a and 8, main text) at 50 kHz MAS. Fitted T₁-values are indicated for each peak.



Figure S29 ²³Na solid-state NMR spectra of Mo_6S_8 discharged against Na metal, taken at 55 and 50 kHz MAS, respectively. Both spectra were measured with recycle delays of 0.1 s. Values of the isotropic resonances are taken from the 50 kHz MAS spectrum for consistency with the rest of the discussion.

S.5 Crystallographic Analysis:

 $Mg[Al(O'Bu)_4]_2$: refinement of the structure was largely routine. The ^tBu groups were restrained to a regular tetrahedral geometry by restraining all C–C distances to a common refined parameter, and all C···C distances to 1.633 times that parameter (both restraints applied with su 0.01 Å). Several of the ADPs for the terminal C atoms were significantly prolate, indicative of rotational disorder. No benefit was perceived in splitting these atom sites. The terminal Al–O bond lengths span the range 1.660(2)–1.704(2) Å, while the bridging Al–O bond lengths span the range 1.8047(18)–1.8131(17) Å. The Mg–O distances are all equivalent within the precision of the measurement: 1.9554(18)–1.9612(18) Å.

 $Mg[Al(OPh)_4]_2(THF)_2 THF$: the molecule is situated on a 2-fold rotation axis. Three of the four unique OPh groups appear well ordered, while the fourth (O2) displayed severely elongated ADPs. The THF molecule coordinated to Mg1 showed similar elongated ADPs. Hence, the phenyl ring C7-C12 and the coordinated THF molecule are refined using two components with isotropic displacement parameters. The components of the phenyl were both constrained to be regular hexagons (AFIX 66), and SAME restraints were applied to the two components of THF. The site occupancies of the two components were refined in both instances as free variables, but the result did not differ significantly from 50:50. In the final refinement, the site occupancies of all components were therefore constrained to 0.5. The disordered ring and THF molecule are in close proximity in the structure, so the disorder may be correlated between adjacent complexes.



Figure S30 Molecular unit in the crystal structure of Mg[Al(O'Bu)₄]₂ with displacement ellipsoids shown at 50% probability. H atoms are omitted.



Figure S31 Molecular unit in the crystal structure of **Mg[Al(OPh)_4]_2(THF)_2·THF** with displacement ellipsoids shown at 50% probability. H atoms and the lattice THF molecule are omitted. The molecule is situated on a crystallographic 2-fold axis.

· · · · ·	$Mg[Al(O^tBu)_4]_2$	Mg[Al(OPh) ₄] ₂ (THF) ₂ ·THF
CCDC number	1856188	1856187
Cambridge data number	DW_B1_0057	DW_B2_0143
Empirical formula	$C_{32}H_{72}Al_2MgO_8$	$C_{60}H_{64}Al_2MgO_{11}$
Formula weight	663.16	1039.38
Temperature / K	180(2)	180(2)
Crystal system	monoclinic	orthorhombic
Space group	$P2_{1}/n$	$P2_{1}2_{1}2$
<i>a</i> / Å	9.9953(3)	14.1081(4)
b / Å	16.5017(5)	21.3826(6)
<i>c</i> / Å	25.7252(8)	8.9782(3)
α / °	90	90
β / °	92.9649(11)	90
γ / °	90	90
Volume / $Å^3$	4237.4(2)	2708.43(14)
Z	4	2
$ ho_{calc}$ / g cm ⁻³	1.040	1.274
μ / mm^{-1}	1.077	1.095
F(000)	1464	1100
Crystal size / mm ³	0.28×0.14×0.11	$0.17 \times 0.08 \times 0.07$
Radiation	$CuK\alpha (\lambda_{ave} = 1.5418 \text{ Å})$	$CuK\alpha (\lambda_{ave} = 1.5418 \text{ Å})$
2θ range / °	6.37 to 133.16	7.51 to 117.87
Reflections collected	28916	16436
Independent reflections	7432	3857
R _{int}	0.028	0.052
Goodness-of-fit on F^2	1.04	1.05

Data/restraints/parameters	7432/48/413	3857/10/300
$R1 [I > 2\sigma(I)]$	0.069	0.049
w <i>R</i> 2 [all data]	0.194	0.109
Largest diff. peak/hole / $eÅ^{-3}$	0.80/-0.78	0.22/-0.25
Flack parameter		0.01(2)

S.6 References:

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