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Electronic Supplementary Information for:

A Magnesium Tetraphenylaluminate Battery Electrolyte Exhibits a Wide Electrochemical Potential Window and Reduces Stainless Steel Corrosion

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General considerations. Phenylmagnesium chloride, trimethylaluminum and phenol were purchased from Sigma Aldrich, and used as received. Tetrahydrofuran solvent was purchased from VWR, and distilled over sodium with a benzophenone-ketyl indicator. ^{27}Al NMR was performed on a Varian VNMRS-700 MHz spectrometer in THF with chemical shifts reported relative to a solution of $AlCl_3$ in D_2O with a drop of concentrated HCl. ^{1}H, and ^{13}C NMR were performed on a Varian MR-400 MHz spectrometer in THF. Conductivity measurements were carried out using a YSI Model 3200 conductivity meter equipped with a 3253 conductivity cell at room temperature. Mass spectrometry was performed on a Micromass LCT Time-of-Flight mass spectrometer with electrospray ionization. X-ray photoelectron spectra were recorded on a Kratos XPS (8 mA, 14 keV, Monochromatic Al). All peaks were calibrated to C(1s) at 284.5 eV. The XPS data was fit using CasaXPS program.

Synthesis. All compounds were prepared and handled using standard Schlenk techniques under N_2 and a N_2-filled glove box (Vacuum Atmospheres). Aluminum triphenoxide was made though the slow addition of 10 mL of $Al(Me)_3$ (2M, 20mmol) to a solution of phenol in THF (10mL, 6M, 60mmol) in a Schlenk flask. The solution was stirred for 3 hours and the solvent removed in vacuo. The powder was brought into the glove box and recrystallized from diffusion of Hexane into a THF solution. The PhMgCl-$Al(OPh)_3$ electrolyte was synthesized through addition of a 0.5 M $Al(OPh)_3$ in THF (2mL, 1mmol) to a solution of PhMgCl (6mL, 4mmol) in THF. The solution was stirred for at least 6 hours.

Electrochemistry. Cyclic voltammograms were recorded using a CH Instruments Electrochemical Workstation 1000A with a Pt-disk working electrode and Mg-foil counter- and reference electrodes. Measurements were carried out at a scan rate of 25 mV/s, starting at OCP (ranging from 1.5 – 1.7 vs $Mg^{2+/0}$) and scaned cathodically. All electrolyte solutions were 0.5 M (based on Mg) in THF, and measurements were performed using a custom-designed sealed cell in an N_2 box to avoid concentration change during the measurements. Referencing to the $Fc^{+/0}$ couple was carried out in a 0.5M $(FMPMC)_2$-$AlCl_3$/THF solution containing 10 mM ferrocene in THF with a Pt wire working electrode, a Mg foil auxiliary electrode, and a Mg foil reference electrode. Electrolyte stability was examined by opening a vial of the electrolyte to air, and allowing it to stir for 1 hour, followed by stirring for an additional 5 hours while lightly capped to minimize solvent evaporation. The slurry of Mo_6S_8 was made by mixing an 8:1:1 weight-ratio mixture of Mo_6S_8, super-P carbon powder, and polyvinylidine fluoride (PVDF) binder in N-methyl-2-pyrrolidinone (NMP). The cathode slurry was placed on a Pt current collector and dried in an oven at 120 ºC. The active material loading was approximately 2 mg/cm^2. The cathode was placed in an electrochemical cell with a Mg foil anode and 0.5M $(FMPMC)_2$–$AlCl_3$/THF electrolyte. The charge-discharge tests of the cell were carried on a Vencon UBA4 battery analyser charger and conditioner (Toronto, Canada) with cut-off voltages of 2.0 and 0.2 V vs. $Mg^{2+/0}$.

X-ray Structure Determination for $C_{28}H_{42}O_6Mg_2Cl_2$ (CCDC # 999561)

Colorless needles of **en52** were grown from a tetrahydrofuran/hexane solution of the compound at 22 deg. C. A crystal of dimensions 0.14 x 0.04 x 0.03 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 4146 images were collected with an oscillation width of 1.0° in ω. The exposure time was 2 sec. for the low angle images, 10 sec. for high angle. The integration of the data yielded a total of 42069 reflections to a maximum 2θ value of 136.48° of which 2810 were independent and 2519 were greater than $2\sigma(I)$. The final cell constants (Table S1) were based on the xyz centroids 26696 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/4) software package, using the space group P2(1)/c with Z = 2 for the formula $C_{28}H_{42}O_6Mg_2Cl_2$. The complex lies on an inversion center of the crystal lattice. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0436 and wR2 = 0.1229 [based on I > 2sigma(I)], R1 = 0.0463 and wR2 = 0.1257 for all data. Additional details are presented in Table 1 and are given as Supplementary Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

X-ray Structure Determination for $C_{60}H_{78}O_{12}Mg_4Cl_2$ (CCDC #999562)

Colorless block-like crystals of **en5153** were grown from a tetrahydrofuran solution of the compound at 22 deg. C. A crystal of dimensions 0.25 x 0.25 x 0.25 mm was sealed in epoxy and mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (l = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 250(1) K with the detector placed at a distance 42.00 mm from the crystal. A destructive phase change prevented data collection at lower temperature. A total of 4088 images were collected with an oscillation width of 1.0° in w. The exposure time was 1 sec. for the low angle images, 8 sec. for high angle. The integration of the data yielded a total of 75202 reflections to a maximum 2q value of 136.50° of which 5663 were independent and 5345 were greater than 2s(I). The final cell constants (Table S2) were based on the xyz centroids 46672 reflections above 10s(I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/4) software package, using the space group P2(1)/n with Z = 2 for the formula $C_{60}H_{78}O_{12}Cl_2Mg_4$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. The complex lies on an inversion of the crystal lattice located at the mid-point of Mg2 and Mg2a. The bound THF ligands show considerable conformational disorder and were each modeled in three discrete resolved positions utilizing suitable restraints and partial occupancy atoms. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0343 and wR2 = 0.0915 [based on I > 2sigma(I)], R1 = 0.0358 and wR2 = 0.0927 for all data. Additional details are presented in Table 1 and are given as Supplementary Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Sheldrick, G.M. SHELXTL, v. 2008/4; Bruker Analytical X-ray, Madison, WI, 2008.

CrystalClear Expert 2.0 r12, Rigaku Americas and Rigaku Corporation (2011), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

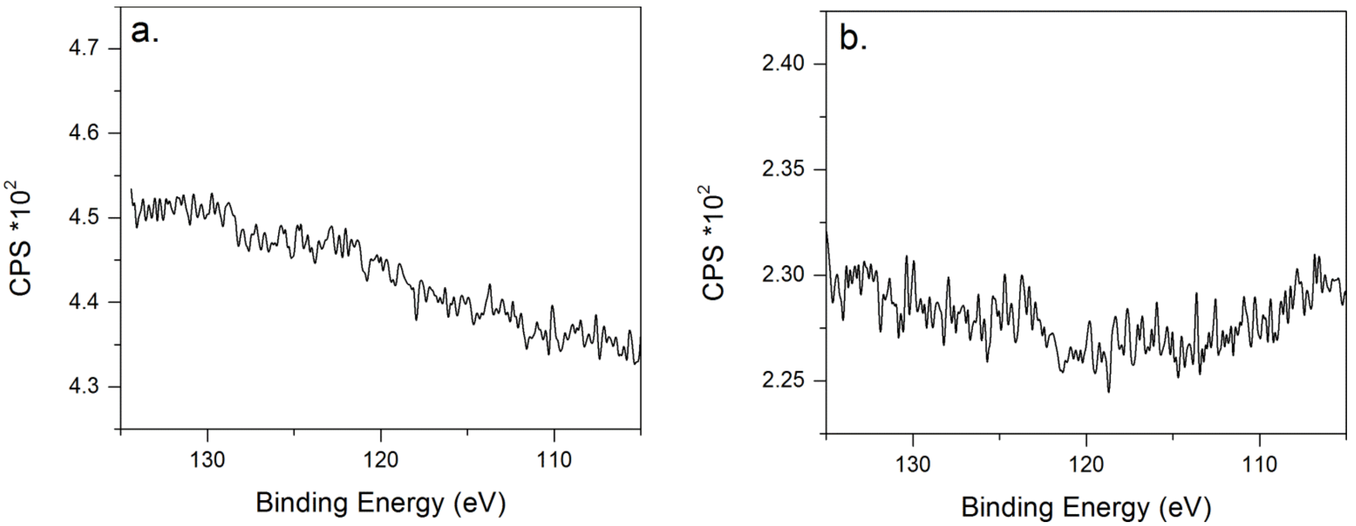

Figure S1. a.) Al 2s XP spectra of Pt soaked in THF for 20 minutes; b.) Al 2s XP spectra of Pt after cycling 20 times in $Al(OPh)_3$:4PhMgCl electrolyte from 0-5V.

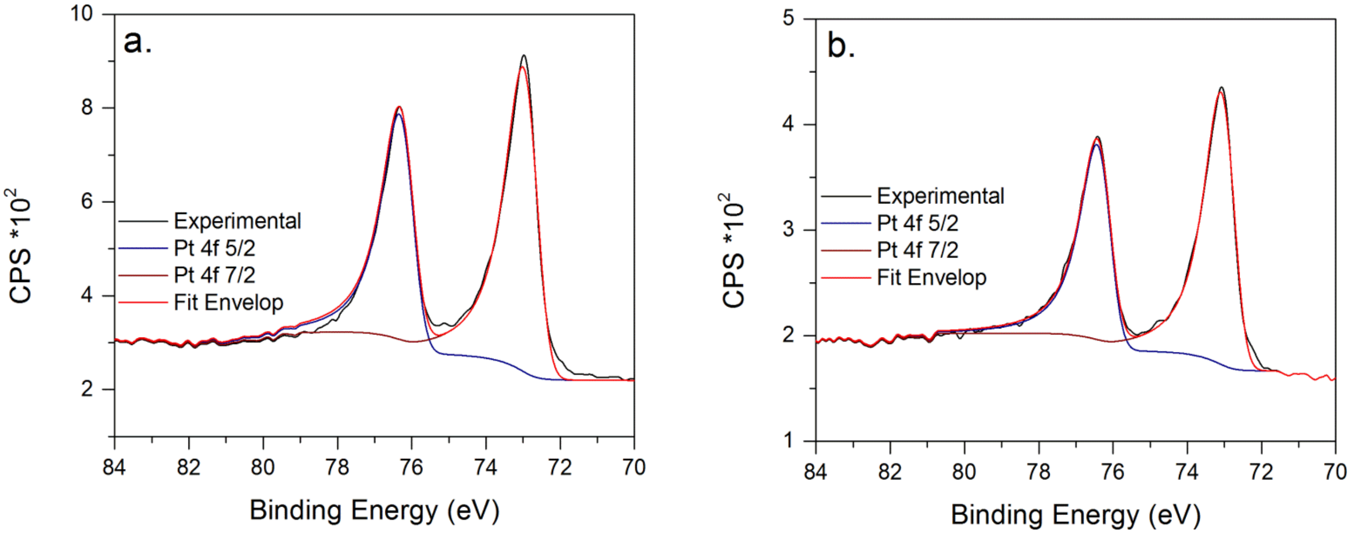

Figure S2. a.) Pt 4f XP spectra of Pt after cycling 20 times in $Al(OPh)_3$:4PhMgCl electrolyte from 0-5 V; b.) Pt 4f XP spectra of Pt soaked in THF for 20 minutes.

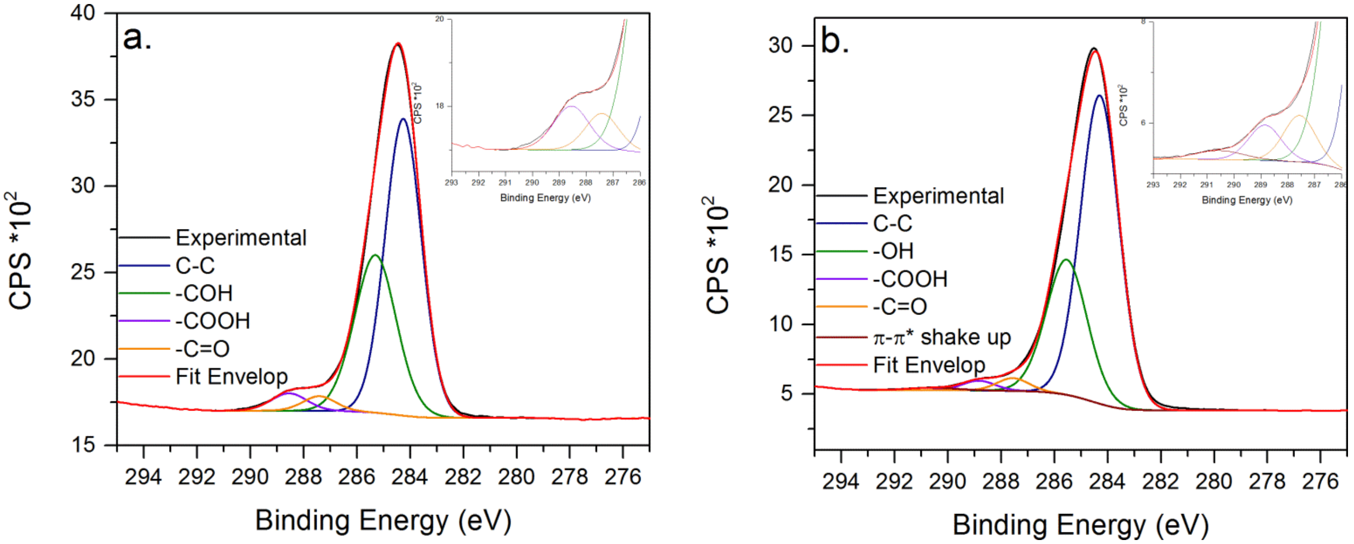

Figure S3. a.) C 1s XP spectra of Pt soaked in THF for 20 minutes, b.) C 1s XP spectra of Pt after cycling 20 times in Al(OPh)$_3$:4PhMgCl electrolyte from 0-5 V.

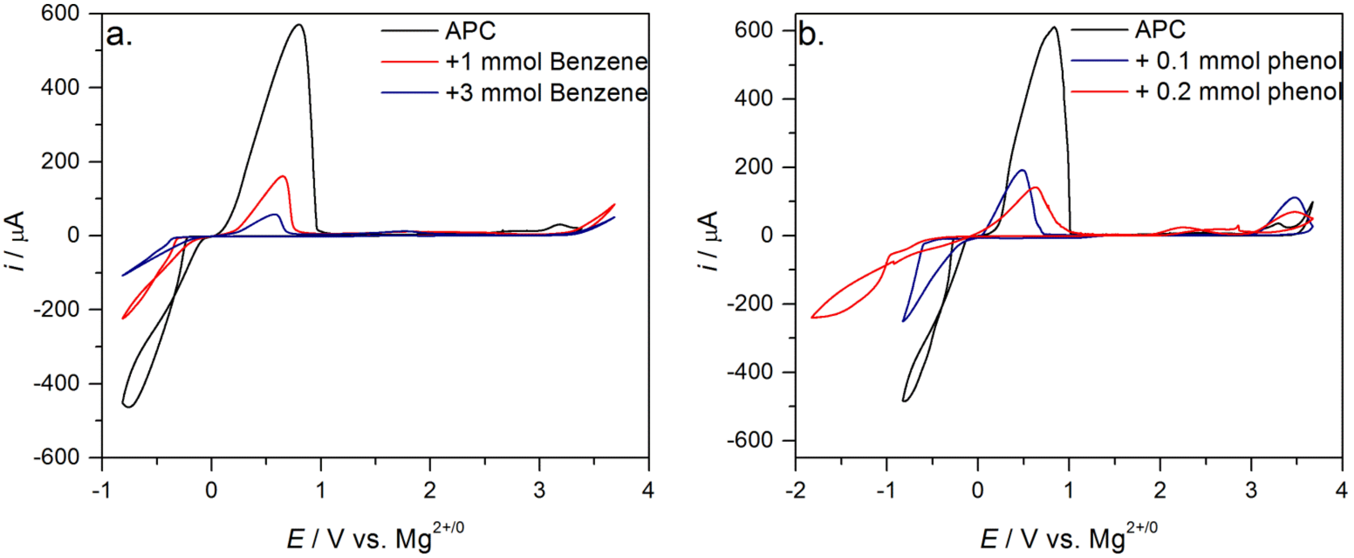

Figure S4. CV of APC electrolyte with the addition of a.) benzene and b.) phenol with Mg foil counter and reference electrode, Pt working and scan rate of 25 mV/s. Note that Adding benzene and phenol to the APC electrolyte does not enhance the oxidative stability of the electrolyte, suggesting benzene and phenol do not play a role in the formation of an electrochemical passivation layer. We note the addition of the ligands to result in a decreased current density of Mg deposition and striping as well as an increased overpotential for Mg deposition, most noticeable with the addition of phenol. If an electrochemical passivation layer if formed in the presence of these ligands, these results suggest it passivates the electrochemistry on the anodic side as opposed to the reactions which occur cathodically.

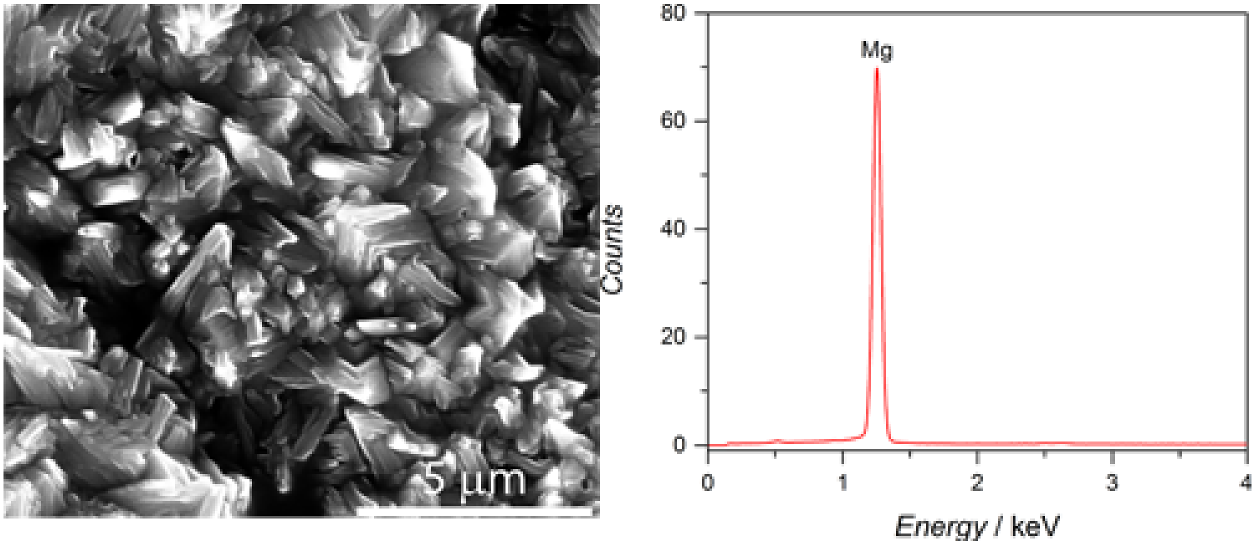

Figure S5. SEM image and EDX spectrum of deposited Mg on Cu foil

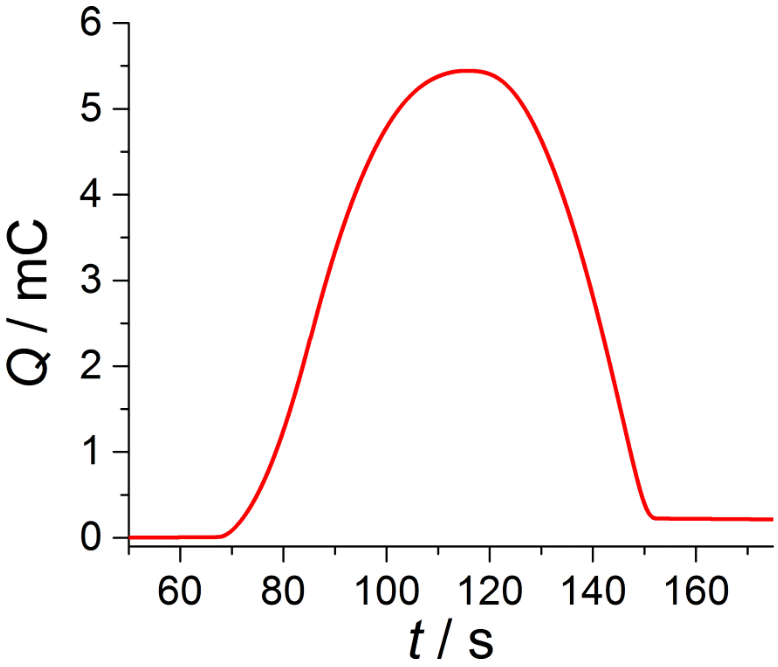

Figure S6. Charge balance of Mg deposition/stripping showing a ~98% coulombic efficiency.

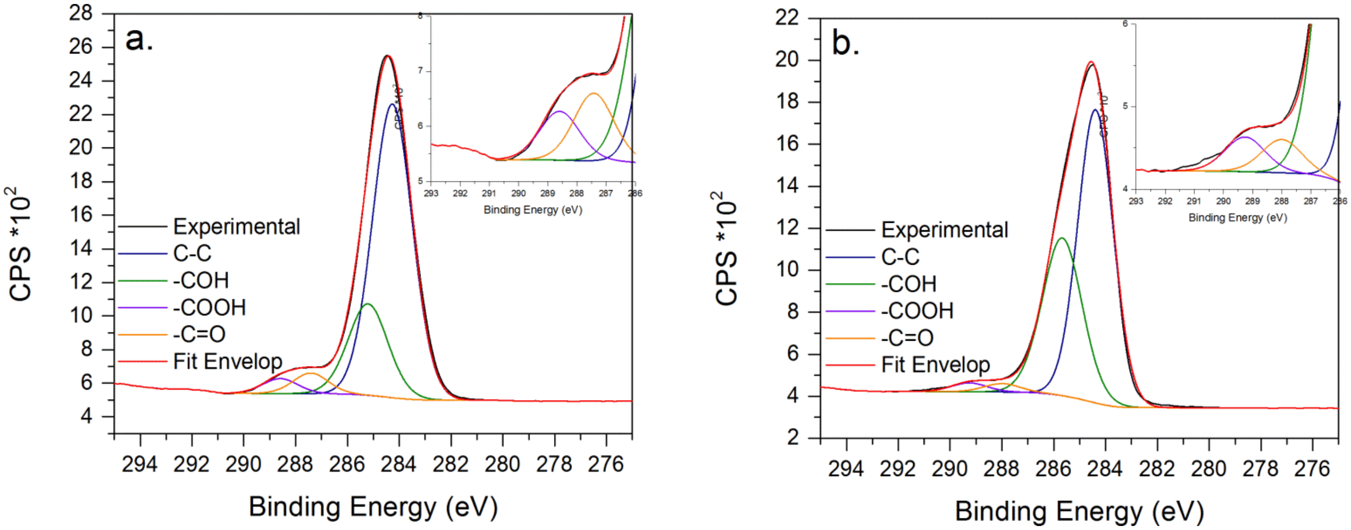

Figure S7. a.) C 1s XPS spectra of stainless steel soaked in THF for 20 minutes; b.) C 1s XPS spectra of stainless steel after cycling 20 times in Al(OPh)$_3$:4PhMgCl electrolyte from 0-5 V.

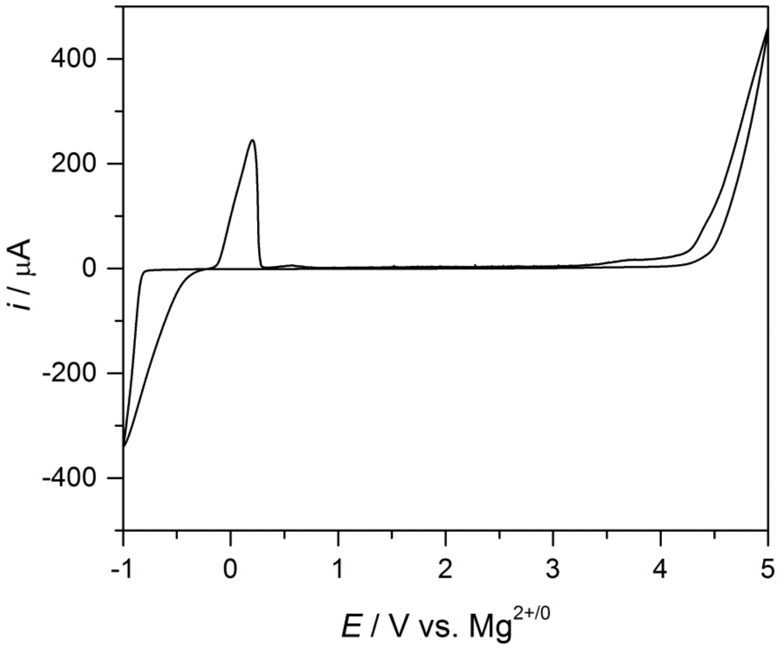

Figure S8. CV of 0.5 M LiPF$_6$ with 0.5 M Al(OPh)$_3$/PhMgCl in THF. The addition of LiPF$_6$ to the Al(OPh)$_3$/PhMgCl electrolyte does not change the deposition or stripping of magnesium. The oxidation potential has decreased by ~500 mV, due to the oxidation of LiPF$_6$.

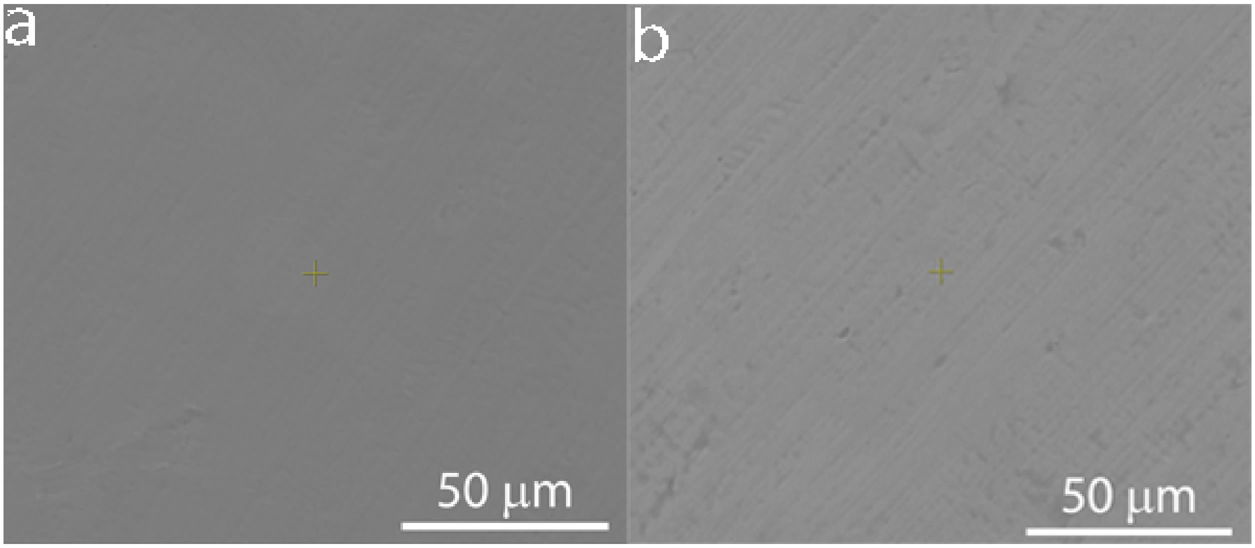

Figure S9. SEM image of stainless steel coin cell casing a) before and b) after 100 cycles with 0.5 M $Al(OPh)_3/PhMgCl$ in THF containing 0.5 M $LiPF_6$, and $LiMn_2O_4$ cathode.

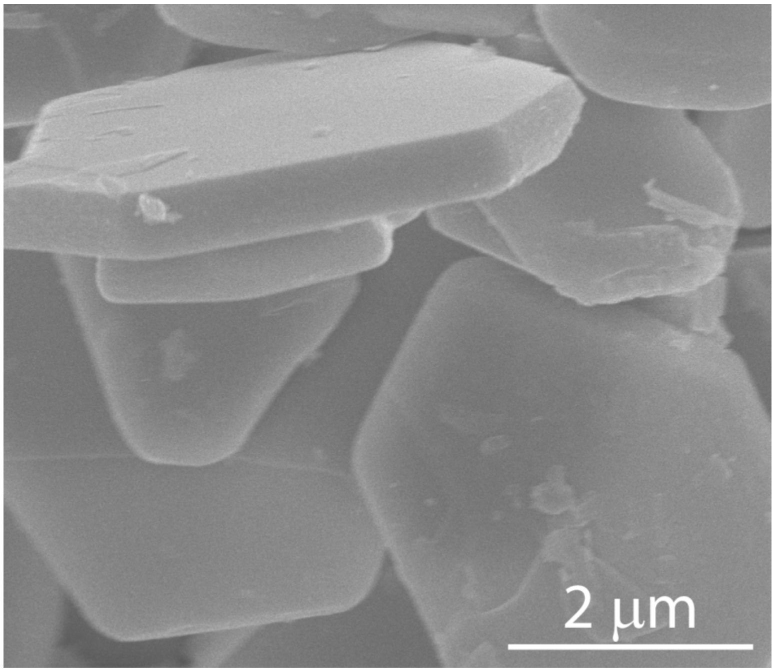

Figure S10. SEM image of WSe_2

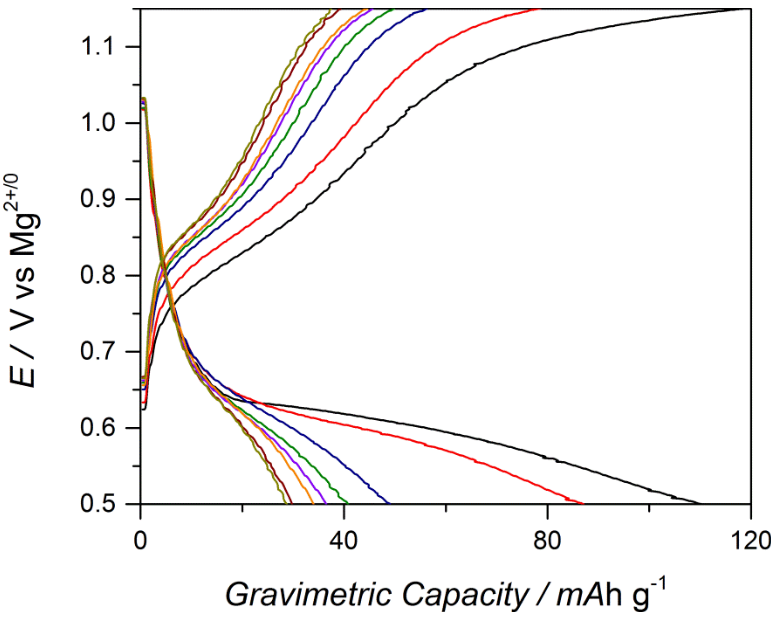

Figure S11. Typical charge/discharge profiles for a rechargeable battery with $Al(OPh)_3$/PhMgCl in THF, a Mg anode, a Mo_6S_8 cathode at a rate of C/20 (10 µA/cm²) cycles 1 (black), 2 (red), 10 (navy), 20 (olive), 40 (violet), 60 (orange), 80 (wine), and 100 (dark yellow).

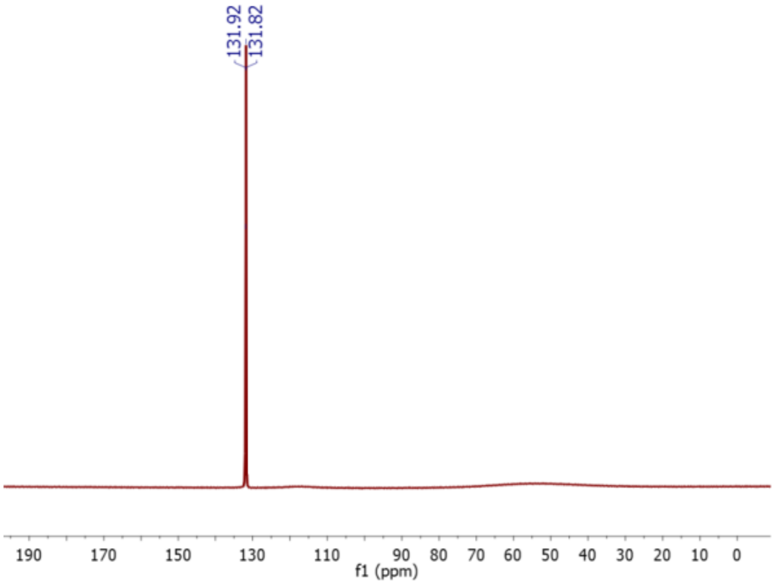

Figure S12. ^{27}Al NMR of 1:4 $Al(OPh)_3$/PhMgCl in THF giving one peak corresponding to $Al(Ph)_4^-$ (131 ppm)

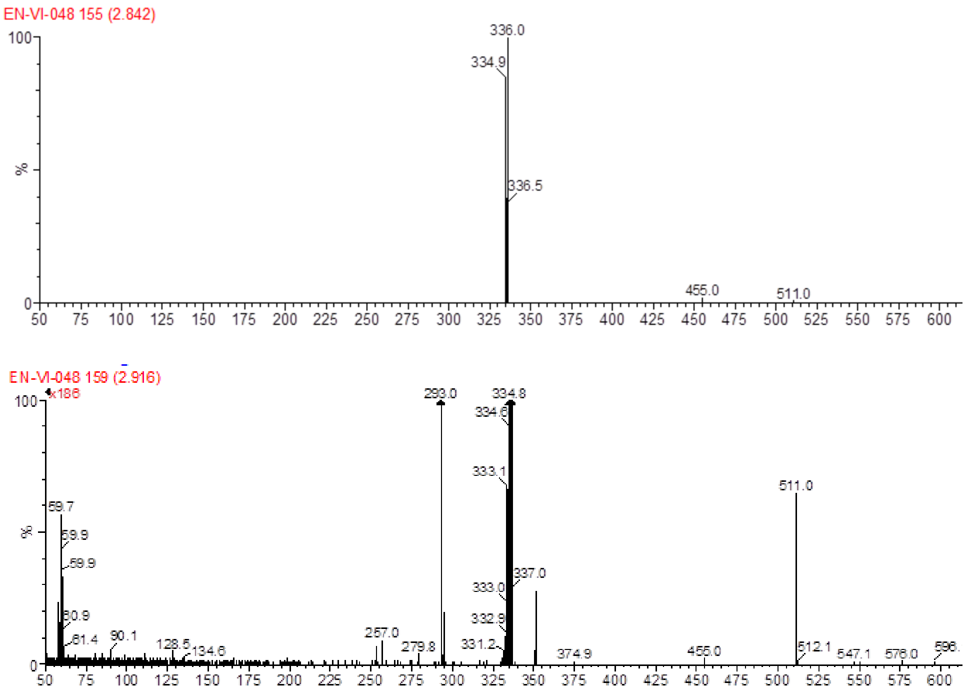

Figure S13. Electrospray ionization mass spectra in negative ionization mode of 1:4 $Al(OPh)_3$/PhMgCl giving $Al(Ph)_4^{-}$ (*m/z* 335); upon magnification the following species are identified: $Al(Ph)_3Cl^{-}$ (*m/z* 294), $Al(Ph)_3(OPh)^{-}$ (*m/z* 352).

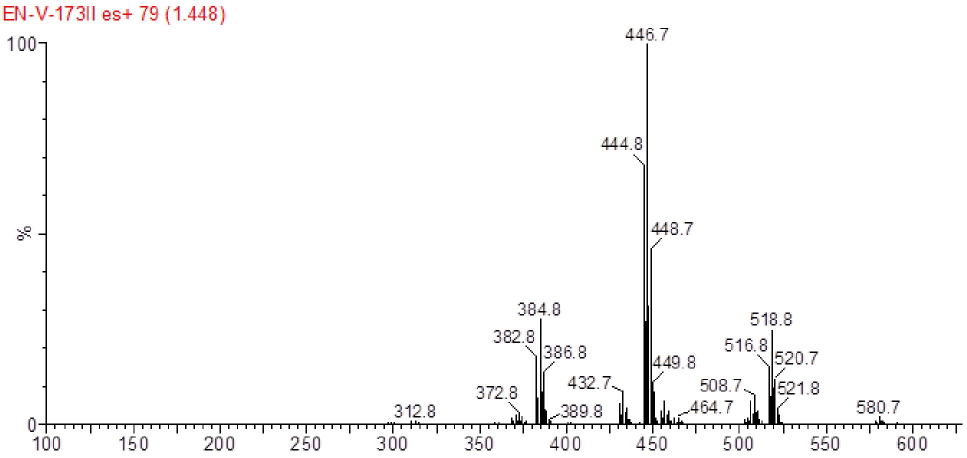

Figure S14. Electrospray ionization mass spectra in positive ionization mode of 1:4 $Al(OPh)_3$/PhMgCl giving the following species: $Mg_2Cl_3(THF)_4^{+}$ (*m/z* 446), $Mg_2(OPh)_3Cl(THF)_2^{+}$ (*m/z* 508), $Mg_2Cl_3(THF)_5^{+}$ (*m/z* 518).

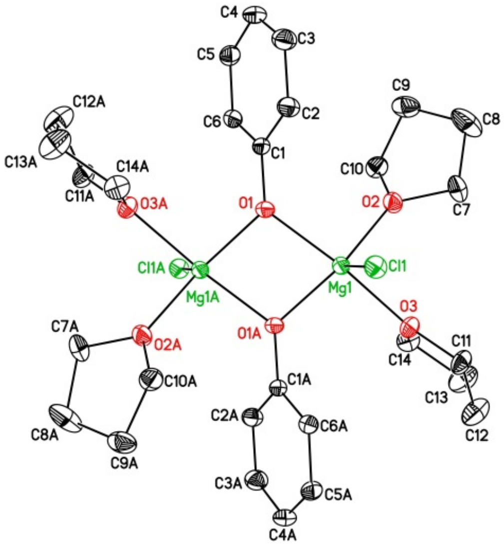

Figure S15. One X-ray crystal structures of the neutral Mg species $C_{28}H_{42}Cl_2Mg_2O_6$ isolated from a 1:4 $Al(OPh)_3$/PhMgCl electrolyte solution.

Table S1. Crystal data and structure refinement for en52 (CCDC #999561)

Identification code	en52
Empirical formula	$C_{28}H_{42}Cl_2Mg_2O_6$
Formula weight	594.14
Temperature	85(2) K
Wavelength	1.54178 Å
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	a = 7.23120(10) Å α = 90°
	b = 10.8165(2) Å β = 92.125(7)°
	c = 19.6313(14) Å γ = 90°
Volume	1534.43(12) Å^3
Z, ρ_{calc}	2, 1.286 g/cm^3
Absorption coefficient	2.616 mm^{-1}
F(000)	632
Crystal size	0.20 x 0.20 x 0.20 mm
θ range for data collection	4.51 – 68.24°
Limiting indicies	$-8 \leq h \leq 8$
	$-13 \leq k \leq 12$
	$-23 \leq l \leq 23$
Reflections collected/unique	42069 / 2810 [R(int) = 0.0751]
Completeness to θ = 68.24°	100%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6228 and 0.6228
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2810 / 0 / 172
$G.o.F.$ on F^2	1.139
Final R incides [$I > 2\sigma(I)$]	$R1$ = 0.0436; $wR2$ = 0.1229
R indices (all data)	$R1$ = 0.0463, $wR2$ = 0.1257
Largest diff. peak and hole	0.836 and –0.548 eA^{-3}

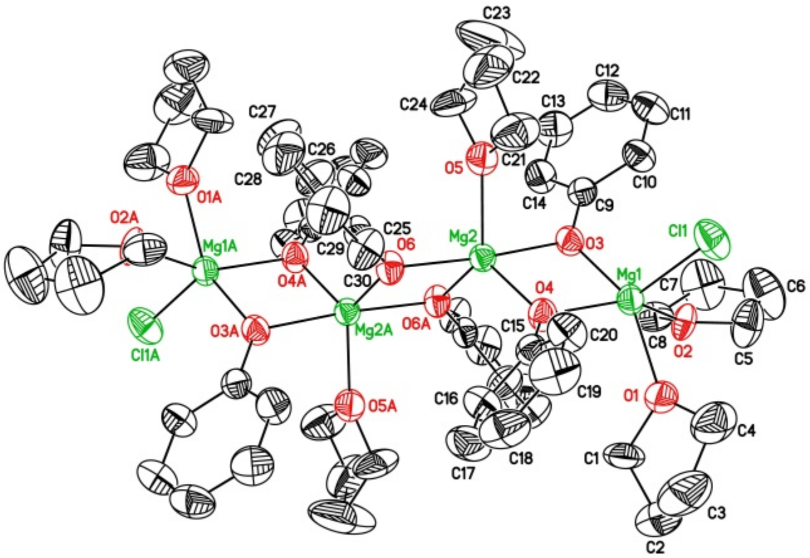

Figure S16. Second X-ray crystal structure of neutral Mg species $C_{60}H_{78}Cl_2Mg_4O_{12}$ isolated from a 1:4 $Al(OPh)_3$/PhMgCl electrolyte solution.

Table S2. Crystal data and structure refinement for en5153 (CCDC # 999562)

Identification code	en5153
Empirical formula	$C_{60}H_{78}Cl_2Mg_4O_{12}$
Formula weight	1159.36
Temperature	250(2) K
Wavelength	1.54178 Å
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions	a = 12.8707(7) Å α = 90°
	b = 19.0698(4) Å β = 102.113(4)°
	c = 12.8991(7) Å γ = 90°
Volume	3095.5(2) Å^3
Z, ρ_{calc}	2, 1.244 g/cm^3
Absorption coefficient	1.810 mm^{-1}
F(000)	1232
Crystal size	0.25 x 0.25 x 0.25 mm
θ range for data collection	4.64 – 68.25°
Limiting indicies	$-15 \leq h \leq 15$
	$-22 \leq k \leq 22$
	$-15 \leq l \leq 15$
Reflections collected/unique	75202 / 5663 [R(int) = 0.0523]
Completeness to θ = 68.25°	99.8%
Absorption correction	Semi-empirical from equivalents

Max. and min. transmission	0.6604 and 0.6604
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5663 / 448 / 631
G.o.F. on F^2	1.053
Final R incides [$I > 2\sigma(I)$]	$R1 = 0.0343$; $wR2 = 0.0915$
R indices (all data)	$R1 = 0.0358$, $wR2 = 0.0927$
Largest diff. peak and hole	0.203 and –0.236 eA^{-3}