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# Electronic Supporting Information for:

# A Fluorinated Dialkoxide-Based Magnesium-Ion Electrolyte

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## Methods

**Materials.** All synthetic procedures were carried out under an atmosphere of argon using standard Schlenk techniques and oven-dried glassware. 1,1,1,3,3,3-Hexafluoro-2-propanol (99%, HFIP, Oakwood Chemical), anhydrous 1,2-dimethoxyethane (99.5%, DME, Sigma-Aldrich), anhydrous inhibitor-free tetrahydrofuran (99.9%, THF, Sigma-Aldrich), and magnesium methoxide (6-10% in methanol, Sigma-Aldrich) were used as received. Ultra-dry aluminum chloride was used as received (99.999%, Alfa-Aesar).

**Electrochemical and surface measurements.** Electrochemical measurements were performed either in an argon-filled glove box (Vacuum Atmospheres) using a standard three electrode setup (Solartron 1287, Gamry Interface 1000E) or in coin cells (Arbin BT2000). Conductivity measurements were acquired with a conductivity meter (Mettler Toledo SevenCompact S230) paired with an InLab 751 conductivity probe. Linear sweep voltammograms for the measurement of oxidative stabilities were acquired at 5 mV $s^{-1}$ in a flooded cell using a standard three electrode setup with various metal electrodes of known area that had been polished with 1 µm alumina. The counter and reference electrodes were magnesium foil that were mechanically abraded in the glove box before use (99.95% GalliumSource, LLC). The commercially available disc electrodes used were platinum (2 mm dia., CH Instruments, Inc.), gold (2 mm dia., CH Instruments, Inc.), and glassy carbon (3 mm dia., CH Instruments, Inc.). In house-made 1/8-inch dia. disc electrodes were made using aluminum 6061, copper 101, and stainless steel 304.

Cyclic voltammograms were performed in 2032-type coin cells that were fabricated using a copper cathode, abraded magnesium anode, and Celgard 2400 separator material. A Teflon ring was used to limit the working electrode area in the coin cell. Sweep rates for cyclic voltammograms were typically 10 mV $s^{-1}$ unless otherwise noted. Limiting cathodic potentials were set either when a defined current value or potential was reached, after which the scan direction was reversed. Coulombic efficiency values were calculated by dividing the charge passed during stripping by the charge passed during plating.

SEM images and EDS spectra were acquired at a 15 keV accelerating voltage (FEI Quanta 200 FEG SEM). XPS spectra were recorded using a ThermoFisher Scientific K-Alpha XPS system. The samples were introduced to the XPS chamber using a vacuum transfer module from the glove box to prevent environmental contamination of the surfaces. The XPS spectra were recorded after sputtering the surface with a 3 kV argon ion beam for 5 minutes. Viscosity measurements were performed at 20°C with a Brookfield LVDV III Ultra rheometer using a cone/plate geometry with a CPE-40 spindle (accurate within ±3%).

Chevrel phase $Mo_6S_8$ was prepared according to a previous report.[35] A slurry of the active material was made that consisted of 85% active material, 7.5% Super-P carbon (TIMCAL), and 7.5% PVDF (Kynar) in 1-methyl-2-pyrrolidinone (99.5%, Sigma-Aldrich), and was mixed using a planetary mixer (DAC 150 FVZ, FlackTek Inc.). The slurry was cast on a copper substrate (McMaster-Carr) at a thickness of 40 µm and heated in a vacuum oven at 120°C for at least 8 hours. Average active material mass loading was 1.7 mg $cm^{-2}$. Full cells used an abraded Mg anode (99.95% GalliumSource, LLC) and Celgard 2400 separator material in a 2032-type coin cell case. The cells were cycled at constant current density of 10 mA $g^{-1}$, with voltage cutoffs of 0.4 V and 1.7 V.

**NMR spectroscopic analysis.** NMR spectra were acquired with a Bruker Avance III 500 MHz spectrometer, with chemical shifts reported in ppm. Solvents for the NMR experiments were the native electrolyte solvent paired with a lock solvent ($CDCl_3$, 99.8%, Cambridge Isotope Laboratories) in a 1.7 mm capillary tube (New Era Enterprises, Inc.). For $^{27}Al$ NMR spectra, a broad shift centered near 70 ppm resulting from aluminum in the NMR probe was subtracted from experimental spectra. Gaussian curve fits for peak deconvolution were performed using MestReNova 11 software.

**Synthetic procedures.** 1:2 $Mg(HFIP)_2$:$AlCl_3$: Electrolyte solutions on the order of 0.25 M by Mg were made by first dissolving one equivalent of $Mg(HFIP)_2$ in DME. $Mg(HFIP)_2$ was synthesized as previously reported.[19] Two equivalents of $AlCl_3$ were very slowly added to this solution due to the exothermicity of the addition process. The solution was electrochemically analyzed after reacting for a minimum of 72 hours, after which the mixture is a clear and colorless solution. $^{25}$Mg NMR (31 MHz, DME, 25 °C): δ 5.71 ($\nu_{1/2}$ = 128 Hz). $^{27}$Al NMR (130 MHz, DME, 25 °C): δ 83.96 ($\nu_{1/2}$ = 508 Hz), 94.50 ($\nu_{1/2}$ = 223 Hz), 104.03 ($\nu_{1/2}$ = 4.4 Hz). $^{1}$H NMR (500 MHz, DME, 25 °C): δ 5.34 (s, br, C*H*), 5.17 (m, C*H*), 4.68 (s, br, C*H*), 4.60 (s, br, C*H*). $^{19}$F NMR (470 MHz, DME, 25 °C): δ -75.88 (d, $^{3}J_{HF}$ = 6.7 Hz, $CF_3$), -76.09 (d, $^{3}J_{HF}$ = 6.5 Hz, $CF_3$), -76.36 (d, $^{3}J_{HF}$ = 6.4 Hz, $CF_3$), -76.65 (d, $^{3}J_{HF}$ = 6.1 Hz, $CF_3$), -77.03 (d, $^{3}J_{HF}$ = 4.3 Hz, $CF_3$).

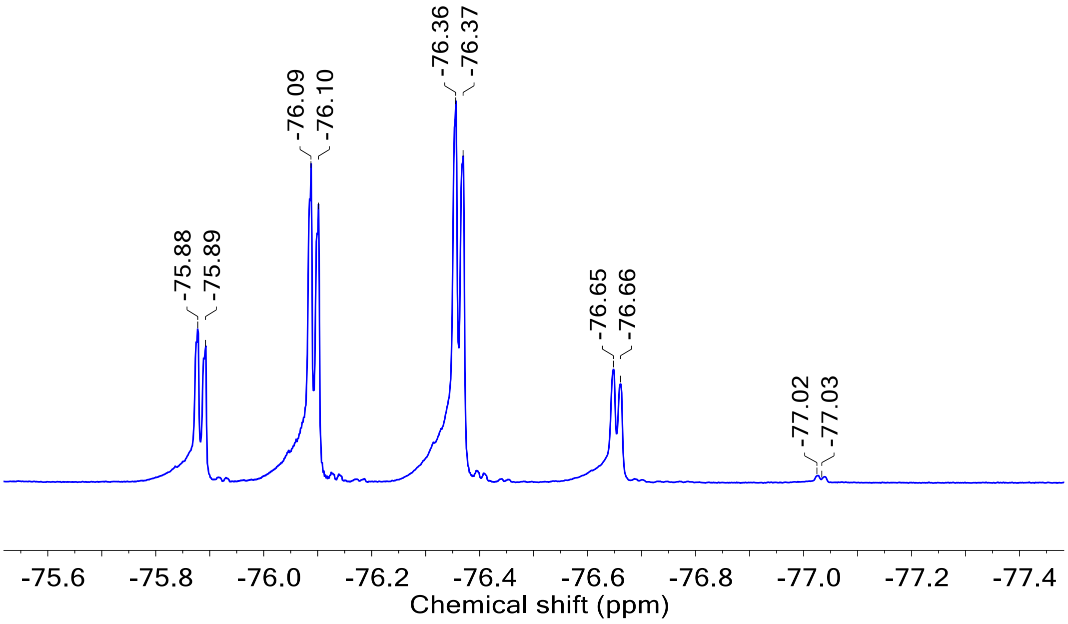

**Figure S1.** $^{19}$F NMR spectrum of 1:2 $Mg(HFIP)_2$:$AlCl_3$ in DME.

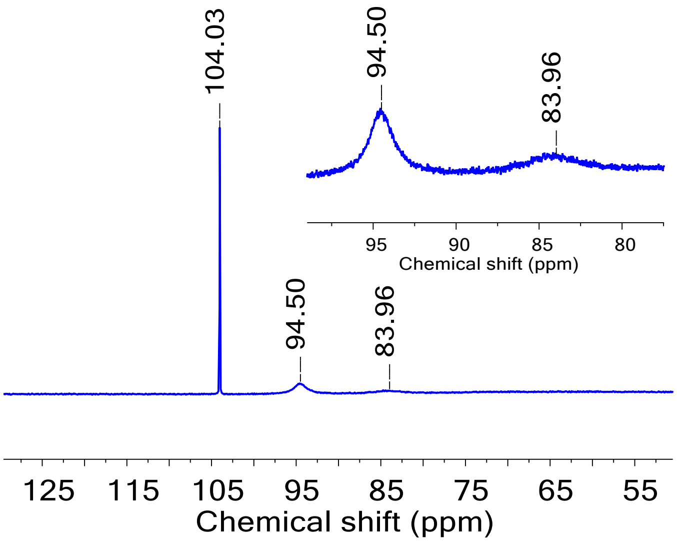

**Figure S2.** $^{27}$Al NMR spectrum of 1:2 $Mg(HFIP)_2$:$AlCl_3$ in DME.

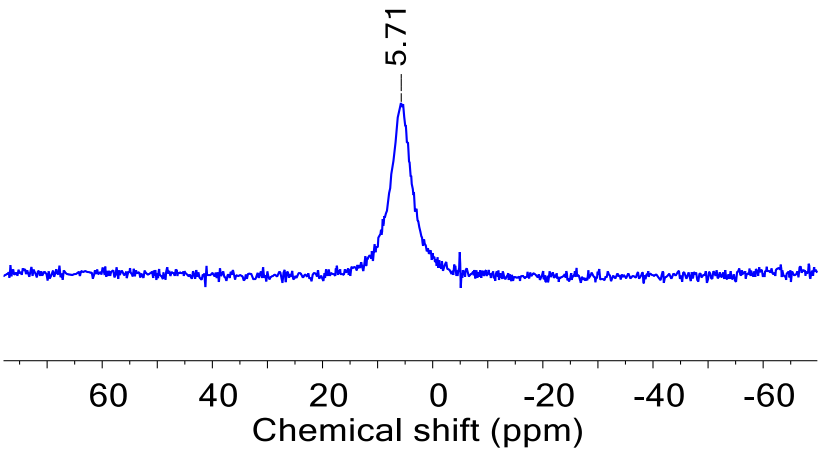

**Figure S3.** $^{25}$Mg NMR spectrum of 1:2 $Mg(HFIP)_2$:$AlCl_3$ in DME.

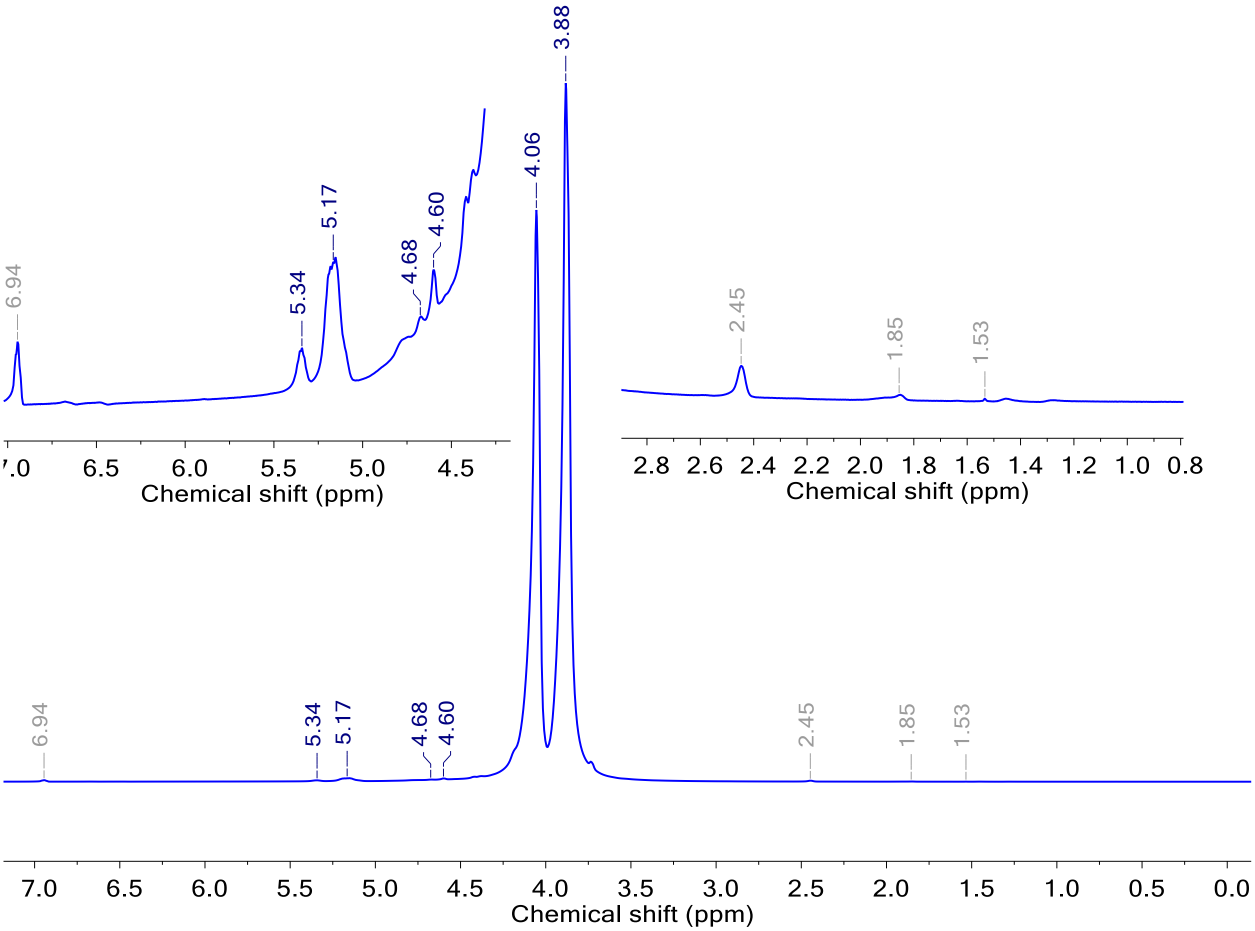

**Figure S4.** $^{1}$H NMR spectrum of 1:2 $Mg(HFIP)_2$:$AlCl_3$ in DME. Minor peaks marked in gray are impurities from the solvent.

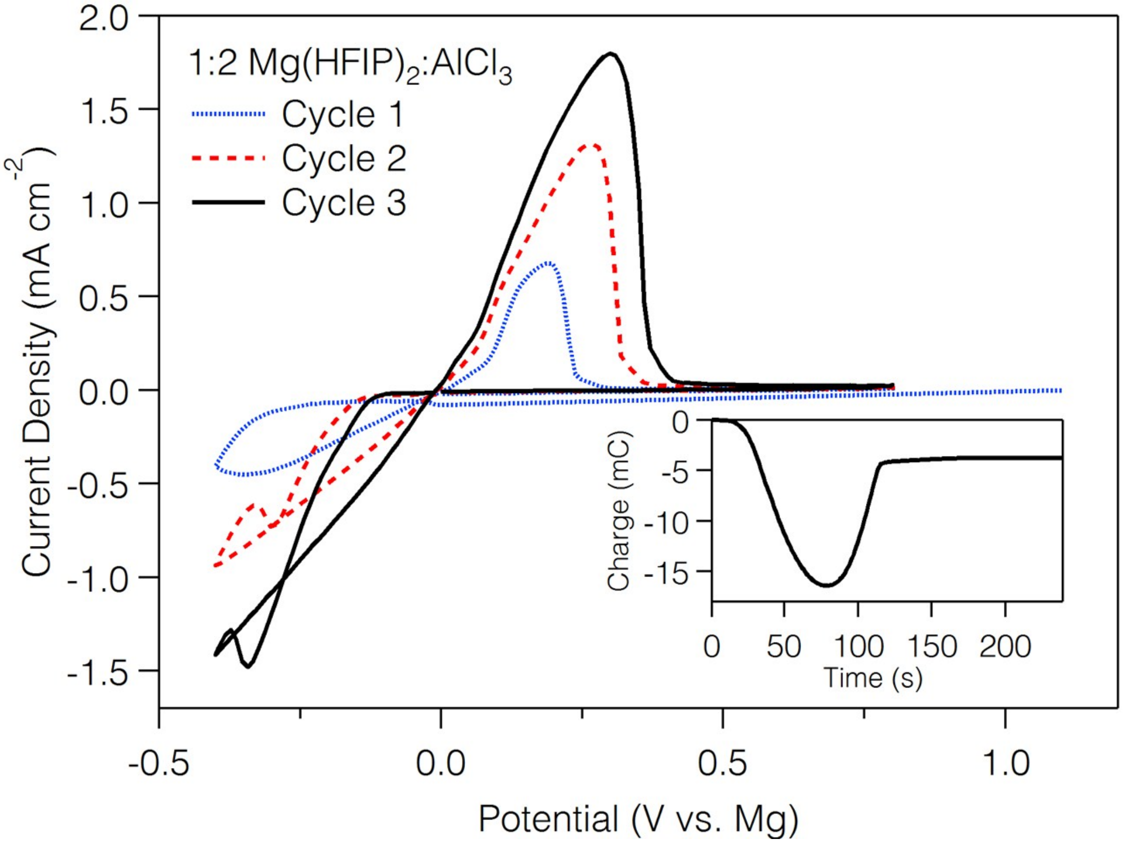

**Figure S5.** Cyclic voltammograms of the first three cycles (10 mV $s^{-1}$ scan rate) of a 0.25 M solution of Mg(HFIP)$_2$:AlCl$_3$ in DME. Inset shows charge passed during cycle 3.

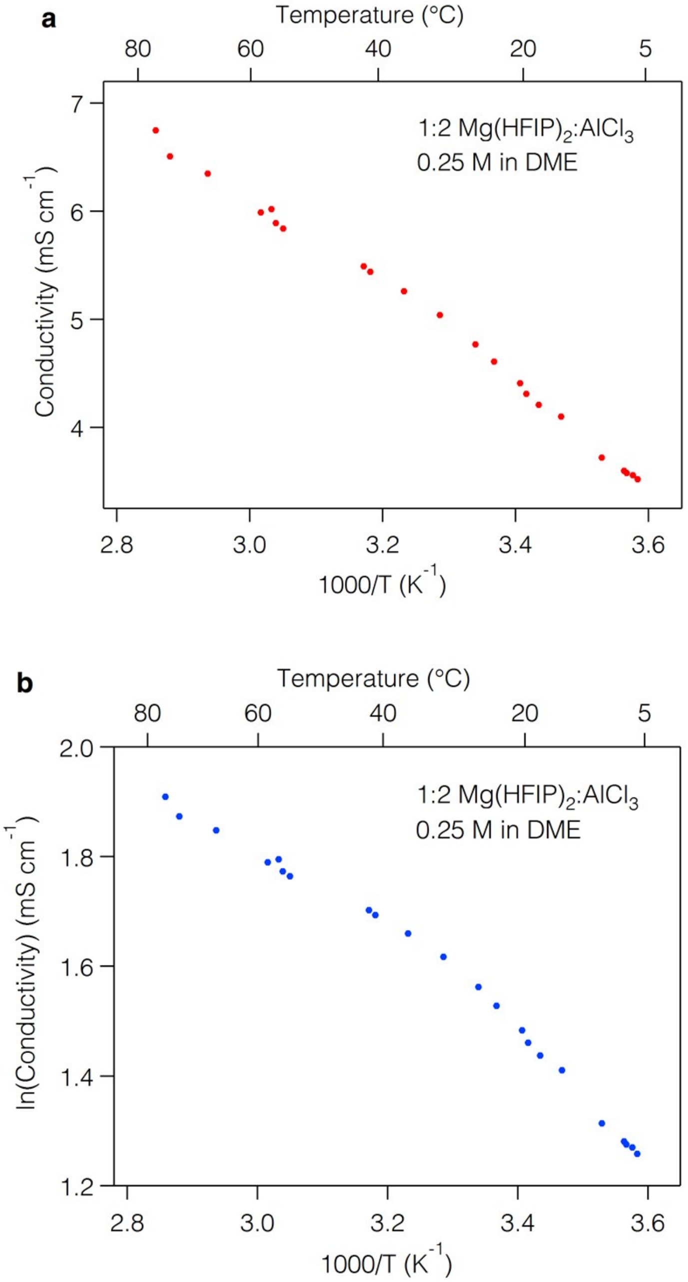

**Figure S6.** (a) Plot of conductivity vs. 1000/T for 0.25 M 1:2 $Mg(HFIP)_2$:$AlCl_3$ in DME (b) Arrhenius plot of the same data.

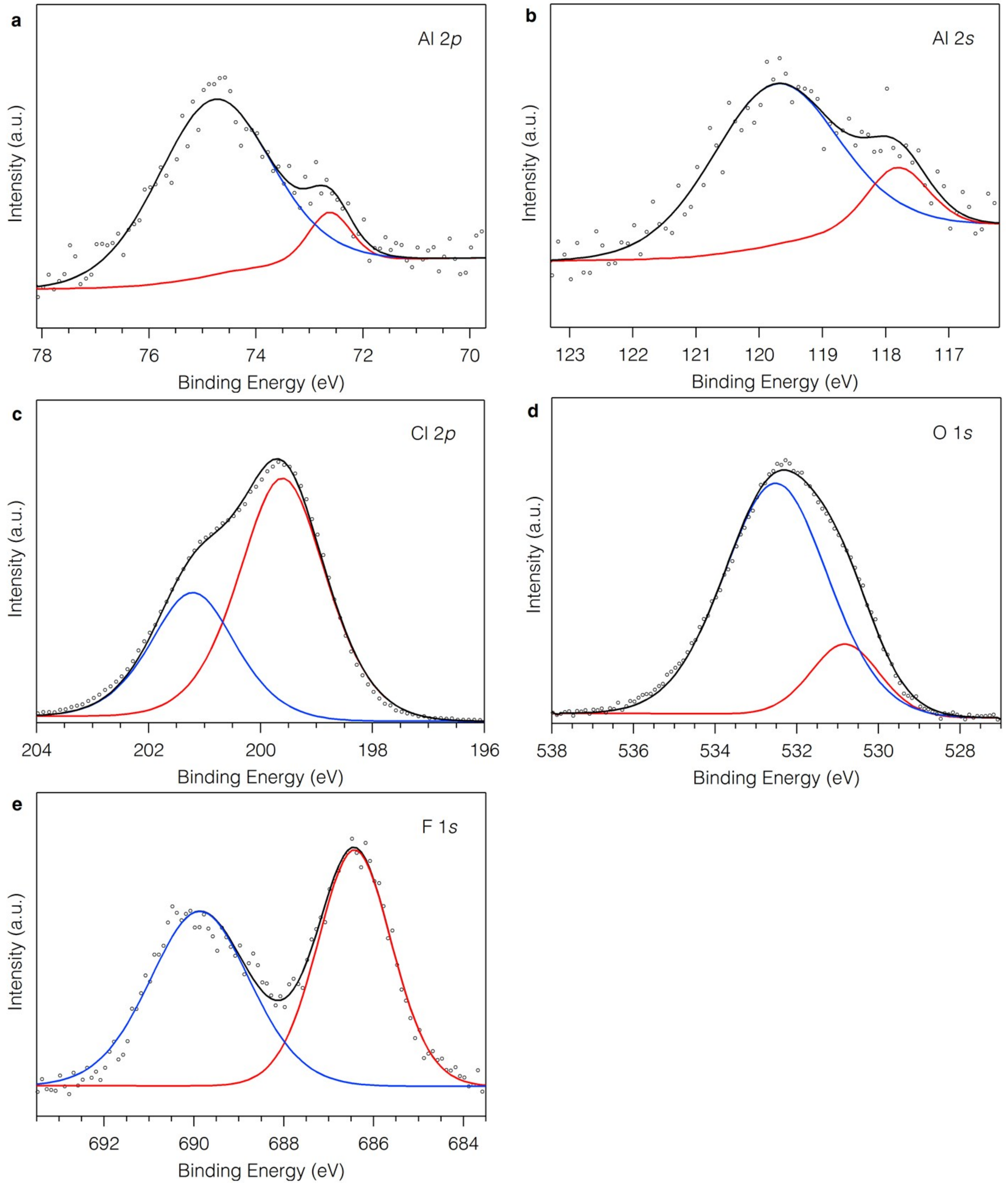

**Figure S7.** Surface characterization of magnesium deposits from 0.25 M 1:2 Mg(HFIP)$_2$:AlCl$_3$ in DME. Fitted XPS spectra of Mg deposit in (a) Al 2*p* (b) Al 2*s* (c) Cl 2*p* (d) O 1*s* (e) F 1*s* regions.

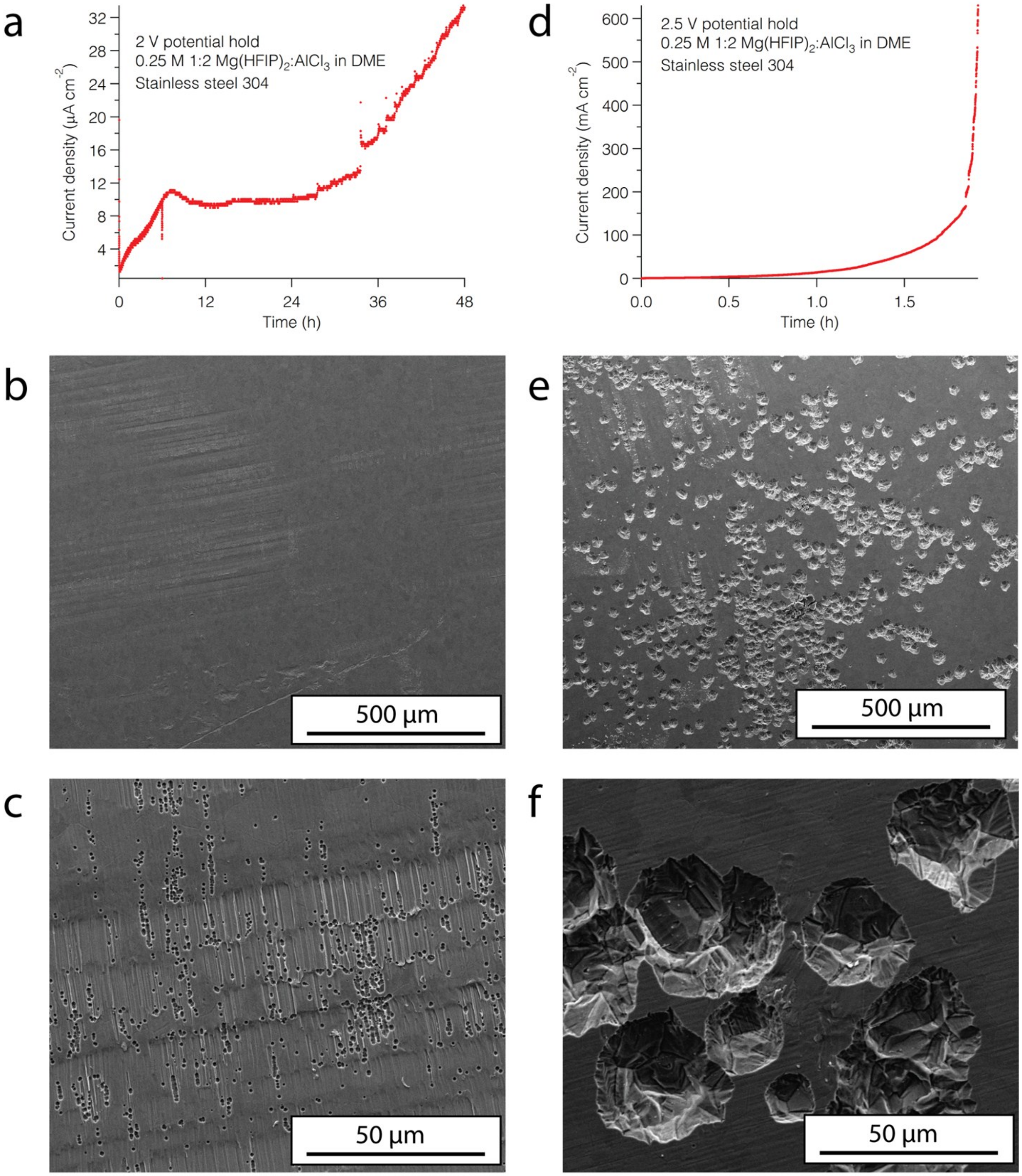

**Figure S8.** Chronoamperometric characterization of 304 SS held at 2 V and 2.5 V. Electrolyte was 0.25 M 1:2 Mg(HFIP)$_2$:AlCl$_3$ in DME. (a) Chronoamperometry data from 2 V, 48 hr coin cell (b) SEM image of oxidized surface at 100x (c) SEM image of oxidized surface at 1000x (d) Chronoamperometry data from 2.5 V, 2 hr coin cell (e) SEM image of oxidized surface at 100x (f) SEM image of oxidized surface at 1000x.