

Supplementary Information

Mg²⁺ ion-catalyzed polymerization of 1,3-dioxolane in battery electrolytes

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Methods

Electrolyte Preparation: All solutions were prepared in an LC Technology glovebox with inert Ar environment and water and oxygen content <0.5 ppm. Mg bis(trifluoromethanesulfonyl)imide (Solvionic, Inc) was dried at 200 °C under vacuum for 24 hours. Magnesium perchlorate and Lithium bis(trifluoromethanesulfonyl)imide (Sigma Aldrich) were dried at 140 °C and 160 °C, respectively under vacuum overnight. Magnesium triflate (STREM chemicals), Aluminum triflate, Lithium triflate, 1,3-dioxolane, and 1,2-dimethoxyethane (Sigma Aldrich) were used as-received. Solutions were mixed in 10 mL glass vials. In making the DOL solutions, micropipettes were used to add exact amounts of 1,3-dioxolane to the salts, e.g. 2 mL DOL added to 0.0474 g Al(OTf)₃ for 50 mM solution. The true molar concentration may be slightly less than 50 mM, but across samples the mole ratio of cation:DOL remains constant.

Electrochemical Testing: The electrolyte was made by mixing the Mg(ClO₄)₂ salt with DOL and fully dissolving it before adding the Mg(TFSI)₂ salt. While still liquid enough to pipette, the solution was drop-casted onto the stainless steel disks (15 mm diameter, 0.5 mm thick, MTI corporation) 62.5 μL at a time, with 125 μL total deposited on each disk. The electrolyte was left to polymerize for 3 hours before sandwiching two halves together and closing in a coin cell (2025, MTI). The thickness was measured after EIS by taking apart the coin cell and measuring the whole stack with a micrometer and subtracting the thickness of the stainless steel disks. Impedance data was collected at the open circuit potential (generally 5-10 mV) between 50 kHz and 10 mHz with 100 mV amplitude, unless otherwise indicated. Fitting was performed using Z-fit in the EC-Lab software. The impedance was monitored over time, but the final reported ionic conductivities are after full polymerization which occurred ~1 week after closing the cells.

H-NMR: All samples were prepared in the inert glovebox environment using d₆-DMSO (Cambridge Isotope Inc.) unless otherwise indicated and referenced to the DMSO solvent residual signal (TMS=0). H-NMR analyses were performed on a Bruker AV-400 MHz spectrometer and analyzed using TopSpin software.

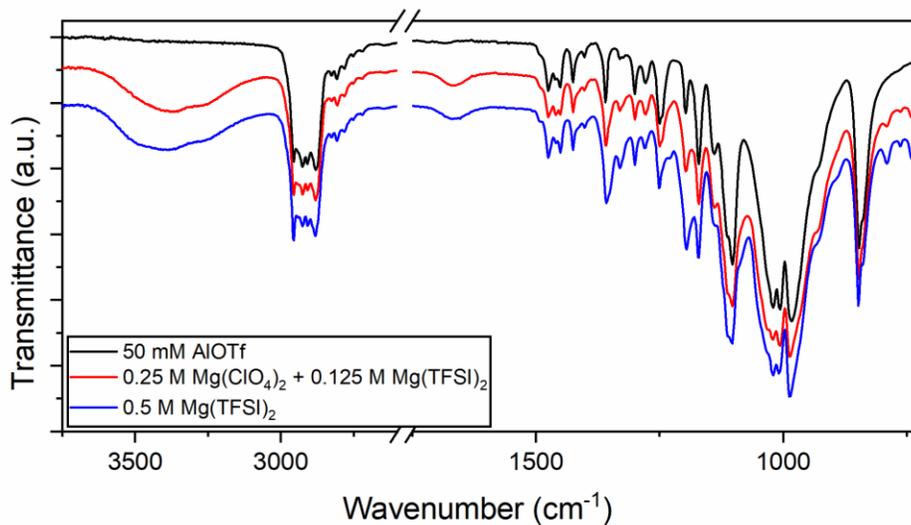


Figure S1. FTIR spectrum of fully polymerized DOL with different amount of salt catalysts. Major C-H and C-O functional groups indicative of poly-DOL structure are visible around 2900 and 1000 cm^{-1} , respectively. The presence of the OH peak around 3400 cm^{-1} is apparent likely due to cleaning of the diamond window with ethanol and collecting the next spectra before it was dry, as all samples were air-exposed for similar times and the 50 mM AlOTf sample, collected first, does not show an -OH peak. The higher salt concentrations in the red and blue samples may also account for slightly more water.

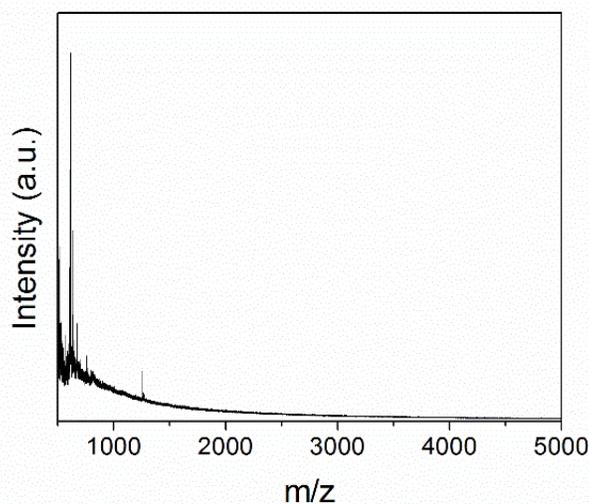


Figure S2. MALDI-TOF mass spectrum of 0.35 M LiTFSI in DOL after 5 days in the glovebox.

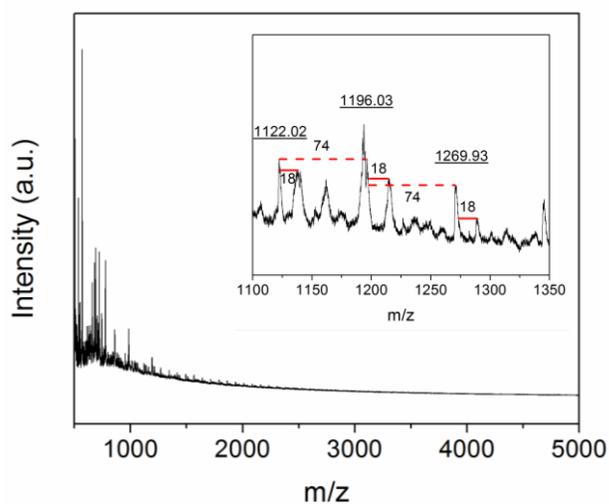


Figure S3. MALDI-TOF mass spectrum of 0.25 M $\text{Mg}(\text{ClO}_4)_2$ in DOL after 5 days.

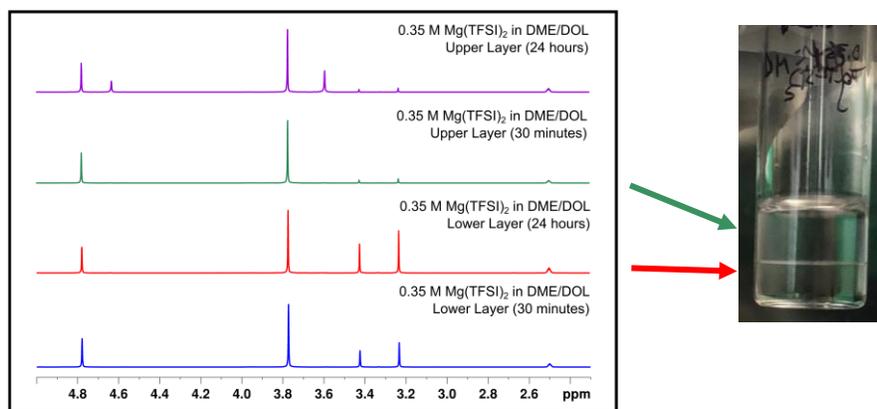


Figure S4. ^1H -NMR spectra of 0.35 M $\text{Mg}(\text{TFSI})_2$ in 1:7 (v/v) DME/DOL of the top and bottom layers of the separated layers after different reaction times.

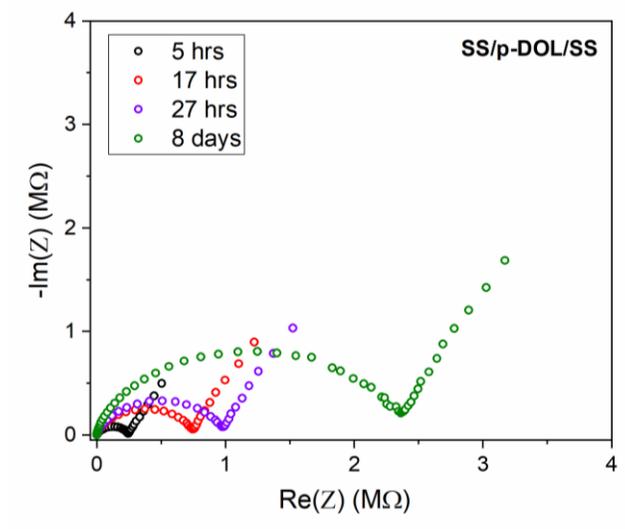


Figure S5. Nyquist Impedance plot for p-DOL (0.125M Mg(TFSI)₂ + 0.25 M Mg(ClO₄)₂ in DOL) polymer sandwiched between two stainless steel electrodes, monitoring the impedance over time. The polymer is 110 μm thick, EIS recorded between 750 kHz and 100 mHz with 100 mV amplitude. The ionic conductivity at 5 hours is $2.5 \times 10^{-8} \text{ S cm}^{-1}$.

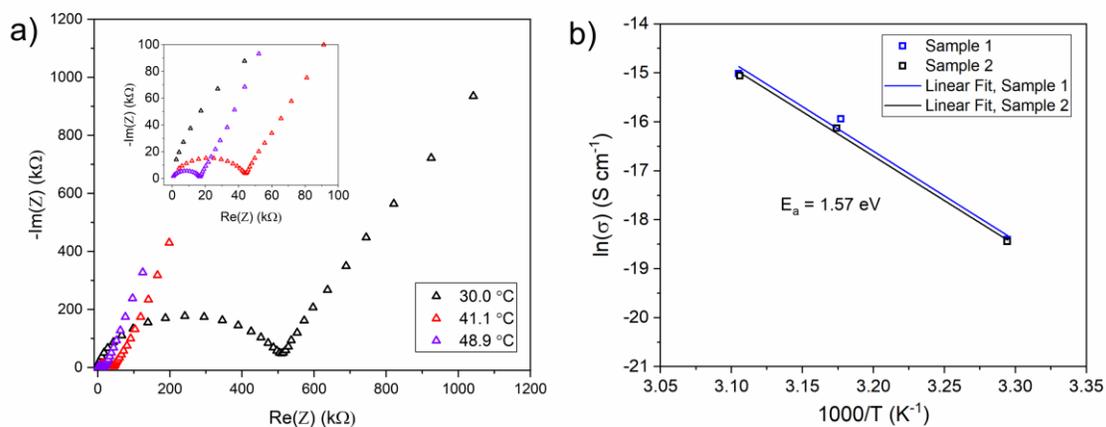


Figure S6. Temperature measurements of p-DOL a) Nyquist impedance plots for p-DOL (0.125M Mg(TFSI)₂ + 0.25 M Mg(ClO₄)₂ in DOL) between two stainless steel electrodes at different temperatures, at frequencies from 50 kHz to 100 mHz with 100 mV amplitude, and b) is the activation energy calculated for two different samples (the EIS data in (a) is from Sample 1).

Table S1. Values from the equivalent circuit model in Figure 3

Sample	R_1 (M Ω)	CPE ₁ Q	CPE ₁ n	CPE ₂ Q	CPE ₂ n	χ^2
Mg-DOL (84 μ m)	1.895	2.05×10^{-9}	0.78	8.30×10^{-7}	0.66	0.84