

Electronic Supplementary Information

Designing Solvate Ionogel Electrolytes with Very High Room-Temperature Conductivity and Lithium Transference Number

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Materials

Poly(ethylene glycol) dimethacrylate (P₇₅₀, average M_n~750Da, Sigma-Aldrich), triethylene glycol monomethyl ether methacrylate (TEGMA, Sigma-Aldrich), poly(ethylene glycol) (PEG₃₃₅₀, 6 mmol hydroxyl end groups, average M_n ~3350, Sigma-Aldrich), benzoyl peroxide (BPO, reagent grade, ≥98%, Sigma-Aldrich), 2,2'-azobisisobutyronitrile (AIBN, 98%, Sigma-Aldrich), acetonitrile (99.9%, extra dry, anhydrous, Fisher), methanol (HPLC, Fisher), hexanes (99%, mixture of isomers, Fisher) and dichloromethane (≥99%, Fisher) were used as-received. Methacryloyl chloride (97%, Sigma-Aldrich) was stored in a freezer with an airtight seal and distilled over CaH₂ under N₂ before use. Tetraethylene glycol dimethyl ether (≥99%, Aldrich) and 1,4-dioxane (≥99%, Fisher) were dried with 3Å molecular sieves and stored in an argon-atmosphere glovebox (Vacuum Technology Inc, <0.01ppm H₂O and O₂) prior to use. LiTFSI was purchased from 3M and dried at 120°C under Ar, then stored/used in an argon-atmosphere glovebox. Lithium chips (99.9%, 15.6mm diameter, 0.45mm thickness) were purchased from MTI Corp and stored/used in an argon atmosphere glove box. N-[2-(2-(2-(Methacryloyloxy)ethoxy)ethoxy)-ethyl]-N-methyl-pyrrolidinium

bis(trifluoromethanesulfonyl)imide (PyrTFSIMA) was synthesized according to literature on similar analogs.¹ All methacrylates and radical initiators were stored in a freezer between uses.

Experimental

Synthesis of Li(G4)TFSI: LiTFSI was weighed into a glass beaker inside of an argon-atmosphere glove box, then an equimolar amount of tetraethylene glycol dimethyl ether ($\geq 99\%$, Aldrich, dried over 3Å molecular sieves) was gradually added with stirring and mild heating. Complete dissolution occurred within several hours, resulting in a clear, viscous liquid, which was subsequently dried under Ar at 120°C for 12 hours, then under vacuum for an additional 12 hours, then stored in an argon-atmosphere glovebox.

Synthesis of poly(ethylene glycol) dimethacrylate, average $M_n \sim 3500$ (P_{3500}): To a stirred solution of PEG₃₃₅₀ (10.05 g, 6 mmol hydroxyl end groups) dissolved in 40 mL anhydrous acetonitrile was dropwise added freshly distilled methacryloyl chloride (1.76 mL, 18 mmol) at 0 °C under an argon atmosphere. The mixture was left stirring at 0 °C for 30 min, then gently heated at 40 °C for 8 hours. The excess methacryloyl chloride was quenched by addition of methanol and the volatiles were removed by rotary evaporation to give the crude product, which was then dissolved in dichloromethane and precipitated by addition of hexanes. The solid was collected by filtration and again dissolved in dichloromethane, followed by addition of activated carbon. The mixture was stirred at room temperature under nitrogen atmosphere for 2 hours. After removal of activated carbon, the solution was again precipitated by addition of hexanes, and filtered to give an off-white powder of P₃₅₀₀ (8.72 g). The product was stored in a freezer and used within 1 month of synthesis.

Fabrication of free-standing ionomer gels: BPO powder was dissolved in 1,4-dioxane in the amount of 3-5%mol relative to the methacrylate content of the desired gel formula; alternately, an identical concentration of AIBN was dissolved in dichloromethane ($\geq 99\%$, Fisher, opened under Ar and used as received). Polymerizable molecules, Li(G4)TFSI, and initiator solution (BPO/dioxane for SIG 1, AIBN/DCM for SIGs 2-5) were sequentially added in appropriate amounts to a glass vial followed by vigorous stirring to ensure homogeneity. The resulting solution was then vacuum dried with stirring at room temperature for 2-3 hours, in order to remove solvent. For DSIG 5, an appropriate amount of 1,4-dioxane was then re-added under argon. This precursor solution was transferred to a mold consisting of soda-lime glass plates (Colorado Concept Coatings) treated with siliconizing agent (Aquaphobe CM, Gelest) and separated by two hollow rectangular Kapton films measuring 5 mils ($\sim 128\mu\text{m}$) each. The mold was sealed shut using permanent magnets over both ends, then transferred into an oven at 80°C for 6 hours to cure the ionogel, followed by cooling overnight. For all gels except DSIG 5, the top plate of the mold was then removed and the exposed gel was vacuum dried for a minimum of 48 hours to remove any traces of solvent remaining. All of the above operations were performed in an argon-atmosphere glove box. All ionogels appeared as transparent, flexible films of approximately 0.25mm thickness. Average film height for each batch of gel was measured using an optical laser microscope (Olympus OLS41).

Conductivity measurements: 7mm diameter gel samples were sandwiched between 15.5mm diameter stainless steel discs and connected to a Gamry 5000E Interface potentiostat/galvanostat via flat clip. Galvanostatic electrochemical impedance spectroscopy was performed (RMS $10\mu\text{A}$) at frequencies ranging from 100kHz to 100Hz, with output voltage measured by the instrument. Resulting data were fitted to an appropriate equivalent circuit (**Figure 1d**) using Gamry EChem

Analyst software, and the limiting resistance at high frequency (R_{bulk}) converted to bulk ionic conductivity using the thickness (l) and cross-sectional area (A) of the sample (**Equation S1**).

$$\kappa = \frac{l}{R_{\text{bulk}}A} \quad (\text{S1})$$

Lithium transference number measurements: Lithium chips were gently polished inside of an argon-atmosphere glovebox using 320 grit followed by 600 grit sandpaper (Norton T414 Blue-Bak) to remove excessive surface oxidation and ensure consistency between samples. The lithium chips were then pressed onto stainless steel discs. A 19mm diameter gel separator (or Whatman GF/C separator with 80 μ L liquid electrolyte) was inserted between the chips, and the whole assembly placed into CR2032 coin cells (Pred Materials) which were sealed using an electric crimping machine (MTI Corp). In order to measure t_{Li^+} of gels, the Evans-Vincent-Bruce method was followed,² with galvanostatic impedance spectra (100kHz-0.1Hz, RMS 10 μ A) collected before and after a potentiostatic polarization of 5mV for 6 hours performed on a Gamry 5000E Interface potentiostat/galvanostat. Polarization and impedance spectroscopy was performed again following this to ensure reproducibility, and this second set of data was used for calculations. Impedance spectra were fitted to a two-semicircle Randles model (with constant phase elements modeling non-ideal capacitive processes) in series with a constant phase element to model the low-frequency diffusive region (**Figure S1g**). For each spectrum, high-frequency real intercept was subtracted from low-frequency real intercept to obtain total interfacial resistance (R_i). The polarization voltage (ΔV), initial interfacial resistance ($R_{i,o}$), interfacial resistance after steady-state current was attained ($R_{i,ss}$), initial current (i_o), and steady-state current (i_{ss}) were plugged into **Equation S2** to determine t_{Li^+} .

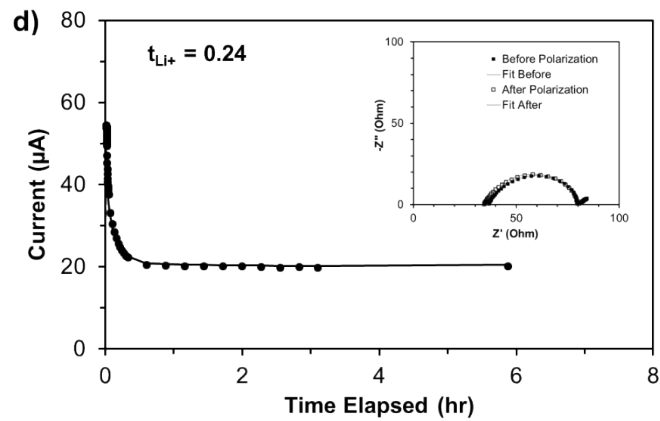
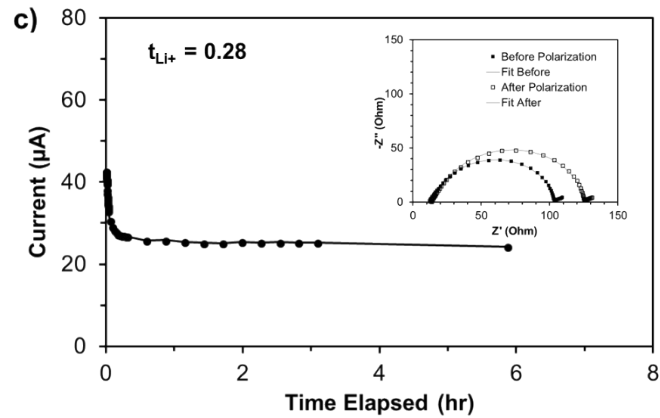
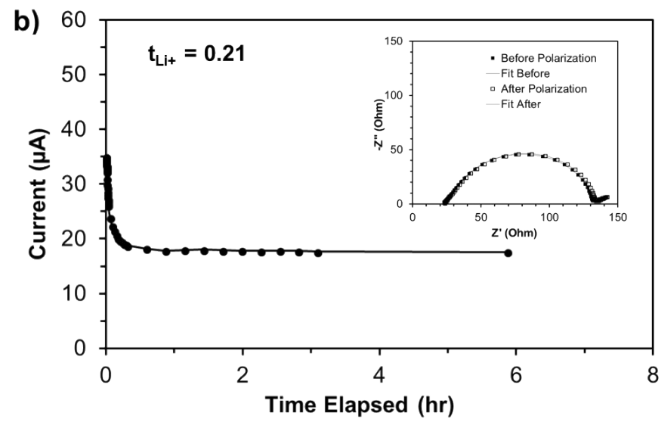
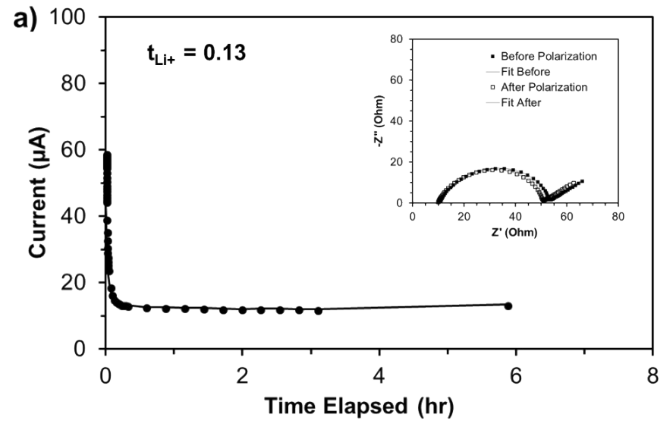
$$t_{\text{Li}^+} = \frac{(\Delta V - R_{i,o}i_o)}{(\Delta V - R_{i,ss}i_{ss})} \cdot \frac{i_{ss}}{i_o} \quad (\text{S2})$$

Time-to-short-circuit and stripping/plating experiments: Li|Li symmetric cells were prepared as above, then either galvanostatically polarized at 0.1 mA/cm² (time-to-short-circuit) or cycled between ±0.1 mA/cm² at 3-hour intervals (stripping/plating) using an Arbin LBT ±5V-200mA battery testing system, and data collected using the included MITS Pro software. A short circuit was considered to have formed when an abrupt, sustained (>5hrs) drop in voltage was observed.

Thermal measurements: TGA experiments were performed under flowing N₂ gas (50mL/min) using a Shimadzu TGA-50 Thermogravimetric Analyzer. Samples (8-10mg) were transferred into pre-weighed aluminum pans in an argon-atmosphere glove box, then weighed on a microbalance and loaded into the instrument within ~1 minute. Samples were then heated at 10°C/min to 80°C, held for 15 minutes to drive off any superficial moisture absorbed during transfer, then heated at 10°C/min to 120°C and held for two hours while weight loss was recorded. DSC thermograms were recorded under flowing N₂ gas (50mL/min) using a liquid-nitrogen-cooled Shimadzu DSC-60 Plus Differential Scanning Calorimeter. Samples (3-5mg) were transferred into aluminum pans and covered, then cooled to below -110°C at -10°C/min. Samples were held at this temperature for 10 minutes, then warmed to 100°C at 10°C/min, resulting in the reported curves.

Mechanical measurements: Uniaxial compression testing was performed using an Instron 5585H test frame equipped with a 50N load cell. 14mm diameter gel samples (thickness determined by a micrometer) were placed between PTFE platens and compressed to 1N applied force at a strain rate of 5µm/min. Response was linear (elastic) for all samples and compression was repeated until slopes converged, the final measurement being reported as elastic modulus. Then, samples were compressed to 50N at 25µm/min and the resulting stress-strain curves plotted as **Figure S2**.

Raman spectroscopy: Raman spectra were collected at $\sim 23^{\circ}\text{C}$ between $500\text{-}1600\text{cm}^{-1}$ on a Renishaw InVia Raman Microscope (785nm laser, 0.5cm^{-1} resolution), and data analysis was performed with Renishaw WiRE 3.4 software. Samples of Li(G4)TFSI (“SIL”), dioxane, and 5:1 + 1:1 volumetric combinations of the two, respectively, were analyzed on a cleaned silicon substrate. In order to normalize signals to Li(G4)TFSI concentration, the $1125\text{-}1150\text{cm}^{-1}$ region was fit with two curves ($\sim 1139\text{cm}^{-1}$ and $\sim 1128\text{cm}^{-1}$) to represent signals from G4 and dioxane, respectively, neither of which show much dependence on Li^{+} coordination state.^{3,4} The intensity of the peak at 1139cm^{-1} was then normalized between all samples, and the resulting data plotted as Figure S6.



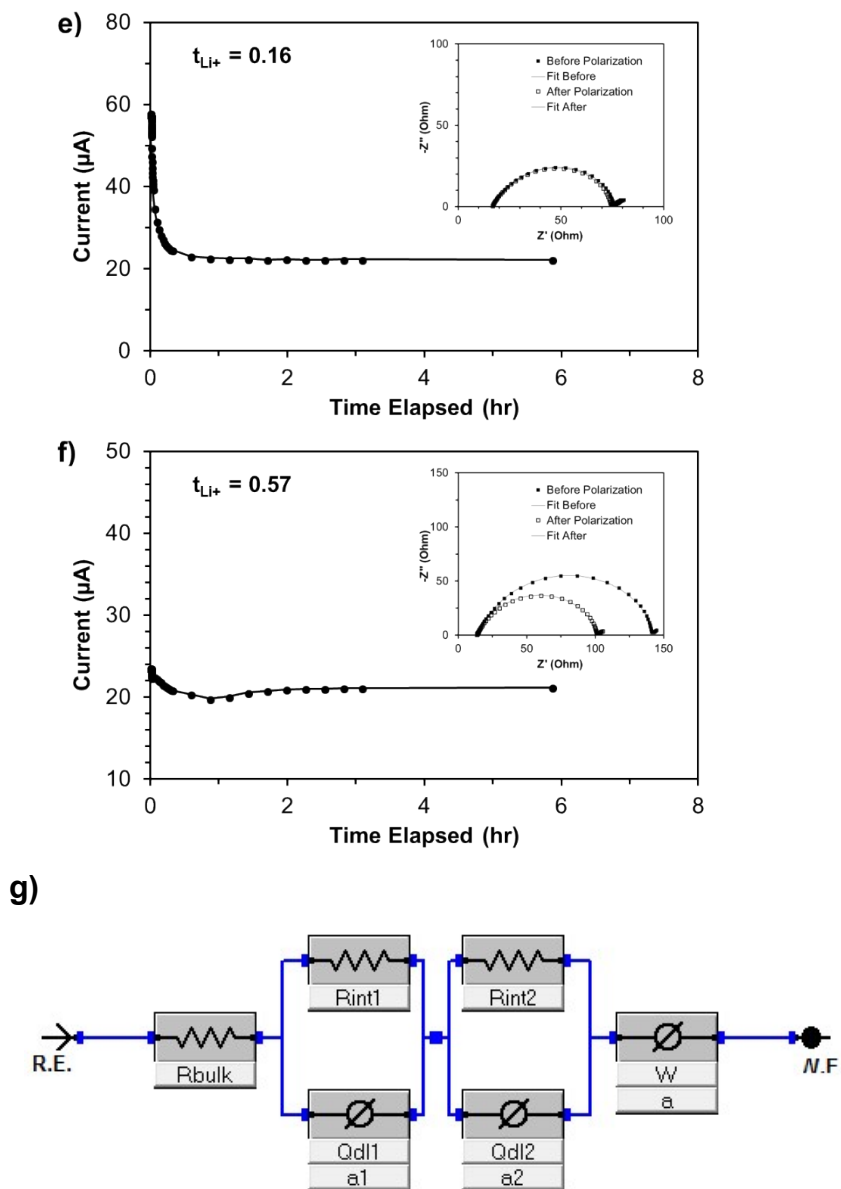


Figure S1. Chronoamperometry data (inset: Nyquist plots of impedance data) used to determine t_{Li^+} for **a)** Li(G4)TFSI, **b)** SIG 1, **c)** SIG 2, **d)** SIG 3, **e)** SIG 4, **f)** DSIG 5. **g)** Equivalent circuit used to fit symmetric cell impedance data.

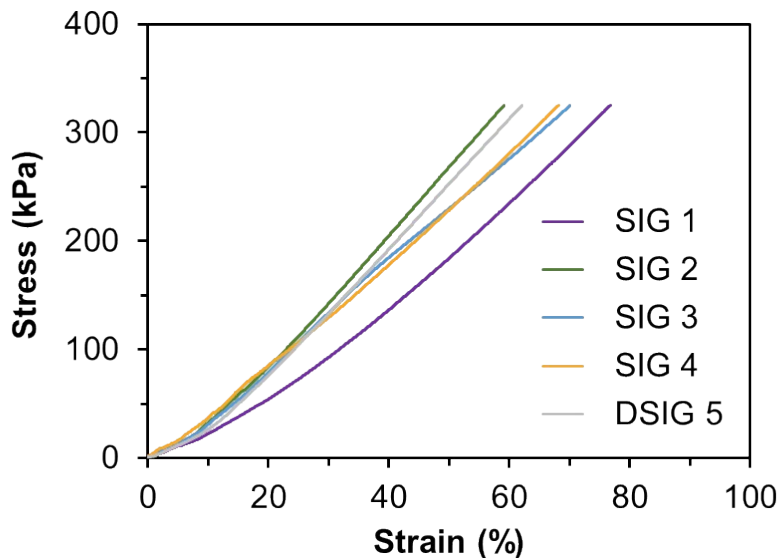


Figure S2. Stress-strain curves for SIGs under uniaxial compression. Curve end points correspond to the pressure limit of the experiment (325kPa), not sample failure.

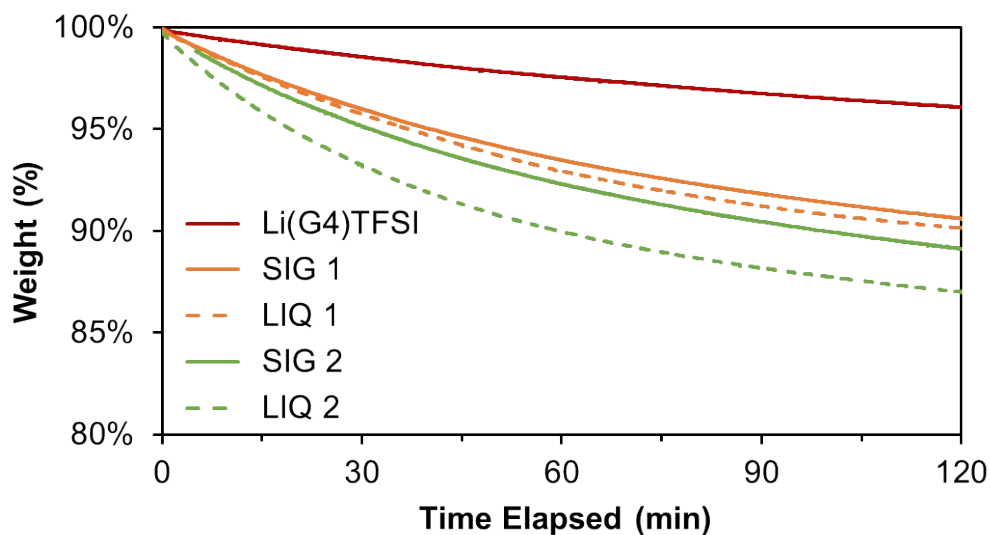


Figure S3. Weight loss of SIGs/LIQs 1 and 2, compared to Li(G4)TFSI, over 2 hours at 120°C. Both LIQs show increased weight loss compared to their crosslinked SIG counterparts, indicating a greater tendency of PEG to compete with G4 for Li^+ binding in the solution vs. solid state. This trend is more significant for the P_{3500} formulas (SIG/LIQ 2), which is above PEG's entanglement molecular weight, than for the P_{750} formulas (SIG/LIQ 1).

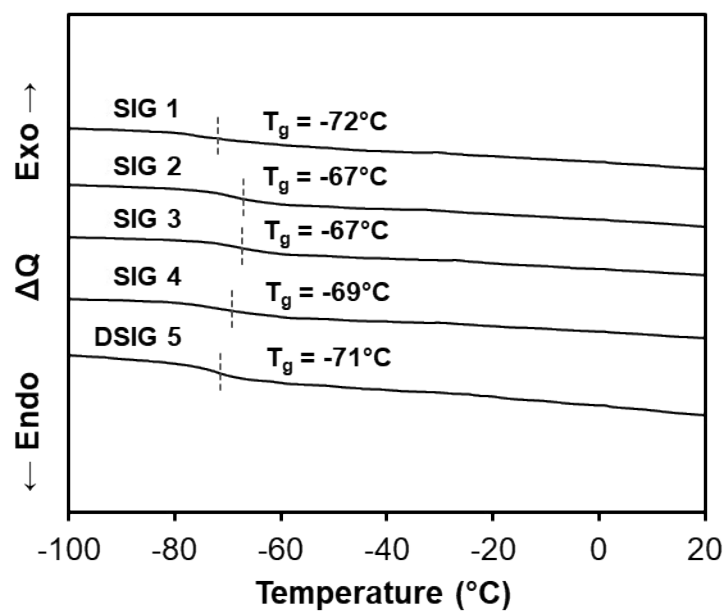


Figure S4. DSC thermograms and glass transition temperature (T_g) values for SIGs 1-5. The dashed vertical lines are a visual aid to mark T_g . Only slight variation of glass transition was observed between SIG formulas, although values for formulas containing P_{3500} tend to be very slightly higher. No melting peak for 1,4-dioxane (lit. 11.8°C) was observed in SIG 5, indicating strong interactions between the solvent and SIL/polymer which prevent crystallization.

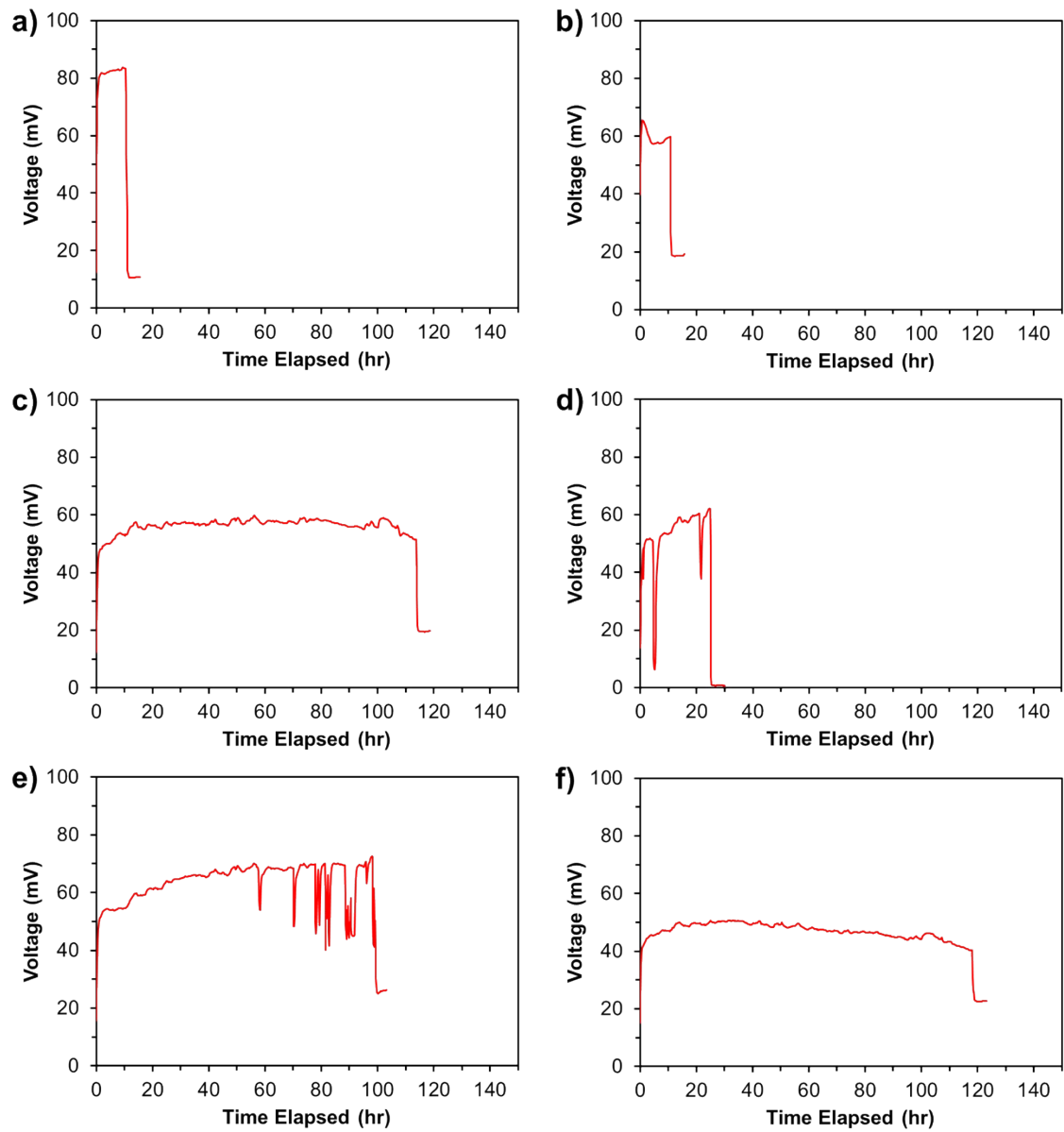


Figure S5. Symmetric cell voltage vs. time elapsed in time-to-short-circuit experiments at 0.1 mA/cm² for **a)** Li(G4)TFSI, **b)** SIG 1, **c)** SIG 2, **d)** SIG 3, **e)** SIG 4, **f)** DSIG 5.

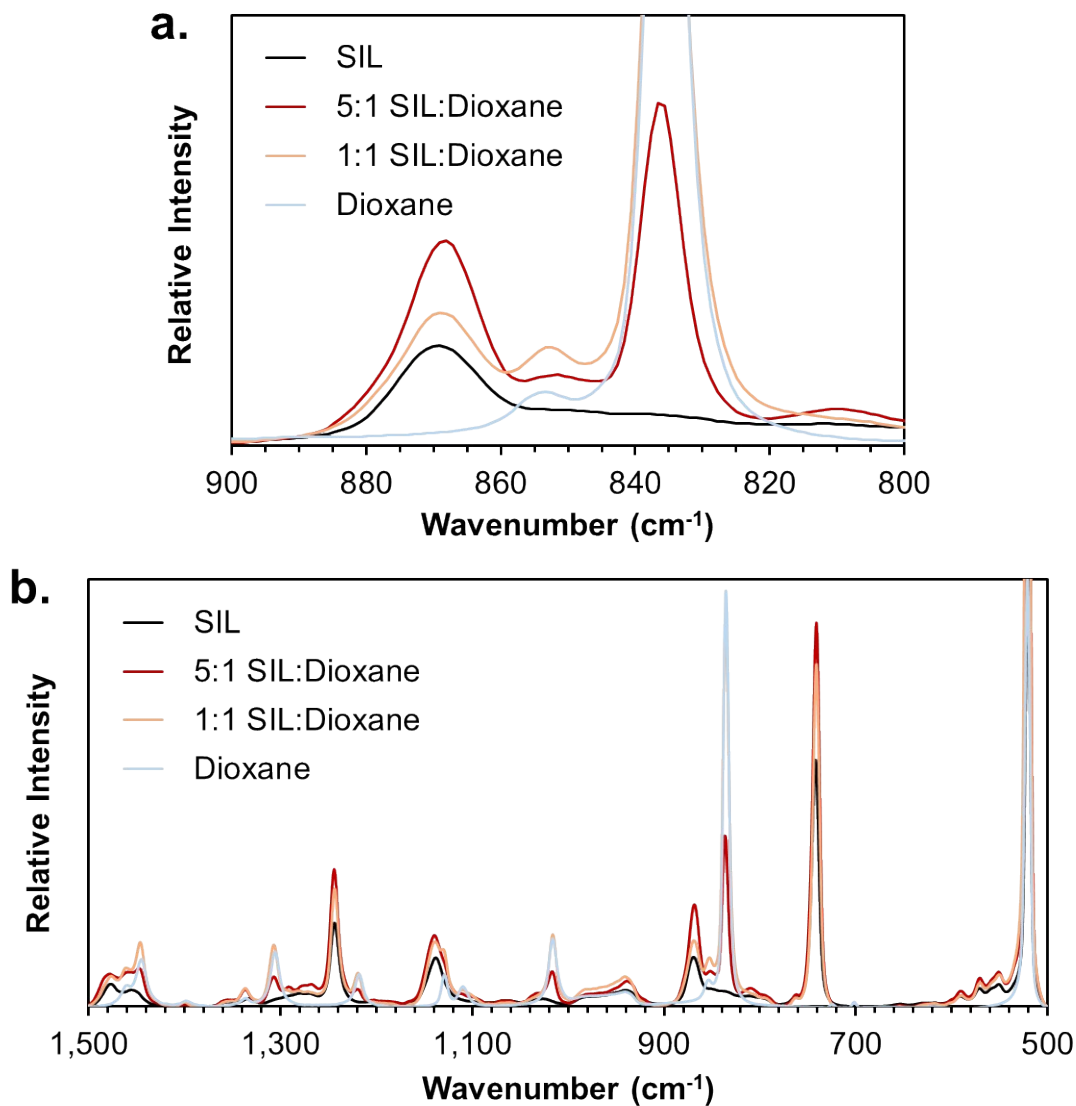


Figure S6. a) Raman spectra of Li(G4)TFSI (“SIL”), 1,4-dioxane, and their 5:1 + 1:1 volumetric combinations between 800-900 cm^{-1} . The “breathing mode” peak at 869 cm^{-1} , corresponding to Li^+ -G4 interaction, appears to intensify upon initial dilution with dioxane. This peak intensity decreases with additional dioxane content, but remains above that of the neat SIL. Such behavior contrasts with “non-innocent” diluents like water, in which a monotonic decrease of the breathing mode peak is observed with increasing dilution due to competition with G4 for coordination of Li^+ .⁵ **b)** Raman spectra for the above samples between 500-1500 cm^{-1} . The intensity of the peaks at 1139 cm^{-1} (deconvoluted from the nearby 1128 cm^{-1} peaks) were used to normalize the data.

Formula	Parameters		Measured Resistances (Ω)	Average κ (mS/cm)	Std. Dev. κ (mS/cm)
	l (μm)	A (cm^2)			
SIG 1	230	0.3848	78.2, 81.2, 91.2, 78.2, 81.2	0.73	0.05
SIG 2	203		48.0, 48.8, 50.3, 56.8, 48.9	1.05	0.07
SIG 3	233		66.9, 70.3, 76.7, 77.8, 66.7, 57.7, 60.3, 67.0, 56.0	0.92	0.11
SIG 4	263		69.9, 55.0, 52.7, 81.6, 89.8, 56.5, 60.0, 62.0	1.07	0.19
(D)SIG 5	257		23.4, 37.2, 37.0	2.15	0.61

Table S1. Individual resistance values measured for SIGs 1-5, along with their average heights (l) and cross-sectional area (A), used to calculate conductivity (Equation S1). The average of these calculations (reported in Table 1) and standard deviation are also included. Small air bubbles, trapped between the samples and electrodes, were a frequent source of error despite efforts to eliminate them. Other sources of error may include: slight deviations from average height for individual samples, slight contractions in height due to the pressure necessary for electrical contact, slight temperature variation between measurements, and (for DSIG 5) variations in dioxane content between samples.

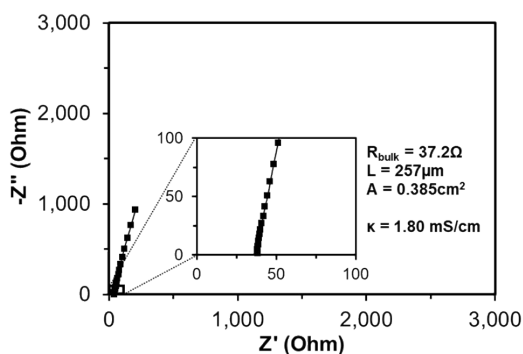


Figure S7. Nyquist plot of representative impedance data (10kHz-100Hz) for a DSIG 5 sample, used to calculate room-temperature conductivity (Equation S1). Fitted equivalent circuit is as shown in Figure 2.

References

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