Supporting Information

Suppression of Lithium Dendrite Growth Using Cross-Linked Polyethylene/Polyethylene Oxide Electrolytes: A New Approach for Practical Lithium-Metal Polymer Batteries

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General Considerations

All reactions and manipulations of air and moisture sensitive compounds were carried out under dry nitrogen using a Braun UniLab drybox or standard Schlenk line techniques unless otherwise specified. ^{1}H NMR spectra were collected in deuterated solvents on a Varian INOVA 500 spectrometer and referenced with residual non-deuterated solvent shifts ($CHCl_3$ = 7.26 ppm) and are reported relative to tetramethylsilane (δ = 0 ppm). ^{13}C NMR spectra were recorded on Varian INOVA (^{13}C, 125 MHz) spectrometer and referenced to chloroform (δ 77.23 ppm). High-resolution mass spectrometry (HRMS) analyses were performed at the Mass Spectrometry Laboratory at the University of Illinois at Urbana-Champaign.

Gel permeation chromatography (GPC) analyses were carried out using an Agilent PL-GPC 50 integrated system, equipped with UV and refractive index detectors, and 2 PL gel Mini-MIX C columns (5 micron, 4.6 mm ID). The GPC columns were eluted with tetrahydrofuran at 30 °C at 0.3 mL/min and were calibrated with monodisperse polystyrene standards. Differential scanning calorimetry (DSC) analyses of polymer samples were performed on a TA Instruments Q1000 instrument equipped with liquid nitrogen cooling system. Polymer samples were made in aluminum pans and heated under nitrogen from −100 °C to 180 °C at a rate of 10 °C per minute and then cooled to −100 °C at a rate of 10 °C per minute, followed heating to 180 °C at a rate of

10 °C per minute. The glass transition temperature (T_g) and the melting temperature (T_m) were recorded from the second heating run.

The thickness of the cross-linked solid polymer electrolytes for all measurement purposes was 200 ± 30 μm. The conductivity data of the polymer electrolytes was obtained over a range of frequency (0.1 to 3×10^6 Hz) and temperature (−5 °C to 100 °C) using a Novocontrol Dielectric Broadband Spectrometer fitted with a Quatro temperature control system. Conductivity measurements were performed using blocking/solid polymer electrolyte (SPE)/blocking cell orientation, using gold plated stainless steel electrodes. Symmetric lithium coin cells (Li/SPE/Li) for short-circuit measurements were prepared in an argon filled MBraun glovebox using Hohsen components, size 2032, with 9.9 mm diameter lithium electrodes and a 12.7 mm diameter cross-linked electrolyte sample. Coin cell crimping was performed with a MTI electric crimping machine to ensure uniformity. Lithium/SPE/Stainless Steel (Li/SPE/SS) coin cells were prepared in an argon filled MBraun glovebox using Hohsen components, size 2032, with 9.9 mm diameter lithium electrodes and a 12.7 mm diameter cross-linked electrolyte sample. The cyclic voltammetric measurements were performed on Li/SPE/SS coin cells using a VersaStat 3 potentiostat (Princeton Applied Research) controlled by VersaStudio software. The potential was scanned from −0.2 V to 4.5 V at 1 mV/s sweep rate and 22 °C. Galvanostatic cyclic short-circuit measurements were performed on Li/SPE/Li symmetric coin cells using a Neware CT-3008 battery tester with wiring into (Fisher Scientific and VWR) convection ovens to maintain T = 90°C. The cells were cycled at constant current density with each half cycle of 3 h until a sudden drop in voltage was observed. Galvanostatic polarization measurements were performed on Li/SPE/Li symmetric coin cells using a Neware CT-3008 battery tester. The storage $G'(\omega)$ and loss $G''(\omega)$ moduli were quantified using small amplitude oscillatory shear measurements. Anton

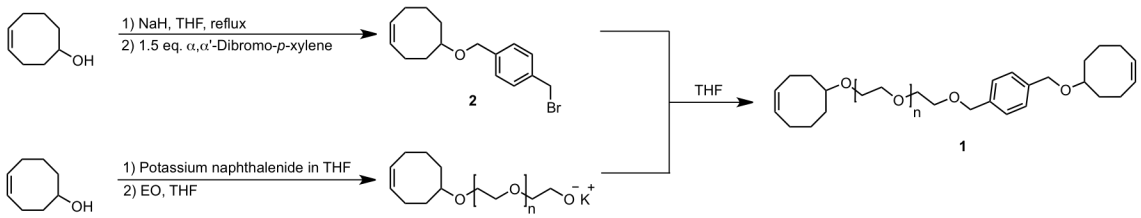
Paar Physica MCR 301 rheometer with 10 mm diameter parallel plates was used for rheological measurements. The ac impedance spectroscopy measurements were made using Li/SPE/Li symmetric coin cells prepared in an argon filled MBraun glovebox, using a Novocontrol Broadband Dielectric Spectrometer fitted with a Quatro temperature control system at frequency ranging from 2 KHz to 900 MHz and at an amplitude of 10 mV.

Materials

Sodium hydride (95%), 1,5-cyclooctadiene, *cis*-cyclooctene (95%), *meta*-chloroperoxybenzoic acid, Grubbs 2nd Generation catalyst (Cl_2(iMes)(PCy_3)Ru=CHPh), and Crabtree's catalyst [(COD)Ir(py)(PCy_3)]PF_6 were purchased from Sigma-Aldrich and used as received. Bis(trifluoromethane)sulfonimide lithium salt, LiTFSI (99.95% trace metals basis) was purchased from Sigma-Aldrich and dried *in vacuo* at 90 °C for 24 h and transferred directly into the glove box. Ethylene oxide was purchased from Sigma-Aldrich and dried over *n*-BuLi before use. Dimethyl poly(ethylene glycol), PEG275 (M_n (NMR) = 275 Da; M_n (Sigma-Aldrich label) = 250 Da) was bought from Sigma-Aldrich, dried over activated 3 Å sieves for 48 hours, and degassed by three freeze pump thaw cycles before use. Dibromo-*p*-xylene (97%) was purchased from Alfa Aesar and used as received. Sodium hydroxide and sodium chloride were purchased from Mallinckrodt and used as received. HPLC grade tetrahydrofuran was purchased from Fischer Scientific and dried over an alumina column and degassed by three freeze pump thaw cycles before use. Chloroform was dried over P_2O_5 and distilled prior to use. Hydrogen (99.99%) was purchased from Airgas. $CDCl_3$ was purchased from Cambridge Isotope Laboratories (CIL) and used as received.

Following a literature procedure,[1] 5-hydroxy-1-cyclooctene was prepared, dried over activated 3 Å sieves, and degassed by three freeze pump thaw cycles before use. Potassium naphthalenide in THF was prepared from naphthalene and potassium at a concentration of 0.59 M (titrated with a standard benzoic acid solution until a persistent green color was observed as an end-point of the titration) and degassed by three freeze pump thaw cycles before use.

General Scheme for the Synthesis of the PEO Functionalized Crosslinker



Scheme S1. General scheme for the synthesis of crosslinker **1**.

Preparation of (Z)-5-((4-(bromomethyl)benzyl)oxy)cyclooct-1-ene (2): A suspension of NaH (2.65 g, 105 mmol) in anhydrous THF (150 mL) was treated dropwise with 5-hydroxycyclooct-1-ene (8.65 g, 68.5 mmol) and heated to 70 °C under N_2 for 16 h. This solution was cooled to room temperature and dropwise cannula transferred to the solution of α,α′-dibromo-*p*-xylene (27.5 g, 104 mmol) in anhydrous THF (150 mL) at 22 °C under N_2, which led to the instantaneous precipitation of salts in a bright yellow solution. The resulting solution was stirred at 22 °C for 16 h and quenched with minimum amount of ethanol until the effervescence ceased. The solution was filtered and the filtrate was concentrated on a rotary evaporator to yield a colorless oil. Hexanes were added (~150 mL) to the crude reaction mixture to recrystallize out excess dibromo-*p*-xylene. Dibromo-*p*-xylene was filtered and the filtrate was concentrated on rotary evaporator to yield colorless oil, which was further purified by column chromatography on

silica using 1:1 CH_2Cl_2/hexanes. Desired product was isolated as colorless oil (7.1 g, 34%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.28 (m, 4H), 5.79 – 5.52 (m, 2H), 4.57 – 4.36 (m, 4H), 3.54 – 3.40 (m, 1H), 2.59 – 1.18 (m, 10H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.71, 136.84, 130.19, 129.50, 129.14, 127.85, 80.32, 69.85, 34.32, 33.57, 33.33, 25.87, 25.68, 22.78. HRMS (ESI) m/z calculated for $C_{16}H_{21}ONaBr$ ($M + Na^+$) 331.0673, found 331.0681.

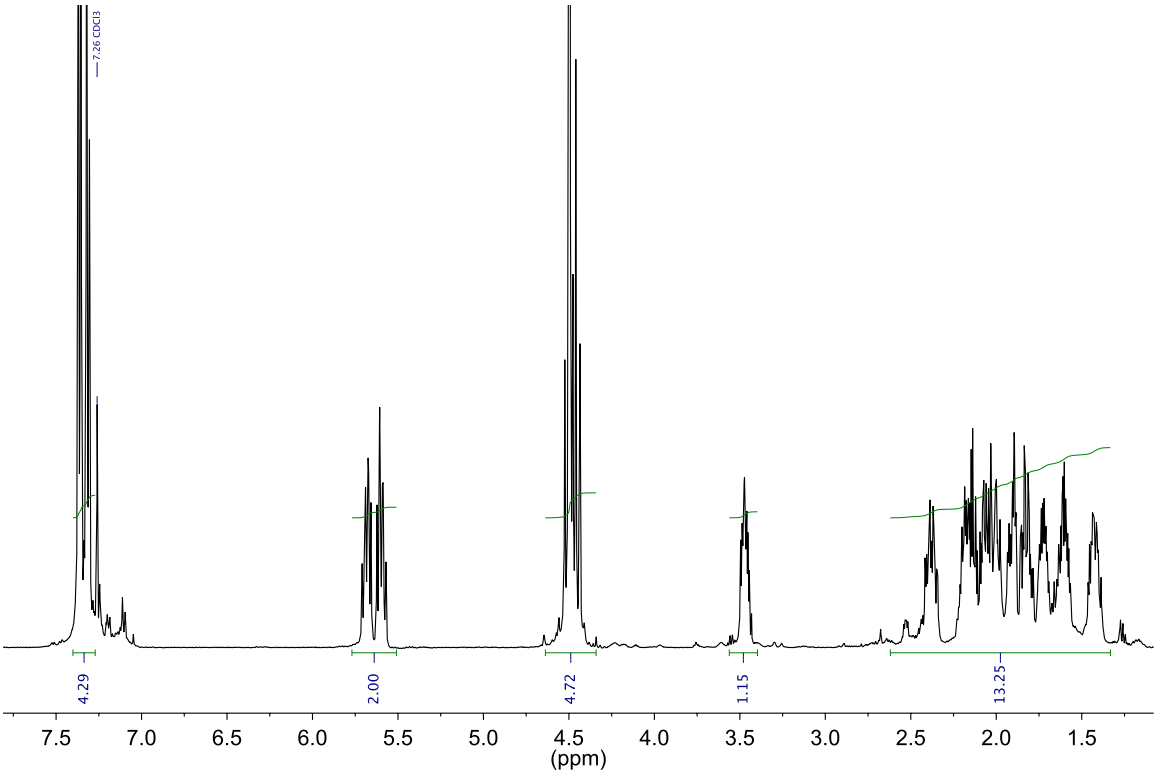


Figure S1. ^{1}H NMR Spectrum of (Z)-5-((4-(bromomethyl)benzyl)oxy)cyclooct-1-ene (**2**). Signal at 7.26 ppm is the residual $CHCl_3$.

Preparation of the PEO functionalized crosslinker (1): In a N_2 glovebox, a Fischer-Porter bottle was charged with 5-hydroxycyclooct-1-ene (144 mg, 1.14 mmol) solution in THF (2.0 mL). 0.59 M THF solution of potassium naphthalenide (1.9 mL, 1.1 mmol) was added to the alcohol solution dropwise resulting in a dark green solution. The vessel was sealed with the reactor head and the apparatus was removed from the box and stirred at 22 °C for 1 h. The solution was cooled to −78 °C and ethylene oxide (3.58 g, 81.3 mmol) was then condensed into

it. The solution was allowed to warm to room temperature over 16 h. After 16 h, the living alkoxide was capped with **2** (0.43 g, 1.4 mmol), which resulted in immediate precipitation of white KBr salt. The reaction mixture was stirred at 50 °C for 5 h and then allowed to warm to room temperature. The salts formed were filtered over a Celite plug and the filtrate was partially concentrated on rotary evaporator. PEO functionalized crosslinker was then precipitated in ~200 mL hexanes. The resulting white powder (3.3 g, 84%) was dried in vacuum at 30 °C for several hours until its mass was constant. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (m, 4H), 5.70 – 5.46 (m, 4H), 4.61 – 4.32 (m, 4H), 3.61 (s, 305H), 3.32 (ddd, J = 9.9, 7.8, 4.3 Hz, 1H), 2.71 – 1.29 (m, 20H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.39, 137.17, 129.95, 129.88, 129.26, 129.21, 127.59, 127.31, 80.75, 79.77, 72.85, 72.35, 70.42, 69.78, 69.18, 67.51, 61.49, 34.10, 33.99, 33.23, 33.06, 25.65, 25.61, 25.47, 25.41, 22.55, 22.51.

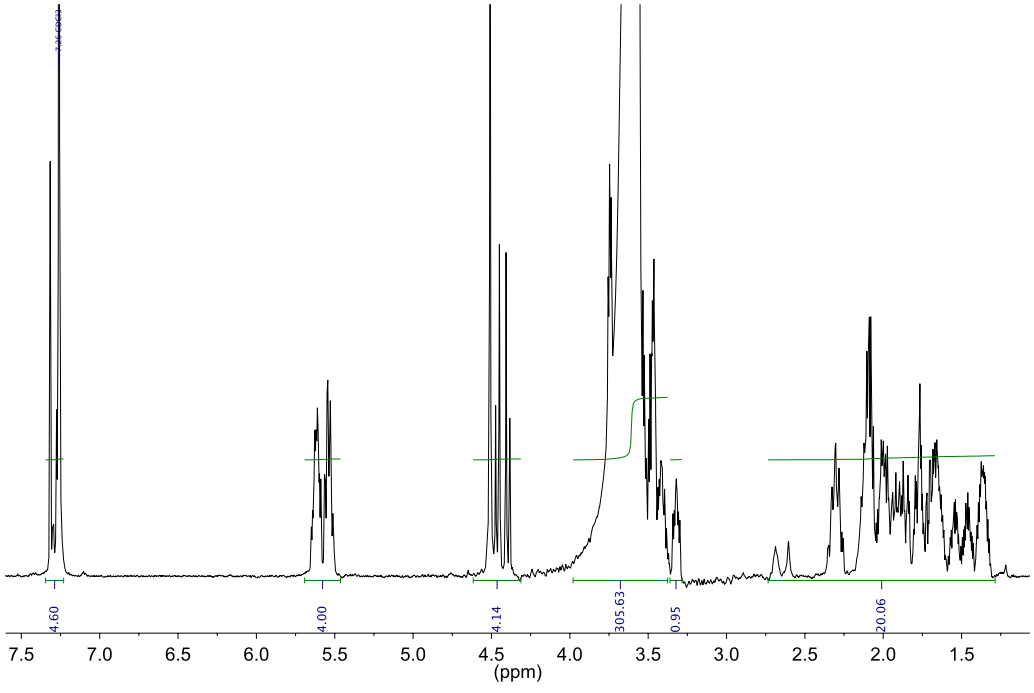
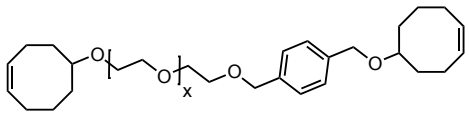


Figure S2. ^{1}H NMR Spectrum of PEO functionalized crosslinker (**1**) of molecular weight 3.7 kg/mol. Signal at 7.26 ppm is the residual $CHCl_3$.

Synthesis of Cross-Linked Solid Polymer Electrolytes (SPEs)

I. PEO Functionalized Crosslinker, 1



1

To study the effect of crosslinker length on the ionic conductivity of the SPE, three crosslinkers of different molecular weights were synthesized using the general procedure described above. The molecular weight and the thermal properties of the crosslinkers are described in Table S1.

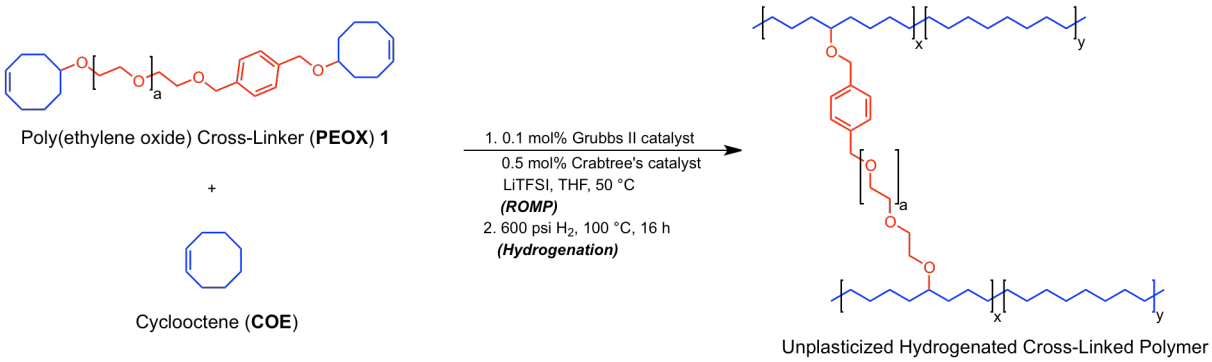
Table S1. PEO functionalized crosslinker.

Entry No.	EO units in the crosslinker[a]	M_n (NMR)[a] kg/mol	M_n (GPC)[b] kg/mol	PDI[b]	T_m[c] (°C)	ΔH_{fus}[c] (J/g)
1	33	1.8	1.3	1.1	34	124.9
2	76	3.7	3.5	1.1	47	132.4
3	123	5.8	5.4	1.1	52	153.7

[a]Determined by ^{1}H NMR spectroscopy. [b]Determined by THF gel permeation chromatography calibrated with polystyrene standards at 30 °C. [c]Determined by differential scanning calorimetry analysis of the second heat cycle.

II. Unplasticized Cross-Linked SPEs

General Scheme for the Synthesis of Unplasticized Cross-Linked SPE



Scheme S2. General scheme for the synthesis of unplasticized cross-linked SPE.

Nomenclature of Unplasticized Cross-Linked SPE

(^{a}PEOX$_{l}$)(^{b}PE$_{m}$)

where

PEOX: PEO in the crosslinker; **PE**: Polyethylene**; a**: average number of ethylene oxide (EO) units in PEOX crosslinker; **b**: average number of ethylene (E) units between the crosslinks; **l**: moles of EO units in the PEOX/ total moles of EO and E units; **m**: moles E units in the PE mainchain/ total moles of EO and E units; **l** + **m** = 1

Calculations for l, m, and n

l′ = (mmoles of PEOX) × a

m′ = [(mmoles of COE) × 4] + [(mmoles of PEOX) × 8]

$$\mathbf{l} = \frac{\mathbf{l'}}{\mathbf{l'} + \mathbf{m'}}$$

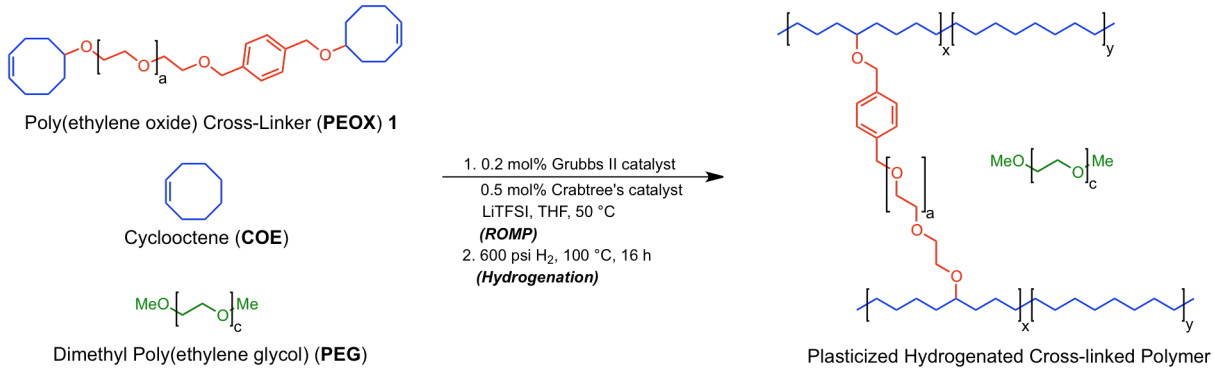
$$\mathbf{m} = \frac{\mathbf{m'}}{\mathbf{l'} + \mathbf{m'}}$$

Sample Procedure for the Synthesis of Unplasticized Cross-Linked SPE, ($^{33}PEOX_{0.32}$)($^{34}PE_{0.68}$): Crosslinker **1** (156 mg, 0.0872 mmol) with 33 EO units in the crosslinker and COE (179 μL, 1.37 mmol) were combined and dissolved in 1.5 mL of THF. Grubbs' 2nd generation catalyst (1.2 mg, 0.0015 mmol) dissolved in 0.5 mL of THF was added to the monomer mixture, followed by addition of LiTFSI (45 mg, 0.16 mmol). Crabtree's catalyst (6.0 mg, 0.0075 mmol) dissolved in 0.5 mL $CHCl_3$ was then added to the resultant solution and shook vigorously for a minute. It was then transferred to a metal dish (fluoropolymer-lined, diameter of 5.25 cm and depth of 3.0 cm) placed in a volume glass chamber bearing two Kontes glass valves on top. The chamber was placed on top of the hot plate equipped with a metal plate to ensure uniform heating and film was casted under N_2 flow at 50 °C (set-up is shown in Figure S3) for 3 h. After the solvent evaporated off, the Kontes valves were closed and the glass chamber was taken in the glove box. Hexane was added to the metal dish in order to release the film from the dish. The film was dried in vacuum at 22 °C for 24 h and then placed in a Parr reactor and sealed. It was pressurized to 600 psig with hydrogen and then vented down to 50 psig. This process was repeated twice more to purge the reactor of air, then pressurized to 600 psig and heated to 100 °C. After 16 h, it was cooled, vented and the hydrogenated film was dried under vacuum at 22 °C.

Figure S3. Experimental set-up for the synthesis of SPE under inert conditions.

III. Plasticized Cross-Linked SPEs

General Scheme for the Synthesis of Plasticized Cross-Linked SPE



Scheme S3. General scheme for the synthesis of plasticized cross-linked **SPE**.

Nomenclature of Plasticized Cross-Linked SPE

(^{a}PEOX$_{l}$)(^{b}PE$_{m}$)(^{c}PEG$_{n}$)

where

PEOX: PEO in the crosslinker; **PE**: Polyethylene; **PEG**: Dimethyl poly(ethylene glycol); **a**: average number of ethylene oxide (EO) units in PEOX crosslinker; **b**: average number of ethylene (E) units between the crosslinks; **c**: average number of EO units in PEG plasticizer; **l**: moles EO units in PEOX/ total moles of EO and E units; **m**: moles E units in PE mainchain/ total moles of EO and E units; **n**: moles EO units in PEG/ total moles of EO and E units; **l** + **m** + **n** = 1.

Calculations for l, m, and n

l′ = [(mmoles of PEOX) × a]

m′ = [(mmoles of COE) × 4] + [(mmoles of PEOX) × 8]

n′ = [(mmoles of PEG) × 5]

$$\mathbf{l} = \frac{\mathbf{l'}}{\mathbf{l'} + \mathbf{m'} + \mathbf{n'}}$$

$$\mathbf{m} = \frac{\mathbf{m'}}{\mathbf{l'} + \mathbf{m'} + \mathbf{n'}}$$

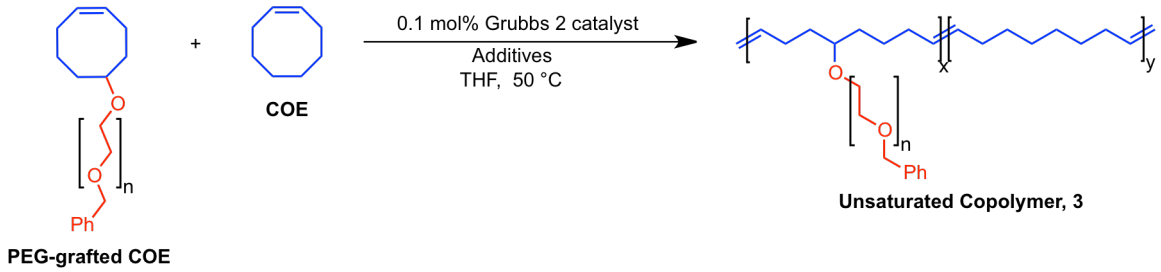
$$\mathbf{n} = \frac{\mathbf{n'}}{\mathbf{l'} + \mathbf{m'} + \mathbf{n'}}$$

Sample procedure for the Synthesis of Plasticized Cross-Linked SPE with the Optimized EO units in the Crosslinker, (^{70}PEOX$_{0.34}$)(^{34}PE$_{0.35}$)(^{5}PEG$_{0.31}$): Crosslinker **1** (121 mg, 0.0352 mmol) with 70 EO units in the crosslinker and COE (73 μL, 0.56 mmol) were combined and dissolved in 1.5 mL of THF. Grubbs' 2nd generation catalyst (1.2 mg, 0.0015 mmol) dissolved in 0.5 mL of THF was added to the monomer mixture, followed by addition of LiTFSI (79 mg, 0.28 mmol) and PEG275 (120 mg, 0.436 mmol). Crabtree's catalyst (2.8 mg, 0.0075 mmol) dissolved in 0.5 mL $CHCl_3$ was added to the resultant solution and shook vigorously for a minute. It was then transferred to a metal dish (fluoropolymer-lined, diameter of 5.25 cm and depth of 3.0 cm) and solution casted in the similar manner to the dry film as described above. The film was dried *in* vacuum at 22 °C for 24 h and then placed in a Parr reactor equipped with an overhead stirrer and sealed. It was pressurized to 600 psig with hydrogen and then vented down to 50 psig. This process was repeated twice more to purge the reactor of air, then pressurized to 600 psig and heated to 100 °C. After 16 h, Parr reactor was cooled, vented and the plasticized SPE was dried under vacuum at 22 °C for 24 h.

Control Experiments

I. Testing the activity of Grubbs' second generation catalyst in the presence of additives

The activity of Grubbs' second-generation catalyst (G2 catalyst) in the presence of additives (LiTFSI and Crabtree's catalyst) was examined by doing control experiments. The cross-linked SPE films discussed above are insoluble and hence cannot be analyzed using NMR and GPC techniques. To gauge the activity of G2 catalyst for the cross-linked system, we studied a solvent processable model copolymer system. COE was copolymerized with PEG-grafted COE[2] using G2 catalyst in the absence and presence of additives to obtain unsaturated copolymers (**3**), which were analyzed by GPC to determine the activity of the G2 catalyst (Scheme S4).



Scheme S4: Copolymerization of COE with PEG-grafted COE.

Sample procedure for the synthesis of copolymers of COE and PEG-grafted COE without any additive: PEG-grafted COE (34 mg, 0.051 mmol) with 10 EO units in the graft and COE (85 mg, 0.77 mmol) were combined in a 5 mL scintillation vial and dissolved in 1.0 mL of THF. G2 catalyst (0.7 mg, 0.0008 mmol) dissolved in 0.5 mL of THF was added to the monomer mixture. The reaction mixture was heated at 50 °C for 3 h, cooled to room temperature, and concentrated under reduced pressure to yield a light brown polymer. The polymer thus obtained was further analyzed by GPC analysis.

Results and discussion

Ring opening metathesis polymerization (ROMP) experiments were done to determine the activity of G2 catalyst in the presence and absence of LiTFSI and Crabtree's catalyst (Table S2, entries 1-3). The GPC results indicate that the molecular weights of the unsaturated copolymers change upon addition of LiTFSI and Crabtree's catalyst to the monomer mixture. However, the G2 catalyst was still very active in the presence of these additives, implying that the ROMP should have proceeded efficiently for the PE-PEO cross-linked polymer system as well.

Table S2: Control experiments to estimate Grubbs' 2nd catalyst activity for the cross-linked system.

Entry No.	LiTFSI (mmol)	Crabtree's catalyst (mol%)	M_n[a] (kg/mol)	M_w/M_n[a]
1	-	-	60	1.8
2	0.038	-	96	1.6
3	0.038	0.5	83	1.4

[a]Number average molecular weight (M_n) and weight average molecular weight (M_w) were determined by THF gel permeation chromatography calibrated with polystyrene standards at 30 °C

II. Testing the activity of Crabtree's catalyst in the polymer film

To estimate the activity of the hydrogenation catalyst (Crabtree's catalyst), a PEG-grafted COE comonomer was used instead of the PEOX crosslinker (**1**) to obtain soluble hydrogenated copolymer that could be analyzed using ^{1}H NMR spectroscopy. COE was copolymerized with PEG-grafted COE using G2 catalyst in the presence of LiTFSI and Crabtree's catalyst to yield the unsaturated polymer film (Figure S4). The unsaturated polymer film was hydrogenated under the same conditions as the cross-linked system to obtain soluble hydrogenated copolymer (**4**). The hydrogenated polymer was analyzed by ^{1}H NMR spectroscopy to determine percent conversion of the hydrogenation reaction.

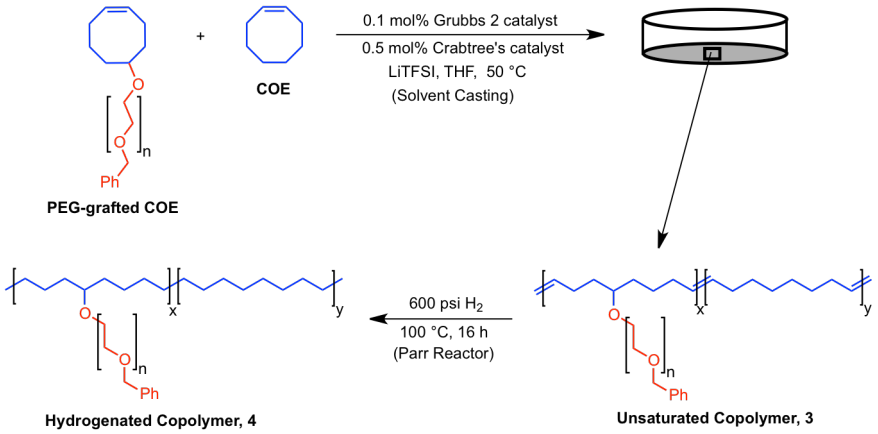


Figure S4: Synthesis of soluble hydrogenated copolymer.

Experimental procedure: PEG-grafted COE (66 mg, 0.14 mmol) with 6 EO units in the graft and COE (245 mg, 2.10 mmol) were combined and dissolved in 1.5 mL of THF. G2 catalyst (2.0 mg, 0.0024 mmol) dissolved in 0.5 mL of THF was added to the monomer mixture, followed by addition of LiTFSI (22 mg, 0.070 mmol). Crabtree's catalyst (9.5 mg, 0.012 mmol) dissolved in 0.5 mL $CHCl_3$ was added to the resultant solution and shook vigorously for a minute. It was then transferred to a metal dish (fluoropolymer-lined, diameter of 5.25 cm and depth of 3.0 cm) and solution casted in the similar manner to the dry film as described for the cross-linked system. The sticky polymer film was dried in vacuum at 22 °C for 24 h and then placed in a Parr reactor equipped with an overhead stirrer and sealed. It was pressurized to 600 psig with hydrogen and then vented down to 50 psig. This process was repeated twice more to purge the reactor of air, then pressurized to 600 psig and heated to 100 °C. After 16 h, the Parr reactor was cooled to room temperature, vented, and the polymer film was dried under vacuum at 22 °C for 24 h.

Analysis of the soluble hydrogenated copolymer (4)

The hydrogenated polymer was analyzed using ^{1}H NMR spectroscopy measurements. The ^{1}H NMR spectra of the unsaturated copolymer and the hydrogenated copolymer are shown in Figure S5. The integrations of the multiplet signal at δ 5.5 ppm (corresponding to the alkene protons in the polymer backbone and highlighted in the Figure S5) were analyzed compared to the integrations of the signal at δ 4.6 ppm (corresponding to the benzylic hydrogens) to determine the percent hydrogenation of unsaturated copolymer. ^{1}H NMR analysis indicated 95% conversion, confirming that the activity of Crabtree's catalyst was still very good in the solid polymer film. This result demonstrated that the catalyst was able to diffuse through the polymer domains of the unsaturated copolymer film and hydrogenate the double bonds along the backbone.

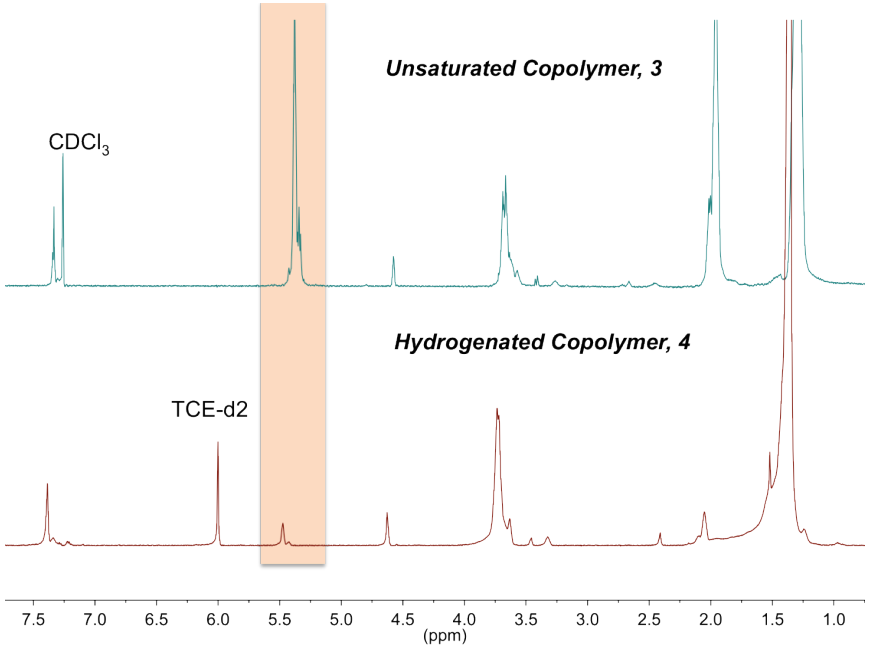


Figure S5: ^{1}H NMR spectra of the unsaturated copolymer, **3** (top) and the hydrogenated copolymer, **4** (bottom). The ^{1}H NMR spectrum for **3** was acquired in $CDCl_3$ at 22 °C and the signal at 7.26 ppm in the top spectrum is the residual $CHCl_3$. The ^{1}H NMR spectrum for **4** was acquired in 1,1,2,2-tetrachloroethane-d_2 (TCE-d_2) at 130 °C and the signal at 6.00 ppm in the bottom spectrum is the residual TCE-d_1.

Differential Scanning Calorimetry (DSC)

DSC analysis was performed using a TA Instruments Q1000 instrument equipped with liquid nitrogen cooling system and automated sampler. Typical DSC samples were made in aluminum pans and the method used was 10 °C/ min ramp, with one cycle of heat, cool, and heat again. The DSC data of the second heat cycle for the unplasticized samples with variable EO units in the PEOX crosslinker (33, 76, and 123) and at [**COE**]:[**1**] loading of 15:1 is shown in Figure S6. Electrolytes containing 76 EO units in the **PEOX** crosslinker exhibited lowest T_g values suggesting that ^{76}PEOX electrolytes had moderately better segmental motion of PEO chains in the SPEs.

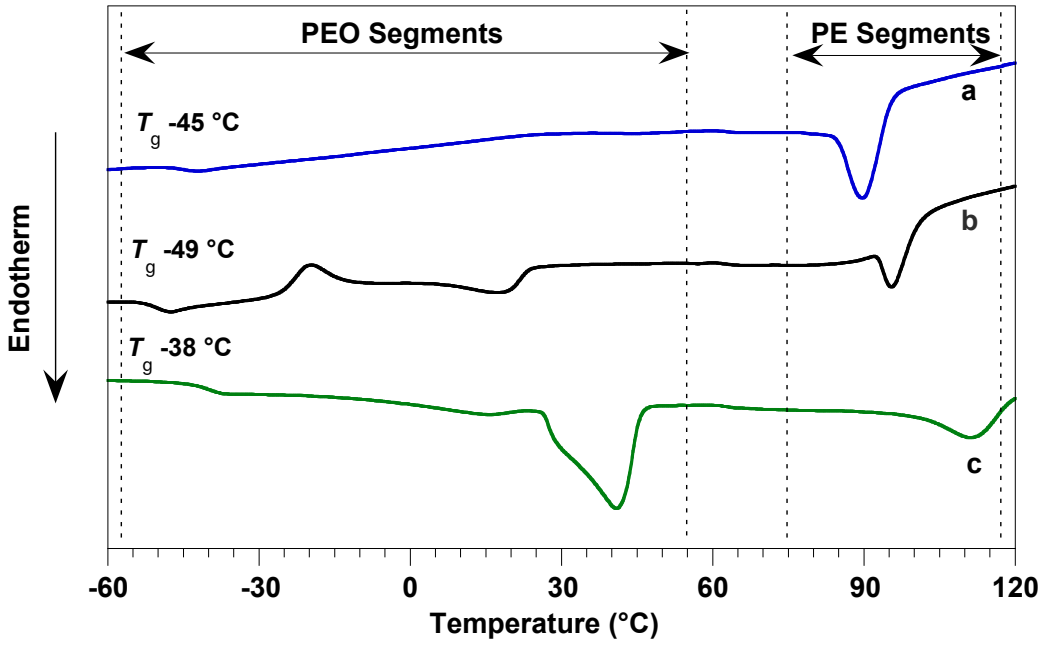


Figure S6. DSC traces of the second heat cycle for unplasticized crosslinked solid polymer electrolytes with variable EO units in the crosslinker, **1**. All films had [**COE**]:[**1**] loading of 15:1, and [EO]: [Li] composition of 18:1. a) 33, b) 76, and c) 123 EO units in the crosslinker.

With the aim of increasing the ionic conductivity of these polymer electrolytes, varied amount of PEG275 plasticizer was added to the polymer framework with the optimized EO units. For the plasticized sample set, a new batch of PEOX crosslinker was synthesized to obtain approximately 76 EO units. Since it is challenging to control the exact amount of EO, the PEOX crosslinker with 70 EO units (^{70}PEOX) was employed instead of ^{76}PEOX crosslinker. DSC traces of the second heat cycle for the ^{70}PEOX electrolytes having different weight% of the PEG275 plasticizer are shown in Figure S7.

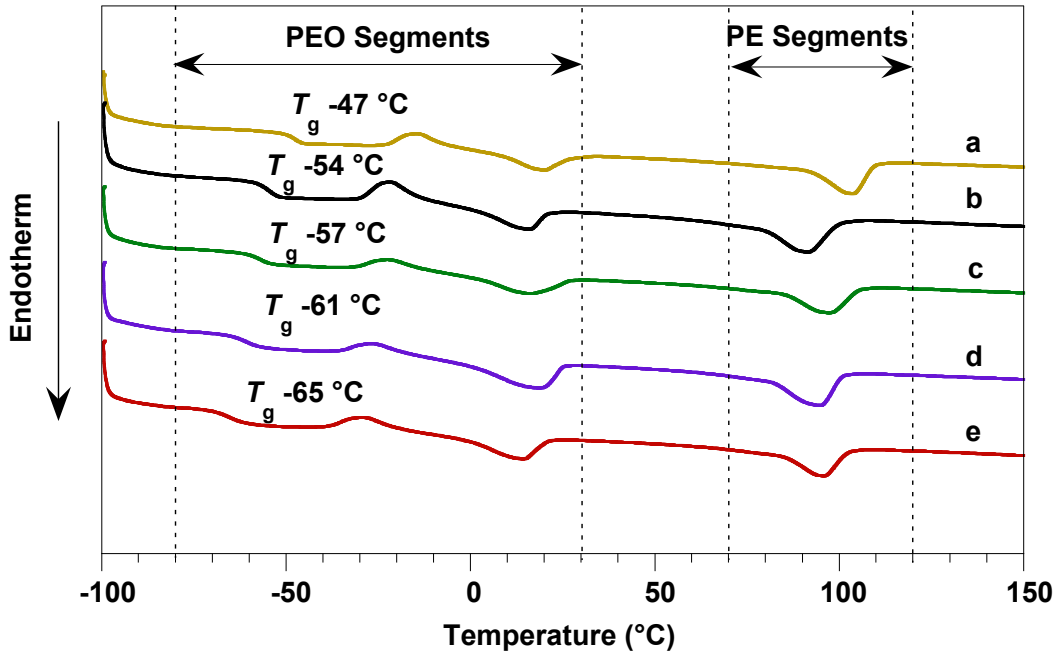


Figure S7. DSC traces of second heat cycle of ^{70}PEOX electrolytes having different weight% of the plasticizer. All films had [**COE**]:[**1**] ratio of 15:1 and [EO]:[Li] composition of 18:1. a) 0 wt%, b) 16 wt%, c) 24 wt%, d) 31 wt%, and e) 39 wt% PEG275 plasticizer in the cross-linked films.

DC Ionic Conductivity

The DC ionic conductivity at each temperature was determined from the plateau value of the plot of real part of the conductivity as a function of frequency, as described in seminal work by Jonscher.[3] A sample plot of Re[conductivity] vs. frequency is shown in Figure S8. The inset shows a plot of Re[conductivity], Im[conductivity], and tan(delta) at variable frequency for the representative sample at 25 °C.

Conductivity measurements are estimated to be accurate to ±5%, the accuracy of determining the film thicknesses. The DC ionic conductivity values of unplasticized SPEs at variable temperature are given in Table S3. ^{76}PEOX electrolytes exhibited highest ionic conductivity values of around 2.7×10^{-5} S/cm (entries 4–6) at room temperature. This is presumably due to better segmental motion of PEO chains in the ^{76}PEOX SPEs as suggested by the lowest T_g of these ^{76}PEOX electrolytes. At higher temperatures (above 50 °C), the crystalline PEO domains in the ^{123}PEOX electrolytes melted, and hence the conductivity values of ^{76}PEOX and ^{123}PEOX are similar in magnitude. Variable temperature DC ionic conductivity values of plasticized ^{70}PEOX electrolytes with different weight% of PEG275 plasticizer are reported in Table S4. The ionic conductivity values for PEO-LiTFSI sample (entry 6) at different temperature are also listed. Below the melting temperature of PEO (<50 °C), all the ^{70}PEOX electrolytes (entries 1–5) showed higher conductivity values than PEO-LiTFSI sample due to the highly crystalline PEO domains in PEO-LiTFSI sample. Most importantly, samples with 31 and 39 wt% of the PEG275 plasticizer (entries 4 and 5) showed conductivity values greater than 1.0×10^{-4} S/cm at ambient temperature.

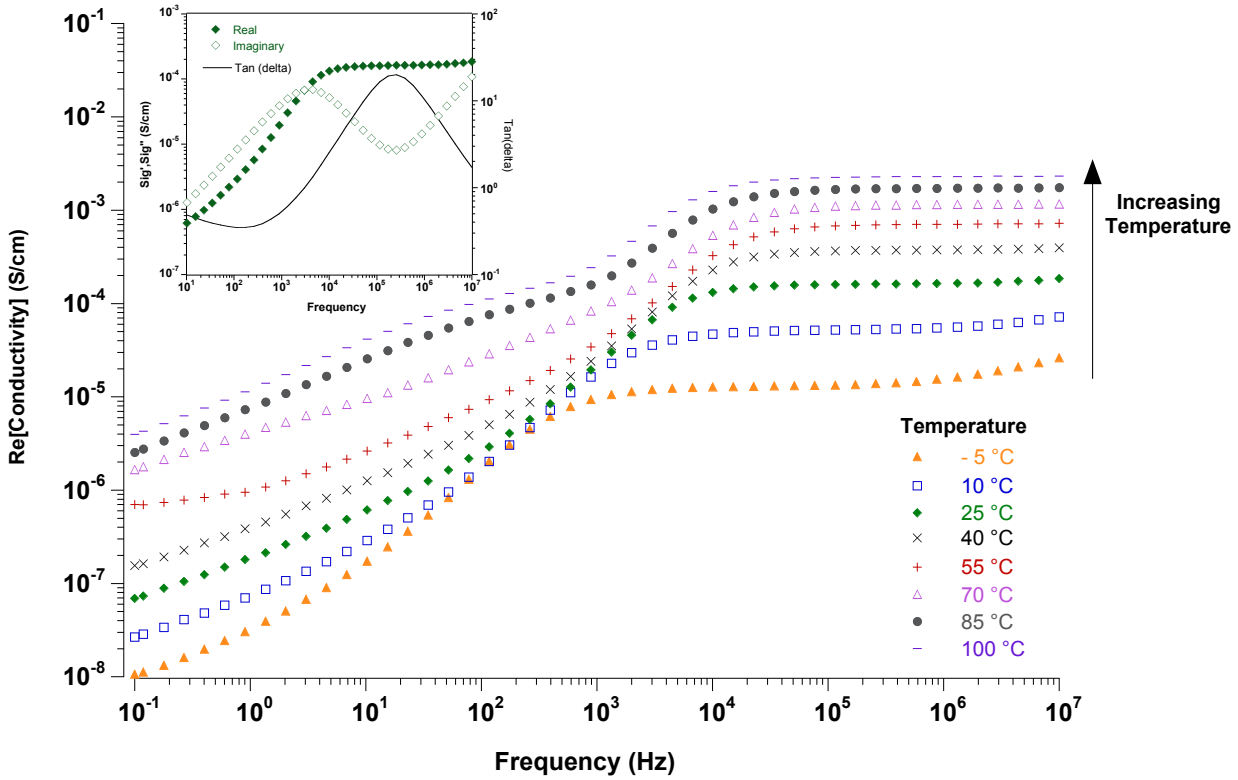


Figure S8. Real part of the ionic conductivity vs. frequency plot for (^{70}PEOX$_{0.34}$)(^{34}PE$_{0.35}$)(^{5}PEG$_{0.31}$) sample at variable temperatures. Inset shows the real conductivity (Sig′), imaginary conductivity (Sig″), and tan(delta) vs. frequency plot for (^{70}PEOX$_{0.34}$)(^{34}PE$_{0.35}$)(^{5}PEG$_{0.31}$) electrolyte at 25 °C.

Table S3. DC ionic conductivities of unplasticized solid polymer electrolytes.[a]

Entry No.	Sample Name	DC Ionic Conductivity (S/cm)[b]							
		−5 °C	10 °C	25 °C	40 °C	55 °C	70 °C	85 °C	100 °C
1	$(^{33}PEOX_{0.32})(^{34}PE_{0.68})$	1.3×10^{-7}	1.1×10^{-6}	5.2×10^{-6}	1.8×10^{-5}	4.5×10^{-5}	9.3×10^{-5}	1.7×10^{-4}	2.5×10^{-4}
2	$(^{33}PEOX_{0.40})(^{24}PE_{0.60})$	1.9×10^{-7}	1.7×10^{-6}	9.0×10^{-6}	3.2×10^{-5}	8.3×10^{-5}	1.8×10^{-4}	3.2×10^{-4}	4.8×10^{-4}
3	$(^{33}PEOX_{0.47})(^{18}PE_{0.53})$	2.0×10^{-7}	1.7×10^{-6}	8.3×10^{-6}	2.8×10^{-5}	7.3×10^{-5}	1.5×10^{-4}	2.6×10^{-4}	4.0×10^{-4}
4	$(^{76}PEOX_{0.51})(^{34}PE_{0.49})$	1.0×10^{-6}	5.0×10^{-6}	2.3×10^{-5}	7.7×10^{-5}	1.9×10^{-4}	3.7×10^{-4}	6.1×10^{-4}	9.0×10^{-4}
5	$(^{76}PEOX_{0.60})(^{24}PE_{0.40})$	2.2×10^{-7}	2.5×10^{-6}	2.8×10^{-5}	1.0×10^{-4}	2.3×10^{-4}	4.6×10^{-4}	7.6×10^{-4}	1.1×10^{-3}
6	$(^{76}PEOX_{0.66})(^{18}PE_{0.34})$	1.3×10^{-6}	8.5×10^{-6}	3.1×10^{-5}	1.1×10^{-4}	2.3×10^{-4}	3.8×10^{-4}	5.3×10^{-4}	7.1×10^{-4}
7	$(^{123}PEOX_{0.64})(^{34}PE_{0.36})$	5.1×10^{-8}	7.8×10^{-7}	8.2×10^{-6}	5.5×10^{-5}	2.0×10^{-4}	4.4×10^{-4}	7.5×10^{-4}	1.1×10^{-3}
8	$(^{123}PEOX_{0.72})(^{24}PE_{0.28})$	4.8×10^{-8}	7.6×10^{-7}	8.4×10^{-6}	5.6×10^{-5}	2.1×10^{-4}	4.0×10^{-4}	6.7×10^{-4}	1.0×10^{-3}
9	$(^{123}PEOX_{0.77})(^{18}PE_{0.23})$	5.2×10^{-8}	7.4×10^{-7}	7.4×10^{-6}	6.2×10^{-5}	2.2×10^{-4}	4.1×10^{-4}	6.7×10^{-4}	1.0×10^{-3}

[a]All films had [EO]:[Li] composition of 18:1; where EO means ethylene oxide units in the PEOX crosslinker. [b]Determined by dielectric spectroscopy measurements.

Table S4. DC ionic conductivities of plasticized solid polymer electrolytes.[a]

Entry No.	Sample Name	DC Ionic Conductivity (S/cm)[b]							
		−5 °C	10 °C	25 °C	40 °C	55 °C	70 °C	85 °C	100 °C
1[c]	$(^{70}PEOX_{0.50})(^{34}PE_{0.50})$	1.2×10^{-6}	7.6×10^{-6}	3.1×10^{-5}	8.8×10^{-5}	1.8×10^{-4}	3.1×10^{-4}	4.5×10^{-4}	6.1×10^{-4}
2[c]	$(^{70}PEOX_{0.43})(^{34}PE_{0.43})(^{5}PEG_{0.14})$	2.6×10^{-6}	1.4×10^{-5}	5.1×10^{-5}	1.4×10^{-4}	3.1×10^{-4}	5.5×10^{-4}	8.6×10^{-4}	1.2×10^{-3}
3[c]	$(^{70}PEOX_{0.39})(^{34}PE_{0.39})(^{5}PEG_{0.22})$	4.4×10^{-6}	2.1×10^{-5}	7.0×10^{-5}	1.7×10^{-4}	3.6×10^{-4}	6.1×10^{-4}	9.2×10^{-4}	1.2×10^{-3}
4[c]	$(^{70}PEOX_{0.34})(^{34}PE_{0.35})(^{5}PEG_{0.31})$	1.3×10^{-5}	5.2×10^{-5}	1.6×10^{-4}	3.7×10^{-4}	7.0×10^{-4}	1.2×10^{-3}	1.7×10^{-3}	2.3×10^{-3}
5[c]	$(^{70}PEOX_{0.30})(^{34}PE_{0.31})(^{5}PEG_{0.39})$	1.8×10^{-5}	7.1×10^{-5}	2.0×10^{-4}	4.3×10^{-4}	7.9×10^{-4}	1.3×10^{-3}	1.8×10^{-3}	2.6×10^{-3}
6[d]	PEO (900 kDa)	3.6×10^{-8}	7.5×10^{-7}	7.2×10^{-6}	6.6×10^{-5}	3.9×10^{-4}	7.6×10^{-4}	1.2×10^{-3}	1.8×10^{-3}

[a]All films had [EO]:[Li] composition of 18:1; where EO includes ethylene oxide units contained both in the PEOX crosslinker and PEG plasticizer. [b]Determined by dielectric spectroscopy measurements. [c]All films had 70 EO units in the crosslinker and [**COE**]:[**1**] loading of 15:1. [d]Sample PEO (900 kDa) is poly (ethylene oxide), M_n 900 kDa polymer doped with LiTFSI salt having [EO]:[Li] composition of 18:1 for comparison purposes.

Cyclic Voltammetry Measurements

The electrochemical stability window of the SPE was determined by cyclic voltammetry. The cyclic voltammogram of $(^{70}PEOX_{0.34})(^{34}PE_{0.35})(^{5}PEG_{0.31})$ is shown in Figure S9. The cross-linked SPE is stable up to 4.0 V versus Li^+/Li, which is in agreement with the previously reported electrochemical stability of PEO-LiTFSI polymer electrolytes.[4]

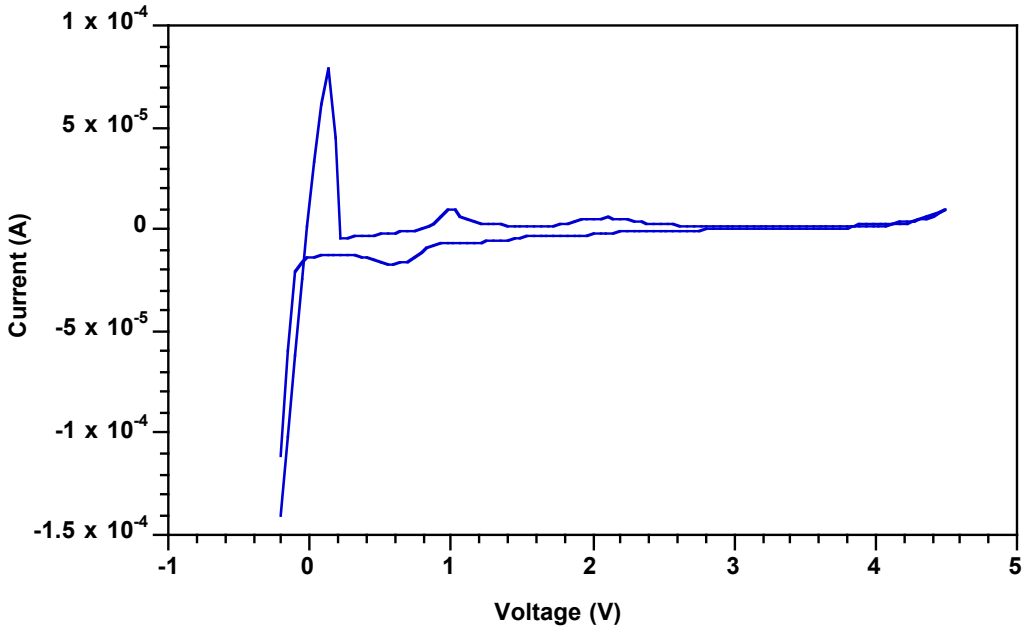


Figure S9. Cyclic voltammogram obtained for ($^{70}PEOX_{0.34}$)($^{34}PE_{0.35}$)($^{5}PEG_{0.31}$) at 1 mV/s and 22 °C.

Galvanostatic Cycling Measurements

Galvanostatic cycling short-circuit measurements were performed on Li/SPE/Li symmetric coin cells using a Neware CT-3008 battery tester with wiring into (Fisher Scientific and VWR) convection ovens to maintain T = 90 °C. Repeated three hour charge and three hour discharge cycles were performed at the specified current density value, with no rest periods, following an initial 24 hour period of three hour charge and three hour discharge cycling at a lower current density (10% of the final value). The cells were cycled at constant current density with each half cycle of 3 h until a sudden drop in voltage was observed. This large decline in voltage was attributed to the formation of dendrite short. The cycling results of ($^{70}PEOX_{0.34}$)($^{34}PE_{0.35}$)($^{5}PEG_{0.31}$) at 0.65 mA/cm^2 current density and 90 °C are illustrated in Figure S10.

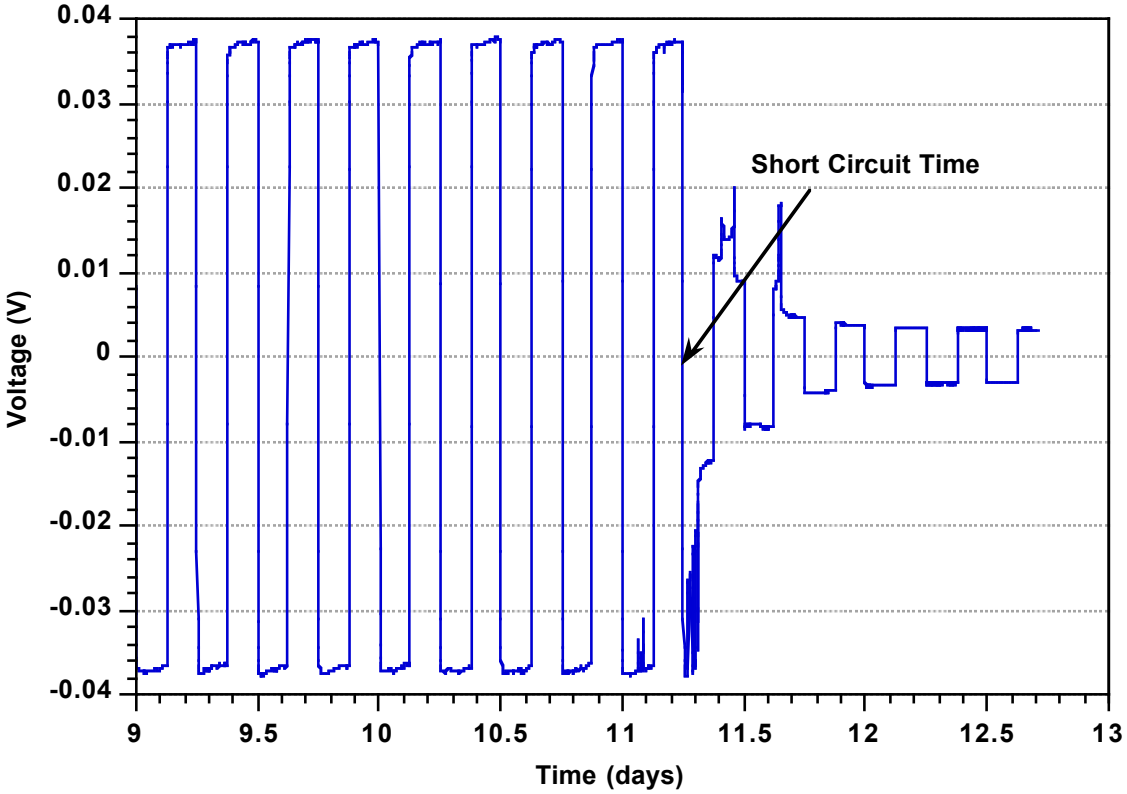


Figure S10. Galvanostatic cycling curve obtained for (^{70}PEOX$_{0.34}$)(^{34}PE$_{0.35}$)(^{5}PEG$_{0.31}$) at fixed current density of 0.65 mA/cm^2 and 90 °C. The short circuit time (t_{sc}) is pointed out; C_d value is 645 C/cm^2.

Galvanostatic Polarization Measurements

Galvanostatic polarization measurements were performed on Li/SPE/Li symmetric coin cells using a Neware CT-3008 battery tester. These tests were conducted to investigate the efficiency of lithium plating from the cross-linked polymer electrolyte. A typical polarization curve at current density (0.65 mA/cm^2) and 90 °C is shown in Figure S11.

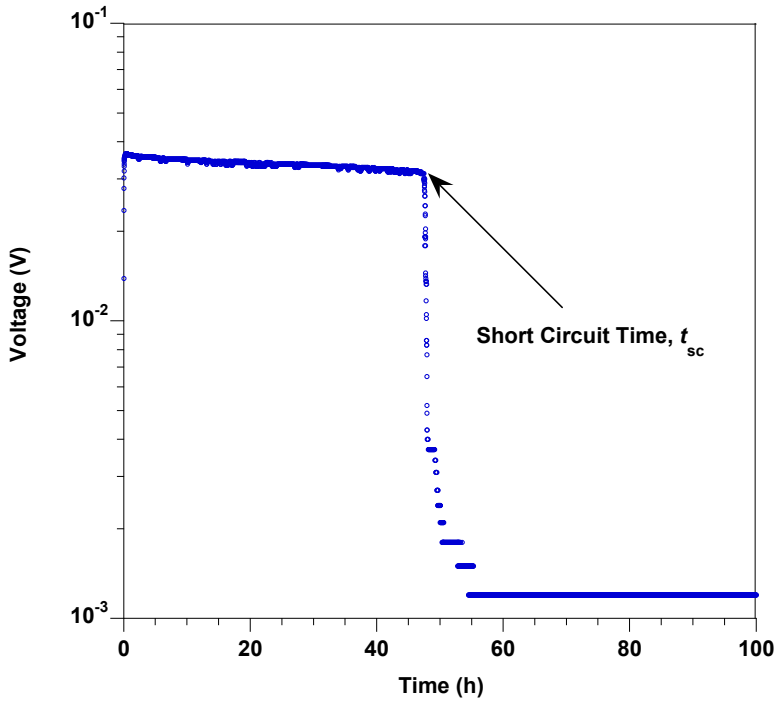


Figure S11. Galvanostatic polarization curve obtained for (^{70}PEOX$_{0.34}$)(^{34}PE$_{0.35}$)(^{5}PEG$_{0.31}$) at fixed current density of 0.65 mA/cm^2 and 90 °C. The short circuit time (t_{sc}) is pointed out.

Calculation of the predicted short-circuit time *via* the Chazalviel model

When a cell containing a binary electrolyte undergoes polarization at high current densities, the concentration of anions approaches zero at the deposition interface and a divergence in the potential occurs at Sand's time, τ_s. Chazalviel predicted that the onset time of the dendrite growth for cells containing dilute, binary, monovalent electrolytes operating at high current density follows a power law as a function of the current density, very similar to the Sand's law given by[5]:

$$\tau_s = \pi D \left(\frac{eC_0}{2Jt_a}\right)^2 \qquad \text{(Equation 1)}$$

where τ_s is the Sand's time, D is the ambipolar diffusion coefficient (m^2/s), e is the elementary charge (C), C_0 is the ion concentration (#/m^3), J is the applied current density (A/m^2), and t_a is the anion transference number (non-dimensional).

Previous reports[6-8] find that the dendrite nucleation time of symmetric lithium cells containing a PEO-LiTFSI electrolyte undergoing galvanostatic polarization at high current density values is roughly equal to Sand's time and thus fit the Chazalviel's model. Experimental work has shown that dendrite onset occurs at this timescale even at low current densities, when finite anion concentrations are predicted at the interface and a stable potential exists in cells being galvanostatically polarized at steady-state.[7]

Optical measurements[9] have indicated that the dendrite front advances at the same rate as the anion depletion zone retreats across the cell, at a speed

$$v = \mu_a E \qquad \text{(Equation 2)}$$

where μ_a is the anion mobility ($m^2/V/s$) and the electric field $E = J/\sigma$ (V/m), where σ is the DC ionic conductivity (S/m), at moderate fields, also as predicted by Chazalviel.[5] The time required for dendrites to traverse the distance L between electrodes can therefore be approximated as

$$t_g = \frac{\sigma L}{\mu_a J} \qquad \text{(Equation 3)}$$

where t_g is the dendrite growth time and L is the interelectrode distance. Therefore, the predicted short circuit time, t_{sc} according to the Chazalviel model is

$$t_{sc\,predicted} \approx \tau_s + t_g = \pi D \left(\frac{eC_0}{2Jt_a}\right)^2 + \frac{\sigma L}{\mu_a J} \qquad \text{(Equation 4)}$$

where t_g is the dendrite growth time and τ_s is the Sand's time (dendrite onset time). The short circuit time has been shown by optical measurements to be equivalent to the drop-off in the potential observed during galvanostatic polarization experiments. No immediate drop in the cell potential is observed before the dendrite spans the interelectrode space and short circuits the cell.[8]

Knowledge of the mobile ion concentration in conjuction with ionic conductivity data allows the ambipolar diffusion coefficient D to be calculated using the Nernst-Einstein equation:

$$D = \frac{\lambda kT}{C_0 q^2} \quad \text{(Equation 5)}$$

where λ is the molar DC ionic conductivity (S-m^2/mol), k is the Boltzmann constant (J/K), T is temperature (K), and q is the charge of the diffusing species (C). The molar DC ionic conductivity, λ, is related to the measured DC ionic conductivity (σ) *via* the following relationship:

$$\lambda = {}^{\sigma}/_{n} \quad \text{(Equation 6)}$$

where n is the molar ion concentration (mol/m^3) and .

For the purposes of this publication, C_o of a given electrolyte is calculated by determining the relative volume fractions of the PE and PEO domains by considering the weight fraction of PE and PEO in the copolymer, and assuming that the density of PE is 0.90 g/cm^3, the density of the PEO is 1.1 g/cm^3, and the density of the PEO/LiTFSI domain is 1.38 g/cm^3. PEO doped with LiTFSI to a concentration of 1:18 Li:EO is calculated to have $n = 1.17$ M, assuming an ideal mixture. It is also assumed that all of the LiTFSI is dissociated, contributing to the effective C_0 and to the ionic conductivity, as has been found experimentally for other PEO-LiTFSI electrolytes.[10]

The lithium transference number, t_{Li+}, of electrolyte (^{70}PEOX$_{0.34}$)(^{34}PE$_{0.35}$)(^{5}PEG$_{0.31}$) was measured via the Bruce-Scrosati method[11] to be 0.16 ± 0.01 at 90 °C. Therefore, the anion transference number for this sample is as follows: t_a = 1 - t_{Li+}= 0.84 ± 0.01 at 90 °C. The anion transference number of the other samples under consideration was assumed to be equivalent to this value.

The interelectrode distance, L, was assumed to be equal to the average electrolyte film thickness, 200 μm. Finally, the anion mobility, μ_a, was computed from the Einstein relation as

$$\mu_a = \frac{qDt_a}{kT} \quad \text{(Equation 7)}$$

The predicted short circuit times ($t_{sc\ predicted}$) for the ^{70}PEOX electrolytes with different weight% of the plasticizer were calculated according to the Chazalviel model as given by equation 4. Table S5 displays the computed parameters that were used to calculate $t_{sc\ predicted}$ at 90 °C and variable current density values (0.25 – 1.0 mA/cm^2). The representative values of the predicted short-circuit times at 0.26 mA/cm^2 are also shown in Table S5.

Table S5: Predicted short-circuit times for ^{70}PEOX electrolytes using Chazalviel model.[a]

Entry	Sample Name	Sigma, σ (S/cm)	C_o (#/m^3)	D (m^2/s)	μ_a (m^2/V/s)	0.26 mA/cm^2 Current Density		
						τ_s (h)	t_g (h)	$t_{sc\ pred}$ (h)
1	(^{70}PEOX$_{0.50}$)(^{34}PE$_{0.50}$)	5.0×10^{-4}	3.6×10^{26}	2.8×10^{-11}	7.4×10^{-10}	4.1	1.5	5.6
2	(^{70}PEOX$_{0.43}$)(^{34}PE$_{0.43}$)(^{5}PEG$_{0.14}$)	9.6×10^{-4}	4.1×10^{26}	4.6×10^{-11}	1.2×10^{-9}	8.9	1.7	11
3	(^{70}PEOX$_{0.39}$)(^{34}PE$_{0.39}$)(^{5}PEG$_{0.22}$)	1.0×10^{-3}	4.3×10^{26}	4.6×10^{-11}	1.2×10^{-9}	10	1.8	12
4	(^{70}PEOX$_{0.34}$)(^{34}PE$_{0.35}$)(^{5}PEG$_{0.31}$)	1.9×10^{-3}	4.6×10^{26}	8.1×10^{-11}	2.2×10^{-9}	20	1.9	22
5	(^{70}PEOX$_{0.30}$)(^{34}PE$_{0.31}$)(^{5}PEG$_{0.39}$)	2.1×10^{-3}	4.9×10^{26}	8.3×10^{-11}	1.0×10^{-9}	23	2.0	25

[a]All films had 70 EO units in the crosslinker and [**COE**]:[**1**] loading of 15:1. The composition of [EO]:[Li] in each of the sample is 18:1; where EO includes ethylene oxide units contained both in the PEOX crosslinker and PEG plasticizer.

The experimentally observed t_{sc} values were compared to the $t_{sc\ predicted}$ values for the ^{70}PEOX SPEs at variable current density values and the data is shown in Figure S12. We observed an order of magnitude higher t_{sc} values than predicted by Chazalviel model for most compositions of the PE-PEO cross-linked SPEs. While the absolute values of the short-circuit times are well above the t_{sc} values predicted by the model, the functional dependence of the t_{sc} with respect to the applied current density is similar to that predicted by the model.

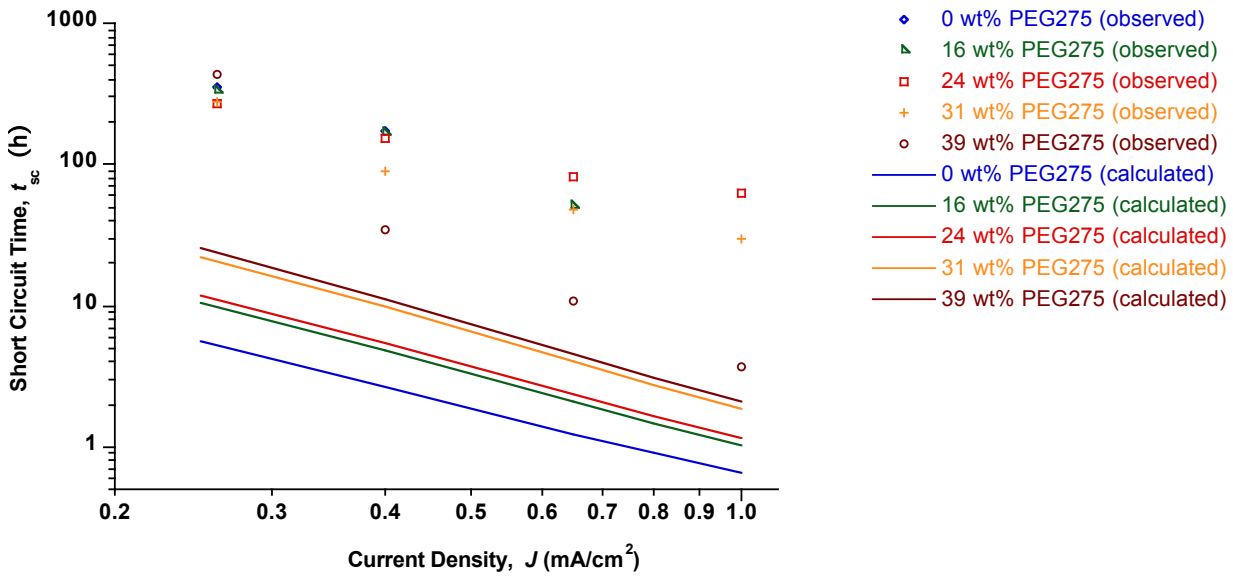


Figure S12. Comparison of measured t_{sc} with the predicted short-circuit times for ^{70}PEOX electrolytes having different weight% of the plasticizer at 90 °C. All films had [**COE**]:[**1**] ratio of 15:1 and [EO]:[Li] composition of 18:1. The observed t_{sc} values are shown with hollow symbols and the calculated values as predicted by Chazalviel model are shown as solid lines.

Rheology

The storage $G'(\omega)$ and loss $G''(\omega)$ moduli were quantified using small amplitude oscillatory shear measurements. Anton Paar Physica MCR 301 rheometer with 10 mm diameter parallel plates was used for rheological measurements. The properties were measured as a function of applied angular frequency at low strain (0.1%) and 90 °C. The shear rheology for the ^{70}PEOX electrolytes (Table 2) is displayed in Figure S13. Both the unplasticized (0 wt% PEG275) and plasticized polymer electrolytes (16, 24, 31 and 39 wt% PEG275) exhibit solid-like properties, as evident by the frequency independent moduli. Also, the $G'(\omega)$ of these SPEs is an order of magnitude higher than $G''(\omega)$, suggesting that these electrolytes act as an elastic solids. The storage moduli, G' of these PE-PEO cross-linked polymer electrolytes is ~ 10^5 Pa at 90 °C.

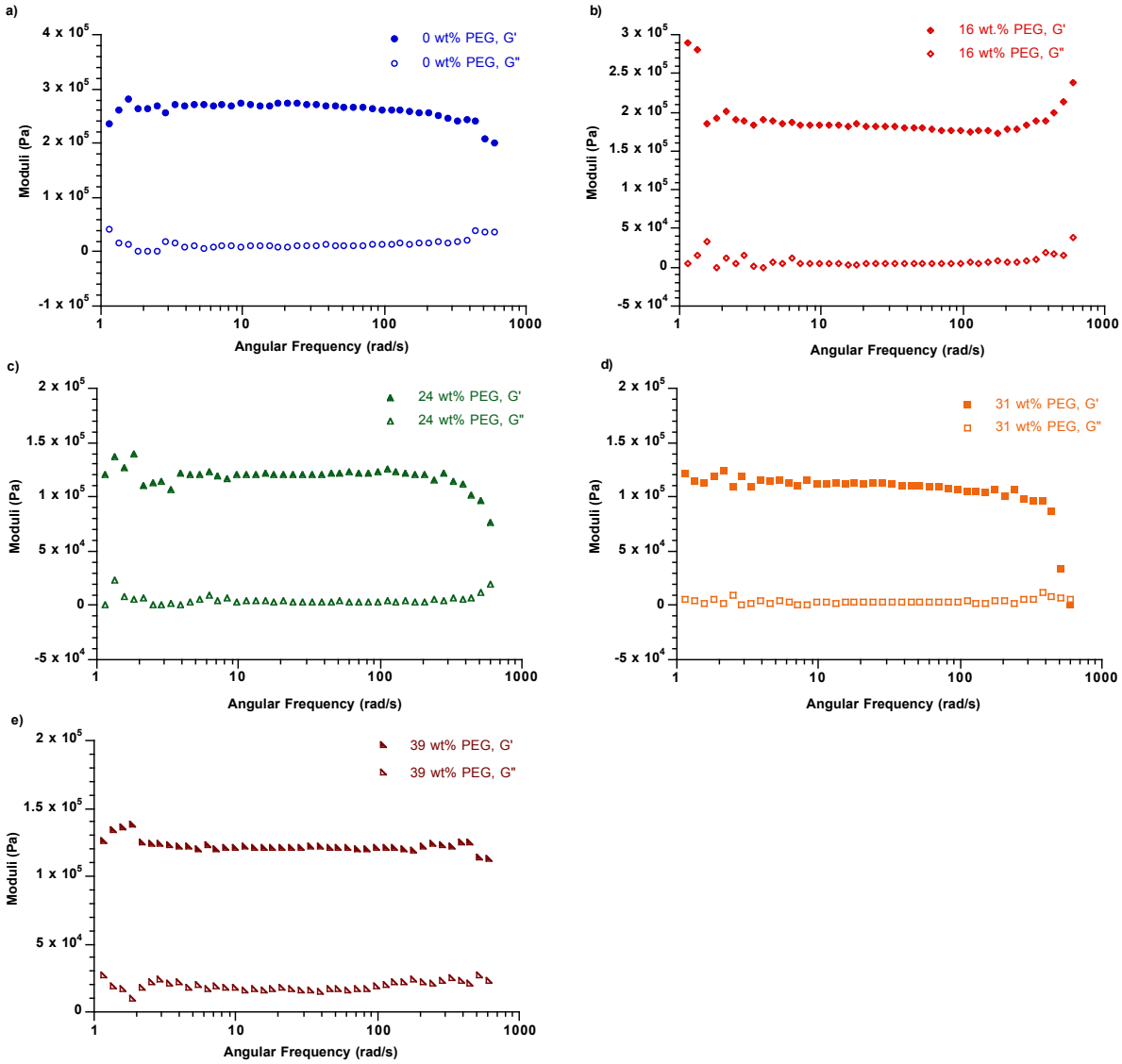


Figure S13. Rheological measurements on ^{70}PEOX electrolytes having different weight% of the plasticizer at 90 °C. All films had [**COE**]:[**1**] ratio of 15:1 and [EO]:[Li] composition of 18:1. Storage modulus $G'(\omega)$ is shown with filled symbols, and the loss modulus $G''(\omega)$ is shown with hollow symbols. a) 0 wt%, b) 16 wt%, c) 24 wt%, d) 31 wt%, and e) 39 wt% PEG275 plasticizer in the cross-linked films.

The shear rheology measurement for PEO 900 kDa sample at 90 °C was also performed and the data is shown in Figure S14. The frequency dependent moduli of PEO sample indicate that it

has fluid-like properties as opposed to the PE-PEO cross-linked samples. The storage moduli, G' of the PEO sample was observed to be ~ 4×10^4 Pa at 10 rad/s, 0.1% strain and 90 °C.

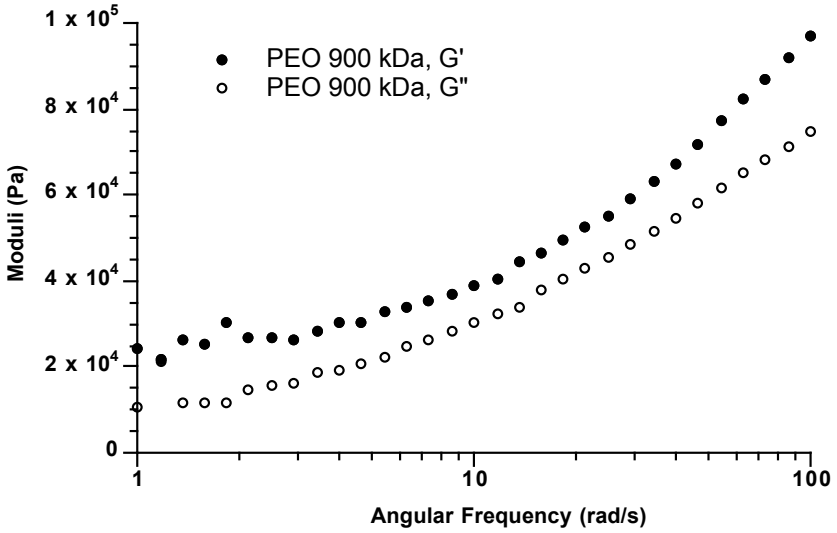


Figure S14. Rheological measurements on PEO 900 kDa sample with [EO]:[Li] composition of 18:1 at 90 °C. Storage modulus $G'(\omega)$ is shown with filled symbols, and the loss modulus $G''(\omega)$ is shown with hollow symbols.

Electrochemical Impedance Spectroscopy (EIS)

The ac impedance spectroscopy measurements were made using Li/SPE/Li symmetric coin cells prepared in an argon filled MBraun glovebox, using a Novocontrol Broadband Dielectric Spectrometer fitted with a Quatro temperature control system at frequency ranging from 2 KHz to 900 MHz and at an amplitude of 10 mV. Impedance spectra for the ^{70}PEOX electrolytes were measured as a function of wt% of the plasticizer at 18 °C (Figure S15a). The bulk resistance (R_b) of the polymer electrolytes decreases significantly with the increase in the amount of PEG275 in the SPEs, while interfacial resistance (R_i) remains relatively constant. The variable temperature impedance spectra for ($^{70}PEOX_{0.34}$)($^{34}PE_{0.35}$)($^{5}PEG_{0.31}$) are shown in Figure S15b. The electrolyte exhibit low interfacial resistance (~10 Ω/cm^2) in contact with lithium metal at 90 °C. Notably, at elevated temperatures the measured interfacial resistance is lower than that of the bulk resistance.

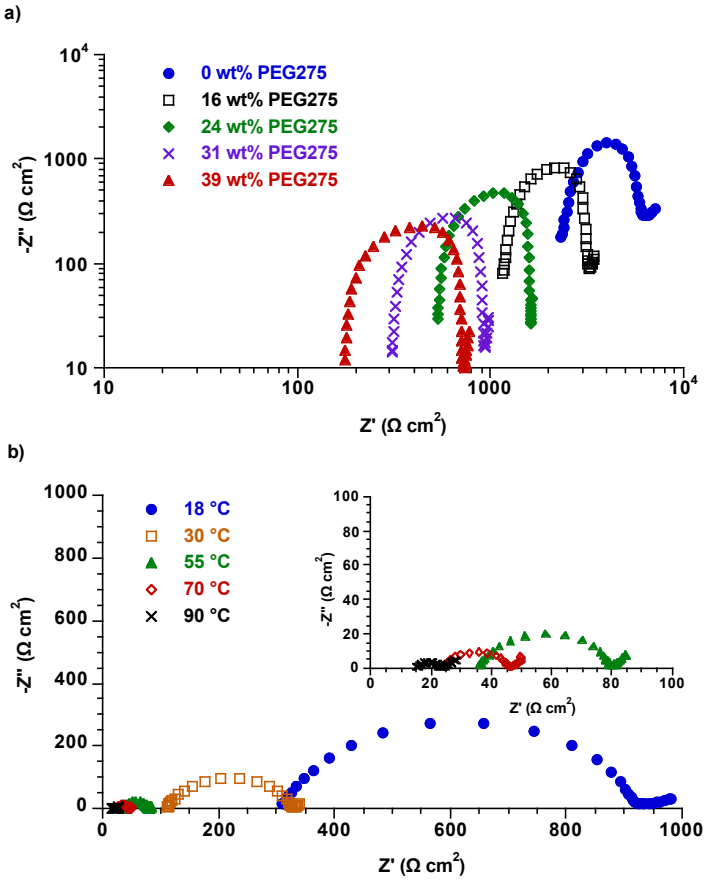


Figure S15. a) Impedance spectra for ^{70}PEOX electrolytes with varied plasticizer weight at 18 °C. All films had [**COE**]:[**1**] ratio of 15:1 and [EO]:[Li] composition of 18:1. b) Impedance spectra for (^{70}PEOX$_{0.34}$)(^{34}PE$_{0.35}$)(^{5}PEG$_{0.31}$) at variable temperature.

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