Supporting Information

Achieving Uniform Lithium Electrodeposition in Cross-linked Poly(ethylene oxide) Networks: “Soft” Polymers Prevent Metal Dendrite Proliferation

Sanjuna Stalin, Hillis E. N. Johnson, Prayag Biswal, Duylinh Vu, Qing Zhao, Jiefu Yin, Brooks A. Abel, Yue Deng, Geoffrey W. Coates, Lynden A. Archer

School of Chemical and Biomolecular Engineering, Olin Hall, Cornell University, Ithaca, NY 14853, USA
Department of Chemistry and Chemical Biology, Cornell University, Baker Laboratory, Ithaca, NY 14853, USA
Department of Materials Science and Engineering, Bard Hall, Cornell University, Ithaca, NY 14853, USA

1. General Considerations
2. Materials
3. Synthesis
3.1 Synthesis of PEG Diallyl Ether (PEGDA)
   Figure S1
3.2 Synthesis of Cross-linked Polymer Electrolyte (XPE)
   Figure S2
   Figure S3
   Figure S4
3.3 Synthesis of Cross-linked Polymer Gel Electrolytes (XPGE)
4. Electrochemical Characterization
5. Supplementary Figures
   Figure S5
   Figure S6
   Figure S7
   Figure S8
   Figure S9
   Table S1
1. General Considerations

All air and water sensitive manipulations for the synthesis of the cross-linked polymer networks were carried out under dry nitrogen conditions. Air and water sensitive manipulations for cell assembly and manipulation of lithium metal were carried out in an argon glovebox with <0.1 ppm of water and oxygen. \(^{1}\)H spectra were collected on a Bruker AV III HD (\(^{1}\)H, 500 MHz) spectrometer with a broad band Prodigy cryoprobe and referenced to residual non-deuterated solvent shifts (CHCl\(_3\) = 7.26 ppm). \(^{13}\)C NMR were collected on a Bruker AV III HD (\(^{13}\)C, 125 MHz) spectrometer with a broad band Prodigy cryoprobe and referenced to chloroform (\(\delta = 77.16\) ppm). FT-IR spectra were recorded on a Bruker Tensor II FTIR Spectrometer equipped with an attenuated total reflectance (ATR) accessory.
Atomic force microscopy (AFM) images were measured at the Cornell Energy Systems Institute (CESI) using Cypher ES, Oxford Instruments Asylum Research, Inc. AC tapping mode was selected to collect topography and phase images using an AC160TS-R3 probe (frequency 300 kHz, spring constant 26 N/m, 7 nm tip radius).

Oscillatory shear measurements were performed using a MCR301 (Anton Paar) rheometer at Cornell Energy Systems Institute (CESI) equipped with a 10 mm parallel plate fixture at temperatures ranging from 40 to 90 °C. A low strain rate of 0.1% was used for the frequency sweeps to remain in the linear viscoelastic regime.

X-ray Photoelectron Spectroscopy measurements were conducted at the Cornell Center for Materials Research (CCMR) using a Surface Science Instruments SSX-100 with an operating pressure of ~2×10⁻⁹ torr. Monochromatic Al K-α x-rays (1486.6 eV) with beam diameter of 1 mm were used. Photoelectrons were collected at an emission angle of 55° and the electron kinetic energy was determined by a hemispherical analyzer, where a pass energy of 150 V was used for wide survey scans and 50V for high resolution scans. CasaXPS software was used for XPS data analysis with Shelby backgrounds and the spectra were referenced to adventitious C 1s at 284.5 eV.

2. Materials

Tetrahydrofuran (THF) was purified over a column of alumina and degassed by three freeze-pump thaw cycles and stored under nitrogen. Poly(ethylene glycol) ($M_n$ 1,000, 3,000, and 4,600 g/mol) (Sigma Aldrich) was dried by azeotroping with toluene at 80 °C under vacuum for 16 h. Sodium hydride (Sigma Aldrich, 90%) and Lithium bis(trifluoromethanesulfonyl)imide (Sigma Aldrich, 99.95 % trace metals basis) were stored under nitrogen in a glovebox. Lithium
foil was purchased from Alfa Aesar and NCM 811 cathodes were provided by Nohms Inc. Celgard 3501 was used for control samples in electrochemical testing and Glass Fibre Separators were obtained from Fischer Scientific. All other reagents were purchased from commercial sources and used as received unless otherwise noted.

3. Synthesis

3.1 Synthesis of PEG Diallyl Ether (PEGDA)

Poly(ethylene glycol)s of $M_n$ 1,000 g/mol, 3,000 g/mol, and 5,000 g/mol were functionalized using the following representative procedure: To a suspension of NaH (1.33 g, 50.1 mmol) in anhydrous THF (50 mL) was added dropwise a solution of PEG ($M_n = 3,000$ g/mol) (50 g, 16.7 mmol) in anhydrous THF (150 mL). The mixture was stirred under N$_2$ at 22 °C for 16 h with an oil bubbler to allow H$_2$ evolution. Allyl bromide (7.2 mL, 83.3 mmol) was then added dropwise over 10 min and the mixture was heated to 50 °C under N$_2$ for 24 h. The solution was quenched with a minimum amount of methanol and the solution was filtered through a pad of celite. The filtrate was concentrated under vacuum and the residue was taken up in DCM (~250 mL) and washed with 20 % NH$_4$OH (2 x 100 mL), 1 M HCl (2 x 100 mL), and brine. The organic layer was dried over MgSO$_4$, filtered, and concentrated under vacuum. The oil residue was then precipitated into cold ether (~500 mL), collected, and dried. Precipitations were repeated as necessary to obtain a white powder (41 g, 80 %).$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 5.93–5.82 ppm (m, 2H), 5.27–5.21 ppm (dd, $J = 17.5, 1.8$ Hz, 2H), 5.17 – 5.11 ppm (dd, $J = 10.4, 1.6$ Hz, 2H), 3.99 ppm (d, $J = 5.7$, 4H), 3.80–3.40 ppm (m, 299 H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 134.75, 117.06, 72.21, 70.61, 70.55, 69.41 ppm. The number average molecular weight ($M_n$) by $^1$H NMR
was determined to be 1065 g/mol, 3300 g/mol, and 5020 g/mol for the three PEGDA macromonomers used in the study.
[a] 1000 g/mol PEGDA $^1$H & $^{13}$C NMR
[b] 3000 g/mol PEGDA $^1$H & $^{13}$C NMR
[a] 5000 g/mol PEGDA $^1$H & $^{13}$C NMR

Diagram of chemical structures and NMR spectra.
**Figure S1.** Representative $^1$H NMR Spectrum (500 MHz, CDCl$_3$) and $^{13}$C NMR Spectrum (125 MHz, CDCl$_3$) of PEG diallyl ether (PEGDA). [a] 1000 g/mol PEGDA. $M_{n \text{ nmr}} = 1065$ g/mol. [b] 3000 g/mol PEGDA. $M_{n \text{ nmr}} = 3300$ g/mol. [c] 5000 g/mol PEGDA. $M_{n \text{ nmr}} = 5020$ g/mol.

### 3.2 Synthesis of Cross-linked Polymer Electrolyte (XPE)

PEGDA was mixed with pentaerythritol tetrakis (3-mercaptopropionate) (4T) in a 2:1 molar ratio to maintain a 1:1 stoichiometry between thiol and allyl reactive groups. Lithium bis(trifluoromethanesulfonyl)imide salt was added in the desired EO:Li ratio and the mixture was stirred at 80 °C until homogeneous. The photoinitiator, 2,2-Dimethoxy-2-phenylacetophenone (DMPA), was mixed into the precursor solution at 1 mol % immediately before casting the monomer mixture between silylated glass plates. A 100 μm spacer was used to control the film thickness. The film was cured at 80 °C under 350 nm of UV light for 12 hours to ensure maximum conversion. We note, however, that films cured for 30 minutes showed identical mechanical properties to films cured for longer times (Figure S2). The films were dried at 80 °C under vacuum for 48 hours and stored in an argon glovebox prior to cell assembly and electrochemical characterization.
Figure S2. Storage and loss modulus of XPE-3k at different cure times.

Figure S3. FT-IR spectra of the XPE networks. Given the relatively low concentration of thiol and allyl functional groups present during the reaction, functional group conversion was difficult to measure.
Figure S4. Differential Scanning Calorimetry (DSC) traces of synthesized cross-linked polymer electrolytes. Heating and cooling was done at 10 °C/min. [a] XPE-1k. [b] XPE-3k. [c] XPE-5k.
3.3 Synthesis of Cross-linked Polymer Gel Electrolytes (XPGE)

PEGDA was mixed with pentaerythritol tetrakis (3-mercaptopropionate) (4T) in a 2:1 molar ratio to maintain a 1:1 stoichiometry between thiol and allyl reactive groups. The mixture was stirred at 80 °C until homogeneous. The photo-initiator, 2,2-Dimethoxy-2-phenylacetophenone (DMPA), was added to the precursor solution at 1 mol % and mixed briefly before film casting. Samples for the lithium deposition visualization studies were cast in a stainless-steel mold (15 mm diameter, 2 mm depth). Samples for full cell battery tests were cast between silylated glass plates at an average thickness of 100 μm. The films were cured at 80 °C under 350 nm of UV light for 16 hours to ensure full conversion. The films were then dried at 80 °C under vacuum for 48 hours. Inside an argon glovebox, the membranes were soaked for 1 hour in an electrolyte solution until equilibrium swelling was achieved. For full cell Li||NCM 622 tests, the liquid electrolyte component was composed of 0.4 M LiBOB, 0.6 M LiTFSI, 0.05 M LiPF₆ in 1:1 (v:v) EC/DMC. For all other experiments utilizing XPGE membranes, the liquid component used was 1 M LiTFSI in 1:1 (v:v) EC/DMC.

4. Electrochemical Characterization

Ionic conductivity and impedance measurements as a function of temperature were measured at Cornell Energy Systems Institute (CESI) with a Novocontrol N40 broadband spectrometer fitted with a Quarto temperature control system. The coin cells were assembled under argon atmosphere (<0.1 ppm water and air) by sandwiching the electrolyte between two stainless steel electrodes (and lithium as the electrodes for impedance measurements) and sealed in the glovebox to prevent contamination. Galvanostatic strip/plate experiments were performed using
coin cells with the electrolyte sandwiched between two lithium electrodes (diameter = 6.35 mm). Cyclic Voltammetry measurements were performed using a high scan rate of 0.2 V/s in symmetric cells with small electrodes (2mm radius) to avoid ohmic drops and polarizations. High temperature measurements were performed by placing the coin cells in a convection oven (VWR). Visualization was performed in a setup previously described.\textsuperscript{1} Analysis of dendrite growth was performed using MatLab. Full cell measurements were performed using a high loading NCM cathode (3mA/cm\textsuperscript{2} from NOHMS Inc.) and lithium foil as the cathode. At the cathode side, a Celgard 3501 layer was soaked with a small amount of liquid electrolyte with the additives mentioned to wet the porous electrode.

5. Supplementary Figures

Figure S5. Phase mapping using Atomic Force Microscopy. [a] Thiol-ene polymer networks. [b] Thiol-ene polymer networks in the presence of LiTFSI.’
Figure S6. Vogel–Fulcher–Tamman plot of conductivity of cross-linked polymer electrolytes with different PEO molecular weights between cross-links.

Figure S7. Rheological properties of crosslinked networks. [a] Storage and loss modulus of XPE-3k networks obtained from frequency sweep at a fixed strain of 0.1%. [b] Storage modulus as a function of temperature for cross-linked polymer electrolytes with varying PEGDA molecular weights.
Figure S8. Galvanostatic stripping-plating of XPE-3k at different temperatures. [a] 40 °C. [b] 60 °C. [c] 90 °C. Tests involve one-hour stripping and plating cycles.
Figure S9. Impedance spectra of XPE-3k at different temperatures. [a] Impedance at 15 °C, separated for clarity. [b] Impedance at 30 °C, 45 °C, 60 °C, 75 °C, and 90 °C. [c] Model used to fit impedance data. See Table S1 for values.
Table S1. Fitted Impedance values$^a$

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>R (Bulk)</th>
<th>R1 (Interphase)</th>
<th>R2 (Charge Transfer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>118.7</td>
<td>4028</td>
<td>3753</td>
</tr>
<tr>
<td>30</td>
<td>91.8</td>
<td>523.6</td>
<td>794.9</td>
</tr>
<tr>
<td>45</td>
<td>66.5</td>
<td>158.3</td>
<td>243.4</td>
</tr>
<tr>
<td>60</td>
<td>46.6</td>
<td>58.9</td>
<td>92.0</td>
</tr>
<tr>
<td>75</td>
<td>33.7</td>
<td>38.9</td>
<td>53.0</td>
</tr>
<tr>
<td>90</td>
<td>24.7</td>
<td>19.0</td>
<td>20.4</td>
</tr>
</tbody>
</table>

$^a$Fitted values were obtained using the depicted model shown in Figure S8.

Figure S10. Galvanostatic polarization of XPE-3k at 0.5 mA/cm$^2$ with different temperatures of operation. Vertical dashed lines indicate where cell failure occurs.
Figure S11. IV curve of XPE-3k at 90 °C. Measurements were done by holding the sample at each potential-step from 0–5 V for five minutes until steady-state current was reached.

Figure S12. Shear rheology of XPGE-1k, XPGE-3k, and XPGE-5k at a fixed strain of 0.1 %. Note that the measured modulus of the gel electrolytes (XPGE) are very similar to the modulus of their non-gelled counterparts (XPE).
Figure S13. Measured conductivity of XPGE-3k (soaked with 1M LiTFSI in EC/DMC) as a function of temperature.

Figure S14. Impedance spectra of XPGE-3k at room temperature.
Figure S15. Comparison of voltage profiles between Celgard 3501 and XPGE-3k at different stages of time. [a] 0–20 h. [b] 650–800 h. [c] 680–920 h.
Figure S16. Galvanostatic strip-plate of XPGE-3k at 1 mA/cm$^2$.

Figure S17. Galvanostatic polarization at 1 mA/cm$^2$ of a soaked glass fiber electrolyte compared to XPGE-3k. Vertical dashed lines indicate where cell failure occurs.
Figure S18. XPS analysis of the solid electrolyte interphase (SEI) formed with a liquid electrolyte composed of 1 M LiTFSI in 1:1 (v:v) EC/DMC. Comparison with the SEI formed in the XPGE system suggests there is little to no polymer degradation relative to the byproducts formed by reaction of the liquid electrolyte component.
**Figure S19.** Voltage profile vs capacity for cells containing XPGE-3k or liquid electrolyte with Celgard 3501 at 1 mA/cm².

![Image of voltage profile](image)

**Figure S20.** Visualization of lithium electrodeposition in XPGE-5k and XPGE-1k at J = 6 mA/cm².

![Image of electrodeposition](image)

**Figure S21.** Diagram of the experimental setup used to model compression of the XPGE networks during the lithium deposition process. The custom-made parallel upper plate had a diameter of 1.5
mm. The upper plate was driven downward at a constant normal velocity to observe the response within the polymer network.

Figure S22. Compressive stress in cross-linked polymer gel electrolytes for three different compression velocities. [a] XPGE-1k. [b] XPGE-3k. [c] XPGE-5k.

Figure S23. [a] Full Cell cycling results for a control cell consisting of only the liquid electrolyte (0.4 M LiBOB, 0.6 M LiTFSI, 0.05 M LiPF6 in 1:1 (v:v) EC/DMC) with no polymer membrane
at a rate of C/5. The cell contained a 750 µm thick lithium metal anode and an NCM 622 cathode.

[b] Voltage profiles for the 5th, 20th and 100th cycles.

References: