
Supporting Information

Nanophase-Separated, Elastic Epoxy Composite Thin-film As Electrolyte for Stable Lithium Metal Batteries

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Experimental

Synthesis of eEP, eEPE and eEPE-PE film

Jeffamine T5000 (donated by Huntsman), DER332 (donated by Dow), and monoisopropanolamine (MIPA, Alladin) were used as received to synthesize the elastomeric epoxy polymer. The molar ratio of the ethylene oxide groups in the DER332 to N-H groups in the T5000 was chosen as 2:1, 3:1, 4:1 and 5:1. The prepolymers were generated via the stepwise addition reactions of T5000 with DER332. The terminal amino groups (-NH_2) in T5000 were reacted with the terminal ethylene oxide groups of DER332 at 100 °C. Then the epoxy-terminated prepolymer was mixed with MIPA in a centrifugal mixer for 300 seconds at 2500 rpm. Finally, eEP-50 μm films were formed by hot-pressing the mixtures for about 2 hours at 110°C in a shaped die. Besides, the mixtures were infiltrated and hot-pressed into the 8 μm PE separator to get eEP-PE films (around 20 μm). These polymer films were immediately transferred to an argon glovebox to minimize absorption of water from air. In the glovebox, bis(trifluoromethane) sulfonimide lithium salt (LiTFSI, Sigma)/propylene carbonate (PC, Sigma) mixture was added and the films were allowed to swell and equilibrate between two glass slides for at least 2 h to obtain the final eEPE-50 μm and eEPE-PE film.

Characterization

A FTIR test was conducted on a Bruker Vertex 70 spectrometer (the frequency range is 400 – 5000 cm^{-1}). Mechanical testing was carried out on an Instron 5565 testing stain using a strain rate of 1 mm/min. Differential scanning calorimetry (DSC, Diamond DSC, PerkinElmer Instruments) measurements were performed to characterize the thermal property of SPEs with a rate of 10 °C min^{-1} (from –60°C to 100 °C). Thermogravimetric analysis (TGA) experiments were carried out on a TGA-SDTA851 (Mettler–Toledo) using a ramp rate of 10 °C min^{-1} from room temperature up to 600 °C under N_2 atmosphere. Scanning electron microscopy was performed on a FEI Nova NanoSEM 450. The small-angle X-ray scattering (SAXS)

measurements on polymer films in transmission geometry were carried out on SAXS ess mc2 (Anton Paar).

Electrochemical Characterization

The electrolyte membranes were sandwiched between two stainless steel (SS) electrodes with a diameter of 15.4 mm, and the coin cells (CR2032) of SS|SPE|SS were assembled to determine the ionic conductivities. The electrochemical impedance spectroscopy (EIS) was measured using a CHI 660E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd) in the temperature range from 20 °C to 80 °C, and the frequency range was set from 0.1 Hz to 1 MHz with amplitude of 10 mV. The ionic conductivity was obtained using the following equation: $\sigma = L/SR$, where L (cm) is the thickness of SPE membrane ($\approx 50 \mu\text{m}$ and measured by the micrometer), R (Ω) is the bulk resistance of the electrolyte obtained from EIS, and S (cm^2) is the contact area of the electrode and electrolyte. The electrochemical stability windows of the SPEs were determined by linear sweep voltammograms from 1 to 5 V at a scan rate of 0.1 mV s^{-1} using Li|SPE|SS.

A Li/SPE/Li cell was tested by AC impedance and DC polarization to calculate transference number t_{Li^+} from Bruce-Vincent-Evans equation: $t_{\text{Li}^+} = \frac{I_{ss}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{ss} R_{ss})}$. The applied polarization voltage is 10 mV (ΔV). I_0 and I_{ss} are read from time-dependence current curve, and R_0 and R_{ss} represent the initial resistance and the steady-state resistance of the passivating layer on the lithium electrode, respectively.

The interfacial compatibility of SPE was measured by monitoring the interfacial resistance of Li|SPE|Li cells at different cycles and temperatures. Two spacers and a wave spring were used on the anode side of the cell to ensure good contact between the electrolyte and the electrodes. Coin cells were assembled in an Ar filled glove box. For cells with the ePEs, Li metal foil and LiFePO_4 (LFP) electrodes were used as the counter and working electrodes, the latter of which consisted of 80 wt% LFP power, 10 wt% polyvinylidene fluoride (PVDF), and

10 wt% Super P with a typical mass loading of $\approx 2 \text{ mg cm}^{-2}$ on an aluminum current collector. 5 μL of liquid electrolyte, LiTFSI: PC (2:3 w/w), was used to wet the surface of the LFP electrodes during battery assembly. Coin cells were loaded into a battery test (a LAND 8 - channel battery tester) and cycled between 3 and 4.0 V.

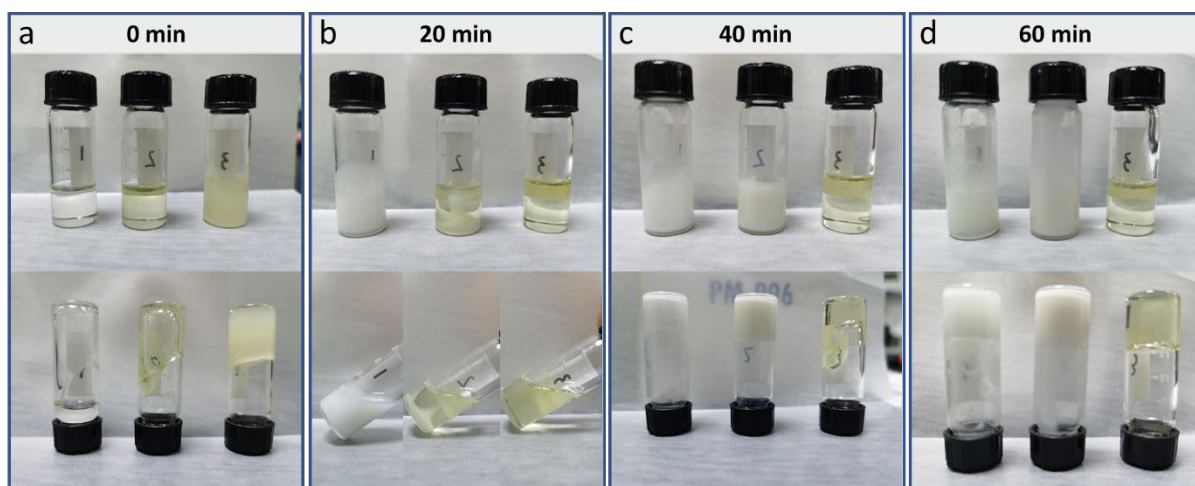


Figure S1. Optical images of curing process in D5T1-M4 (No. 1), pD5T1-M4 (No. 2), and pD5T1-M4-Z (No. 3). (left to right)

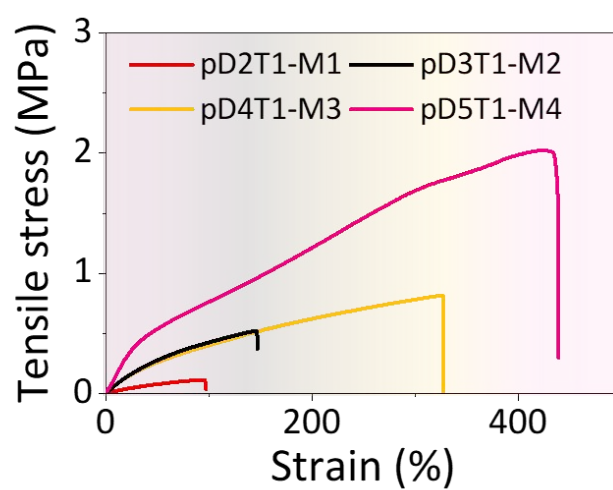


Figure S2. Stress-strain curves of pD2T1-M1 to pD5T1-M4

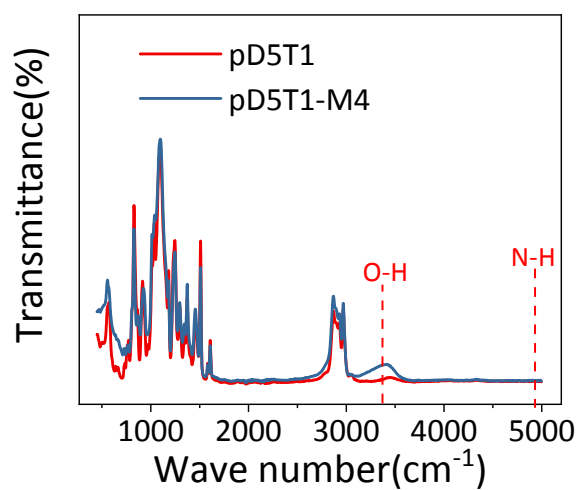


Figure S3. FTIR Characterization of pD5T1 prepolymer and pD5T1-M4.

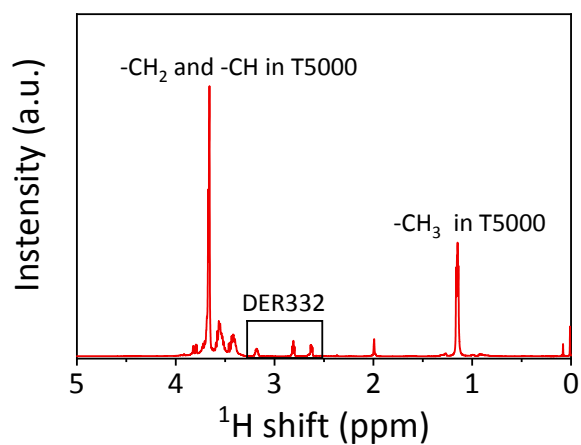


Figure S4. NMR Characterization of pD5T1 prepolymer.

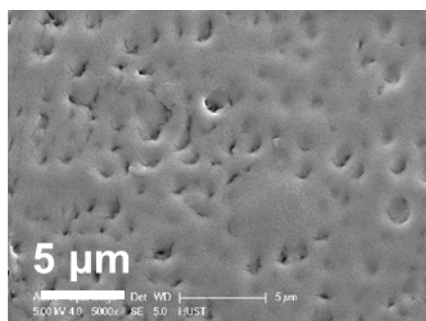


Figure S5. SEM image with higher magnification of pD5T1-M4-Z.

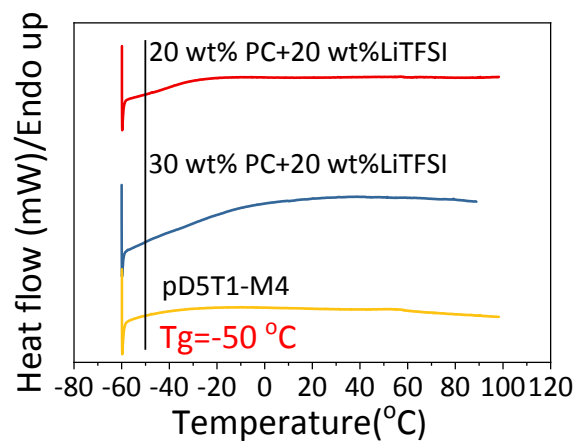


Figure S6. DSC curves of pD5T1-M4-Z with different content of Li salt and PC plasticizer

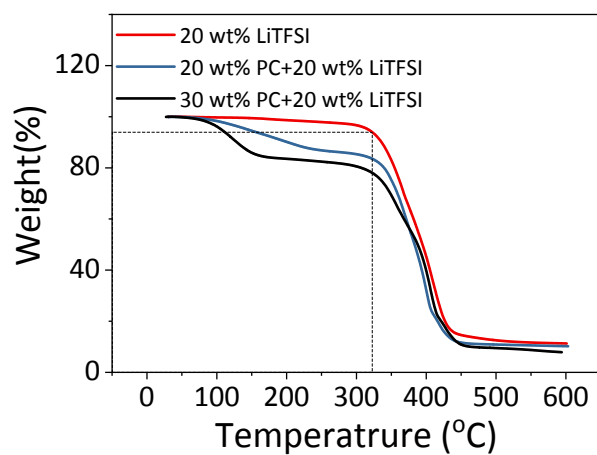


Figure S7. TGA curves of pD5T1-M4-Z with different content of Li salt and PC plasticizer

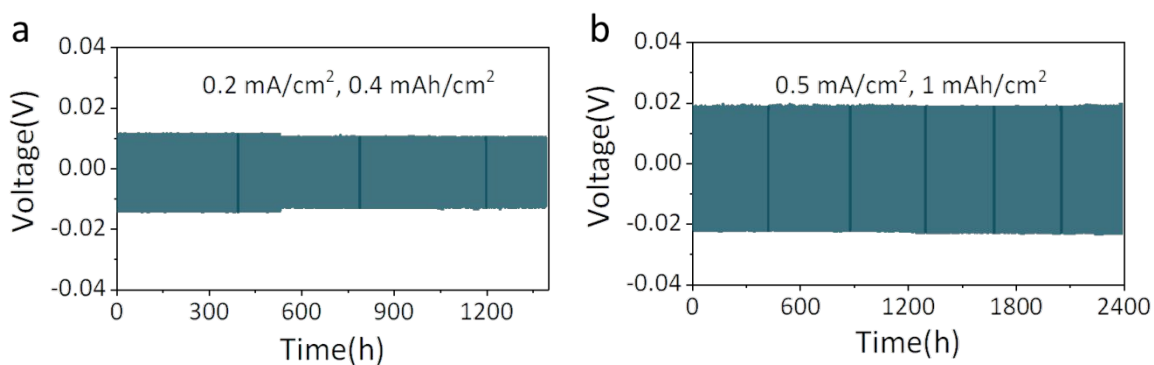


Figure S8. Li/Li symmetric cells with ePE-50 μ m electrolyte at a current density and a capacity of (a) 0.2 mA cm⁻², 0.4 mAh cm⁻², (b) 0.5 mA cm⁻², 1 mAh cm⁻²

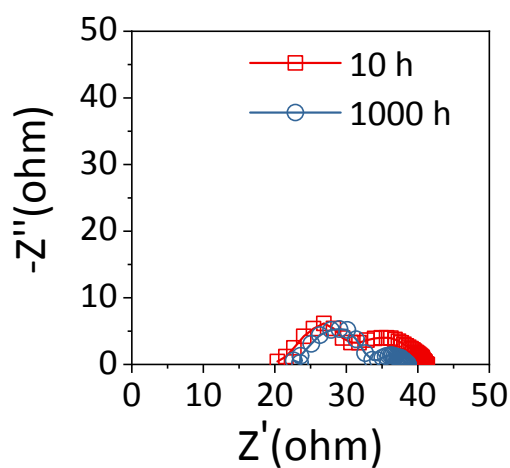


Figure S9. Nyquist plot of cycled Li/Li symmetric cells at 2 mA cm^{-2} and 2 mAh cm^{-2} .

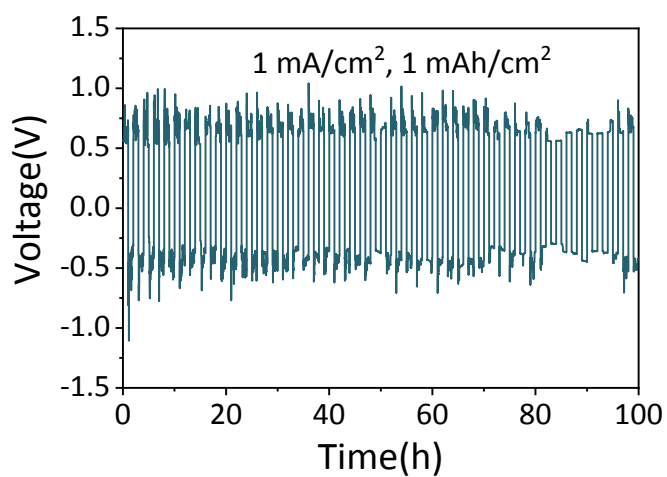


Figure S10. Li/Li symmetric cells with 1M LiTFSI PC electrolyte at a current density and a capacity of 1 mA cm^{-2} , 1 mAh cm^{-2} .

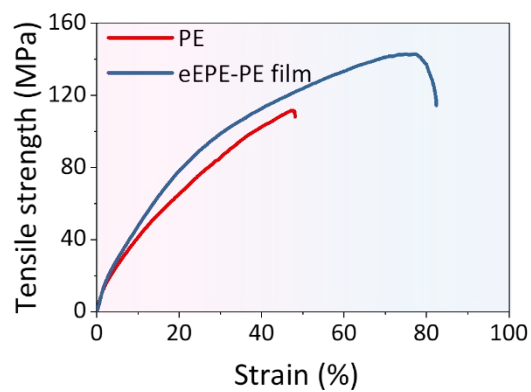


Figure S11. Stress-strain curves of PE separator and eEPE-PE film

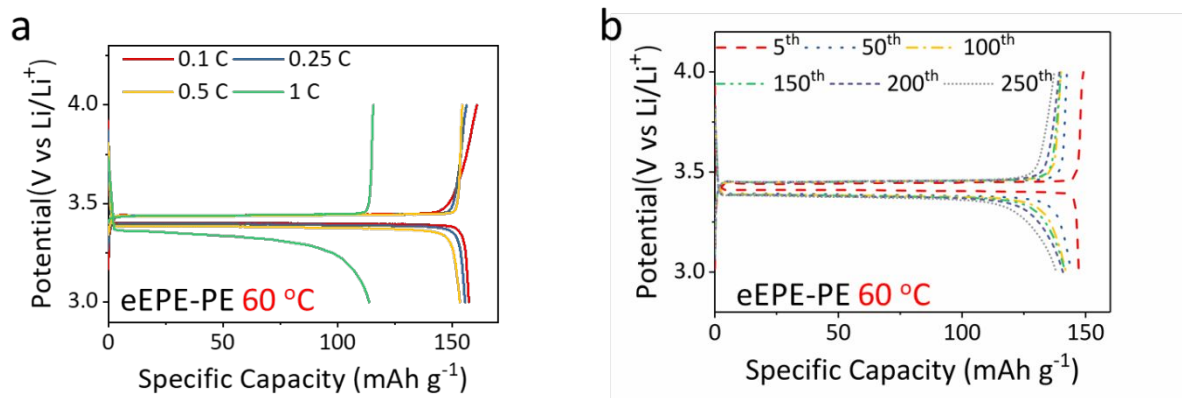


Figure S12. Charging/discharging curves of (a) selected rate and (b) selected cycle of SLMBs with at eEPE-PE film 60 °C.

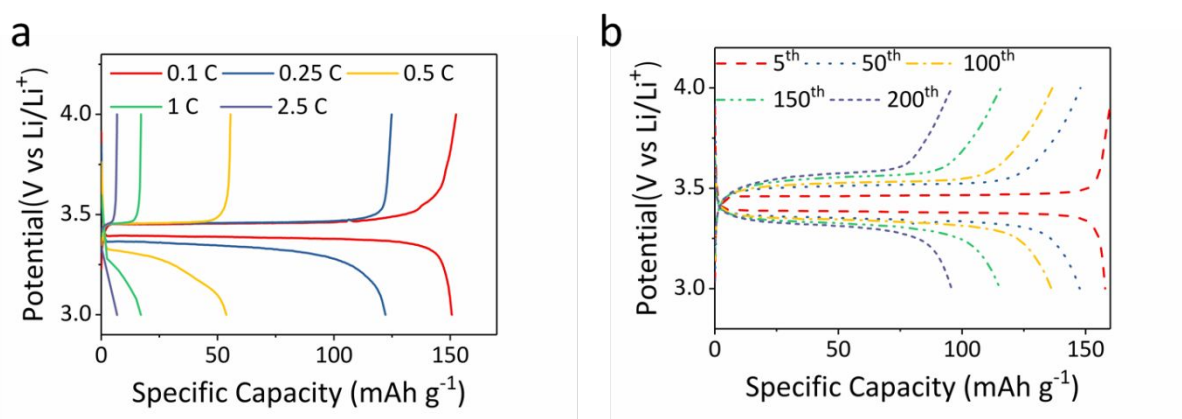


Figure S13. Charging/discharging curves of (a) selected rate and (b) selected cycle of SLMBs with eEPE-50 μm at 60 °C.

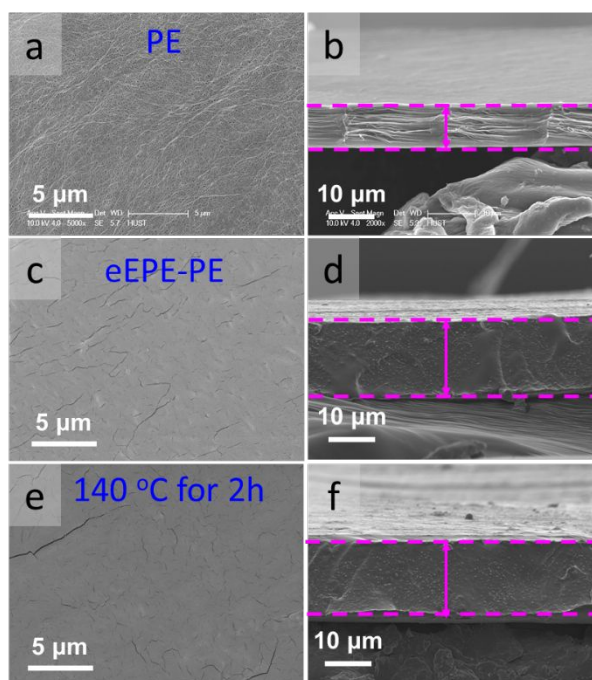


Figure S14. SEM images of the PE separator (a and b), eEPE-PE film (c and d) and eEPE-PE film after exposing at 140 °C for 2 h (e and f). (a, c, e) top view, (b, d, f) cross view.

Table S1. Characteristic of designed eEPs. (x: y: z denotes the molar ratio of the ethylene oxide groups in DER332 to N-H in T5000 and N-H in MIPA)

eEP	x: y: z	PO wt/% in network	Young's Modulus (MPa)	Yield Stress (MPa)	Elongation at break (%)
pD2T1-M1	2:1:1	71%	0.2	0.1	97
pD3T1-M2	3:1:2	61%	0.71	0.52	147
pD4T1-M3	4:1:3	54%	0.62	0.69	330
pD5T1-M4	5:1:4	48%	1.53	2.02	440

Table S2. Comparison of the mechanical properties and ionic conductivity of eEPE compared to commercial and previously-reported tough polymer electrolytes. For the polymer electrolytes in our work, the modulus of resilience is defined as the integrated area under the curve of tensile strain. For previously-reported works, this integral can be approximated using the yield stress and the Young's modulus, according to the reference.¹

Description	Salt	Plasticizer	Ionic Conductivity (S cm ⁻²)	Young's Modulus (MPa)	Yield Stress (MPa)	Resilience (MJ cm ⁻³)	Reference
eEPE	20 wt% LiTFSI	20 wt.% PC	2 E-5	4.12	5.63	12.44	This work
eEPE	20 wt% LiTFSI	30 wt.% PC	3.5 E-4	1.01	1.89	3.4	This work
SLIC	20 wt.% LiTFSI	20 wt.% DEGDME	1.2 E-4	14.5	0.58	29.3	Nat. Commun. 2019, 10 (1), 5384.
ePPO	27 wt% LiTFSI	30 wt.% PC	2.5 E-4	0.3	0.45	0.32	Adv. Mater. 2018, 30 (43), 1804142.
PEO	40 wt.% LiTFSI	None	2 E-5	0.4	0.04	0.003	Adv. Mater. 2018, 30 (43), 1804142.
Crosslinked PEG Diacrylate	30wt. % LiTFSI	35 wt.% SCN	1.1 E-3	0.5	0.24	0.0576	J. Memb. Sci. 2016, 498, 208.
Aramid fiber in PEO	Not reported	None	5 E-6	4950	61	0.38	Nat. Commun. 2015, 6 (1), 6152.

Reference

1. Lopez, J.; Sun, Y.; Mackanic, D. G.; Lee, M.; Foudeh, A. M.; Song, M. S.; Cui, Y.; Bao, Z., A Dual-Crosslinking Design for Resilient Lithium-Ion Conductors. *Adv. Mater.* **2018**, *30* (43), e1804142.