Supporting Information

Flexible, Self-Healing, and Fire-Resistant Polymer Electrolytes Fabricated *via* Photopolymerization for All-Solid-State Lithium Metal Batteries

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1. EXPERIMENTAL SECTION

Materials. 4-hydroxyphenethyl alcohol (98%), hexachlorocyclotriphosphazene (HCCP, 98%), 4-(2-methoxyethyl)phenol (99%), *p*-toluenesulfonic acid monohydrate (98.5%), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), acrylic acid (99.5%), and 2-hydroxy-2-methylpropiophenone (97%) were purchased from Aladdin and used as received. PEGMA ($M_n = 500$ g mol⁻¹, Sigma-Aldrich) and poly(ethylene glycol) diacrylate ($M_n = 575$ g mol⁻¹, Sigma-Aldrich) were filtered through a basic alumina column before use. Sodium bicarbonate, sodium sulfate, sodium chloride, and potassium carbonate were purchased from Sinopharm Chemical. All other solvents were freshly distilled prior to use. UPyMA was synthesized according to a reported method.¹

Synthesis of hexa (4-ethyl acrylate phenoxy) cyclotriphosphazene (HCP). The HCP is synthesized via two steps. First, 4-hydroxyphenethyl alcohol (3.45 g, 25 mmol) and acrylic acid (2.15g, 30 mmol) were dissolved in toluene (50 mL) containing 4-(2-methoxyethyl) phenol (56 mg) and p-toluenesulfonic acid monohydrate (200 mg). The solution was stirred for 5 h under reflux condition. After the reaction, the solution was washed using the aqueous solution of sodium bicarbonate and the saturated sodium chloride solution to form a two-phase mixture. The combined organic layer was dried with Na₂SO₄. The toluene was removed under reduced pressure to obtain the tyrosoyl acrylate. Second, the mixture of tyrosoyl acrylate (5.53 g, 28.8 mmol), HCCP (1.25 g, 3.6 mmol), potassium carbonate (7.46 g, 54 mmol) and acetonitrile (50 mL) was added into an autoclave. The reaction mixture was degassed and backfilled with argon gas. Then, the mixture was stirred at 90 °C for 48 h. After the reaction, the ethyl acetate was added into the mixture under stirring to dissolve the product. The suspension was filtered, and the filtrate was washed with deionized water and NaOH solution (5 wt%) three times. The combined organic layer was dried with Na₂SO₄. Then, the solvent was removed to obtain a slightly yellow liquid (HCP). ¹H-NMR (CDCl₃, TMS, ppm): 6.83–7.10 (dd, 24H), 6.36 (d, 6H), 6.08 (m, 6H), 5.80 (d, 6H), 4.32 (t, 12H), 2.90 (t, 12H).

Preparation of CPSHPEs. The cyclophosphazene-based self-healing polymer electrolytes(CPSHPEs)werepreparedbyphotopolymerizationwhileusing

2-hydroxy-2-methylpropiophenone as the photoinitiator. Typically, HCP (384 mg, 0.3 mmol), UPyMA (168 mg, 0.6 mmol), PEGMA (1.5 g, 3 mmol), LiTFSI (407 mg, with the EO/Li⁺ molar ratio of 16:1) and 2-hydroxy-2-methylpropiophenone (41 mg, 2 wt%) were dissolved in 4 mL DMSO. The mixture was stirred for 2 h, and then was ultrasonicated in water at 50 °C for 1 h to make the mixture form a homogeneous solution. The homogeneous solution was cast onto a Teflon mold and exposed to a UV light for 10 min at a wavelength of 365 nm. The obtained membrane was dried under a high vacuum condition at 80 °C for 48 h to remove the solvent of DMSO. A series of CPSHPEs were obtained by adjusting the ratios of UPyMA relative to HCP, and the ratio of PEGMA and UPyMA was held constant. The flexible membranes were stored in a glove box.

Characterization. ¹H NMR spectroscopy was recorded on a Bruker AV400 spectrometer. The FT-IR spectroscopy was conducted using Fourier transform infrared spectroscopy (FT-IR, Equinox 55, Bruker) from 4000-400 cm⁻¹ at room temperature. The thermal stability of CPSHPEs was assessed using a thermogravimetry instrument (TGA, 4000 PerkinElmer) under nitrogen flow at a heating rate of 10 °C min⁻¹ from 30 to 600 °C. The glass transition temperature (T_g) was evaluated by differential scanning calorimetry (DSC, Q2000) at a ramp rate of 10 °C from -90 to 100 °C. A field emission scanning electron microscope (FESEM, Hitachi SU8010) was employed to detect the morphologies of the surface of CPSHPE and the lithium metal foil.

All the electrochemical properties were evaluated using an Autolab PGSTAT302N electrochemical workstation. The ionic conductivities were evaluated by electrochemical impedance spectroscopy (EIS) with the frequency ranged from 1MHz to 0.1 Hz from 30 °C to 80 °C. The ionic conductivity was calculated from the equation, $\sigma = L/(SR_b)$, in which *L* is the thickness of the CPSHPEs, *S* represents the effective contact area, and R_b is the bulk resistance of

polymer electrolyte membrane. Linear sweep voltammograms (LSV) was performed to mensure the electrochemical stability window at a scanning rate of 1 mV s⁻¹. The Li⁺ transference number (t_{Li^+}) was measured using the Li/CPSHPEs/Li cell. The cell was subjected to a polarization bias of 10 mV (ΔV) to determine the currents from the initial (I_0) to the steady state (I_s). The impedance of R_0 and R_s were respectively measured before and after the polarization. The t_{Li^+} was calculated using the equation: $I_s(\Delta V - I_0R_0)/I_0(\Delta V - I_sR_s)$. The galvanostatic test was used to evaluate the interfacial stability of CPSHPE1/lithium metal. The mechanical properties of CPSHPE was measured using an electronic universal testing machine (CMT4104, Shenzhen San Testing Machine Co.) at a crosshead speed of 5 mm min⁻¹.

Self-Healing and Flame Retardancy Properties. The circular specimens of CPSHPE were formed in a Teflon mold. Two membranes were stained with red and blue color dyes and cut into two parts using a doctor blade. Then, the two parts with different colors were reattached carefully for self-healing over time. To evaluate the flame retardancy of CPSHPE, the rectangular strip was formed in Teflon mold and hanged by a plier. A burning torch was used to ignite the strip for 10 s. Then the burning torch was removed to evaluate the flame-retardant properties of the strip. Furthermore, another rectangular strip formed by PEGDA was used to compare the flame-retardant properties.

Battery Fabrication and Performance. To evaluate the performance of the solid-state lithium batteries, LiFePO₄ (LFP) coin cells were fabricated. The charge and discharge performance of LFP cells were evaluated using a battery testing system (LANHE CT2001A). The LFP cathode was prepared by mixing LiFePO₄, carbon black and PVDF in 8:1:1 weight ratio in NMP. The aluminium current collector was coated with the viscous slurry. The obtained electrode (the thickness is 35 μm) was dried at 120 °C for 24 h in an oven. The obtained cathode,

CPSHPE and lithium metal (the diameter of 15 mm, the thickness of 0.5 mm) were assembled in an argon-filled glove box to form batteries. The teat of charge/discharge performance was conducted from 2.5 V to 4.2 V at 60 °C.



Figure S1. The ¹H NMR spectrum of HCP.





Figure S2. Surface morphology of the CPSHPE membrane.

Figure S3. Optical images of self-healing behavior of CPSHPE1.



Figure S4. The ionic conductivity of CPSHPE1 with various molar ratios of LiTFSI.



Figure S5. Chronoamperometry profile of the Li/CPSHPE1/Li cell at 60 °C. The inset shows the

impedance spectra before and after chronoamperometry.



Figure S6. Chronoamperometry profile of the Li/CPSHPE1.2/Li cell at 60 °C. The inset shows

the impedance spectra before and after chronoamperometry.



Figure S7. Chronoamperometry profile of the Li/CPSHPE1.4/Li cell at 60 °C. The inset shows

the impedance spectra before and after chronoamperometry.



Figure S8. Chronoamperometry profile of the Li/PEGDA1/Li cell at 60 °C. The inset shows the

impedance spectra before and after chronoamperometry.



Figure S9. Surface morphology of the lithium metal foil after cycling.

Table S1. The	Molar feeding ratio,	$T_{\rm g}$ and ionic conductivity	at 30 °C of the CPSHPEs
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Polymer	PEGMA : UPyMA :	_ / _		
Electrolytes	HCP/PEGDA	T _g /°C	σ at 30 °C / S cm ⁻¹	
CPSHPE1	10:2:1	-46.2	8.95 × 10 ⁻⁵	
CPSHPE1.2	10:2:1.2	-43.2	5.66 × 10^{-5}	
CPSHPE1.4	10:2:1.4	-33.4	4.28×10^{-5}	
PEGDA1 ^a	10:2:1	-45.3	2.40×10^{-5}	
^a The mole ra	atio of vinyl gro	oups in p	olymer is same	
with CPSHPE1.				

4.90	2.32	1293	1382	0.26
5.51	3.01	1231	1310	0.29
3.16	1.33	1489	1592	0.28
5.51	2.48	1224	1301	0.22
	4.905.513.165.51	4.902.325.513.013.161.335.512.48	4.902.3212935.513.0112313.161.3314895.512.481224	4.902.32129313825.513.01123113103.161.33148915925.512.4812241301

Table S2. Measure values for the corresponding calculated values of t_{Li^+} .

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 Yamauchi, K.; Lizotte, J. R.; Long, T. E. Thermoreversible Poly(alkyl acrylates) Consisting of Self-Complementary Multiple Hydrogen Bonding. *Macromolecules* 2003, *36*, 1083-1088.