Electronic Supplementary Information

Chemically Inert Covalently Networked Triazole-based Solid Polymer Electrolytes for Stable All-solid-state Lithium Batteries

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Experimental Procedures

Materials Poly(ethylene glycol) (PEG) (M_n = 2050, Sigma-Aldrich) was dissolved in toluene and dried by azeotropic distillation. Glycidyl POSS (Hybrid), propargyl bromide (80% in toluene, 97%, Alfa Aesar), sodium hydride (60 % dispersion in mineral oil, Alfa Aesar), sodium azide (>99.5%, Sigma-Aldrich), acetonitrile (AN, Alfa Aesar), *N,N*-dimethylformamide (Sigma-Aldrich) were used as received.

Synthesis of POSS-$(N_3)_8$ Glycidyl POSS (5 g, 3.7 mmol) was dissolved in 50 mL DMF. Sodium azide (2.6 g, 40 mmol) and ammonium chloride (2.14 g, 40 mmol) were then added into solution. The mixture was stirred at 50 °C for 48 h. The product was precipitated into an excess of water three times. The final product was dried under vacuum to a constant mass at room temperature.

Synthesis of PEO-dialkynyl Dried PEG (15 g, 14.6 mmol –OH group) was dissolved into 150 mL anhydrous THF and then converted into sodium alkoxide by reaction with sodium hydride (60 % dispersion in mineral oil) (1.75 g, 43.9 mmol) at 30 °C for 2 h. Propargyl bromide (5.44 g, 36.6 mmol) was then added to the mixture which was refluxed for 12 h. Then the supernatant was purified by ultracentrifugation and then precipitated into diethyl ether three times. The final product was dried under vacuum to a constant mass at room temperature.

Synthesis of PEO-diamino Dried PEG (15 g, 14.6 mmol –OH group), triethylamine (5.0 mL, 36.6 mmol) and 200 mL dried methylene chloride were charged in a 500 mL dried round bottom flask. This flask was immersed in a thermostatic ice bath at 0 °C. The solution was magnetically stirred for 10 min before slow addition of 1.5 equivalent methanesulfonyl chloride (1.7 mL, 21.9 mmol) over a period of 30 min. The reaction was allowed to proceed for 24 hours at room temperature before the solution was washed three times with 100 mL brine. The organic solution was dried by anhydrous $MgSO_4$ before removing the solvent and then precipitated into diethyl ether three times. The final product was then dried under vacuum to a constant mass at room temperature. Equal mole of above product and ammonium chloride (NH_4Cl) were dissolved in 10 times excessive amount of ammonium (NH_3) solution and stirred at room temperature for 96 h. Then the solution was extracted by dichloromethane. The extracted solution was washed by saturated NaCl solution, and then dried by anhydrous $MgSO_4$ over 12 h. The dried solution was precipitated into excessive diethyl ether and the precipitation was collected and washed twice with diethyl ether. The final product was dried under vacuum at room temperature 24 h. The yield was approximately 95%.

Preparation of PEO-*ta*-POSS membrances A typical procedure to prepare 4PEO-*ta*-POSS membrance at PEO:POSS = 4:1 was following: PEO-dialkynyl (1.0 g, 0.470 mmol), POSS-$(N_3)_8$ (198 mg, 0.117 mmol), LiTFSI (354 mg, 1.23 mmol) (EO:Li = 16:1) and AN (10 mL) were added in a 20 mL vial. The vial was sealed and reaction was carried out in an oil bath at 80 °C for 12 h. The solution was then divided into four parts and drop casted into four molds (34 mm diameter, 3 mm deep). After the majority solvent was evaporated at room temperature in 12 h, samples were transferred into a vacuum oven at 90 °C for 18 h and then at 120 °C for 6 h to make sure the click reaction was completed. After cooling to room temperature under vacuum, the membrances were transferred to an argon-filled glove box. The procedures for preparing 2PEO-*ta*-POSS, 6PEO-*ta*-POSS and 4PEO-*amine*-POSS membrances were the same.

Model reactions The model reaction between PBQS and diethylamine: PBQS (20 mg) was dispersed in 1 mL THF, and then diethylamine (100 mg) was added and the mixture was stirred at room temperature for 12 h. The product was then filtrated and washed by THF three times. The final product was then dried under vacuum to a constant mass at 80 °C. The procedure for model reaction between V_2O_5 and diethylamine was similar to those described above.

Materials characterizations Proton nuclear magnetic resonance (^{1}H NMR) spectra were collected on a JEOL ECA-500 spectrometer using $CDCl_3$ as the solvent. Differential scanning calorimetry (DSC) data were collected on a TA Instruments Q2000 under dry N_2 atmosphere. The samples were heated and cooled between -80 and 150 °C at 10 °C min^{-1}. The reported DSC data were collected on the third heating cycle. X-ray diffraction (XRD) patterns were collected using a Rigaku MiniFlex 600 with Cu Kα radiation (λ = 1.5418 Å) under 40 kV and 15 mA. Small-angle X-ray scattering (SAXS) data were collected at Argonne National Laboratory at Advanced Photon Source Beamline 12-ID-B. Dynamic Mechanical Analysis (Model Q800, TA Instruments) was carried out in an extension mode with a heating rate of 2 °C min^{-1}, strain of 1%, and frequency of 1 Hz. The length, width, and thickness of testing samples were 20, 4, and 1 mm, respectively.

Electrochemical measurements All electrochemical measurements were performed at 90 °C unless otherwise specified. The ionic conductivity (σ) was evaluated by stainless steel (SS)|PEO-POSS SPE|SS symmetric cells from room temperature to 90 °C. The electrochemical impedance spectroscopy (EIS) was recorded on an electrochemical workstation (VMP3, Bio-Logic Co.) ranging from 1 MHz to 0.1 Hz with an amplitude of 7 mV. The ionic conductivity was calculated by $\sigma = L/(S \cdot R)$, where *L* (cm) was the thickness of SPE separator, *S* (cm^2) was the area of SPE, and *R*(Ω) was the measured impedance. The temperature-dependent ionic conductivity was further fitted using Vogel-Tammann-Fulcher (VTF) formula:[1]

$$\sigma = AT^{-1/2} exp\left(\frac{-E_a}{R(T - T_0)}\right)$$

where *σ* is ionic conductivity, *A* is a constant number proportional to the charge carrier density in the system, E_a is activation energy, *R* is gas constant, *T* is temperature. T_0 is usually 50 °C below glass transition temperature.[1]

Li|PEO-POSS SPE|Li symmetric cells were used to evaluate the Li/SPE interfacial stability. Galvanostatic Li stripping and plating performance was recorded at 0.3 mA cm^{-2} with a constant specific capacity of 0.3 mAh cm^{-2}. The galvanostatic charge-discharge cycling was performed at a CT2001A battery tester (LAND Electronics Co., Ltd.)

Li⁺ transference number The Li$^+$ transference number *t*(Li$^+$) were determined by direct current (DC) polarization combined with alternating current (AC) impedance using Li|PEO-POSS SPE|Li symmetric cells. The *t*(Li$^+$) was calculated by the Bruce-Vincent equation:[2]

$$t(Li^+) = \frac{I^s(\Delta V - R_i^0 I^0)}{I^0(\Delta V - R_i^s I^s)}$$

where ΔV was polarization potential (10 mV) applied to the cell. I^0 was initial current, and I^s was steady-state current after 3-hour polarization. R_i^0 and R_i^s were initial and steady-state interfacial resistances, respectively (Figure S7).

Li/PEO-POSS SPE/LFP full cells For Li/PEO-*ta*-POSS SPE/LFP cells, the $LiFePO_4$ (LFP) cathode electrode was composed of LFP, PEO-*ta*-POSS SPE, and conductive carbon (Timcal Super C65) at a mass ratio of 6:3:1. PEO-dialkynyl, POSS-$(N_3)_8$, and LiTFSI (EO:Li^+ molar ratio of 16:1) were dissolved in AN solvent at 80 °C for 12 h before mixing with LFP and C. For Li/4PEO-*amine*-POSS SPE/LFP cells, the LFP cathode electrode was composed of LFP, PEO-*amine*-POSS SPE, and C65 at a mass ratio of 6:3:1. PEO-$(NH_2)_2$, POSS-epoxy, LiTFSI (EO:Li^+ = 16:1) were dissolved in AN solvent at 60 °C for 3 h before mixing with LFP and C. Both slurries were cast on carbon-coated Al foils and dried under vacuum at 120 °C for 24 h. The active material mass loading is ~2.0 mg cm^{-2}. The Li/PEO-POSS SPE/LFP cells were assembled in an argon-filled glove box (O_2 < 0.5 ppm, H_2O < 0.5 ppm) using CR2032 coin-type cells by a lamination process. The corresponding PEO-POSS SPE was employed as the separator. The current density of 1C corresponds to 170 mA g^{-1}. The galvanostatic cycling test were conducted in a potential window of 2.5–4.0 V and 2.8–3.7 (vs. Li/Li^+) respectively.

Li/PEO-POSS SPE/PBQS full cells The PBQS cathode electrode of Li/4PEO-*ta*-POSS SPE/PBQS and Li/4PEO-*amine*-POSS SPE/PBQS cells was composed of PBQS:4PEO-*ta*-POSS SPE:C and PBQS:4PEO-*amine*-POSS SPE:C at a mass ratio of 3:6:1, respectively. The electrode fabrication and cell assembly were similar with those of Li/PEO-POSS SPE/LFP cells. The cycling performance was measured at 0.1C (1C = 388 mA g^{-1}) in a potential window of 1.7–3.8 V (vs. Li/Li^+). Cyclic voltammetry curves were collected at a scan rate of 0.2 mV s^{-1} in a potential window of 1.5–4.0 V (vs. Li/Li^+).

Li/PEO-POSS SPE/V_2O_5 full cells The V_2O_5 cathode electrode of Li/4PEO-*ta*-POSS/V_2O_5 and Li/4PEO-*amine*-POSS/V_2O_5 cells was composed of V_2O_5:4PEO-*ta*-POSS SPE:C and V_2O_5:4PEO-*amine*-POSS SPE:C at a mass ratio of 6:3:1, respectively. The electrode fabrication and cell assembly were similar with those of Li/PEO-POSS SPE/LFP cells. The cycling performance was measured at 0.2C (1C = 294 mA g^{-1}) in a potential window of 2.3–4.0 V (vs. Li/Li^+).

Li/PEO-POSS SPE/C cells for testing anodic stability of SPEs The cathode of Li/4PEO-*ta*-POSS SPE/C and Li/4PEO-*amine*-POSS SPE/C cells was composed of 4PEO-*ta*-POSS SPE:C and 4PEO-*amine*-POSS SPE:C at a mass ratio of 3:1, respectively. The electrode fabrication and cell assembly were similar with those of Li/PEO-POSS SPE/LFP cells. Cyclic voltammetry curves were collected at a scan rate of 0.2 mV s^{-1} in a potential window of 1.5–4.0 V (vs. Li/Li^+).

Table S1. VTF equation fitting parameters of Figure S5.

SPEs	T_0 (K)	E_a (kJ mol^{-1})	A (S cm^{-1} K$^{1/2}$)
2PEO-*ta*-POSS	193.5	8.4	1.15
4PEO-*ta*-POSS	189.1	8.2	3.24
6PEO-*ta*-POSS	193.0	7.8	6.76
4PEO-*amine*-POSS	191.6	8.3	2.47

Table S2. Bruce-Vincent Equation parameters from Figure S7.

SPEs	ΔV (mV)	R_i^0 (Ω)	R_i^s (Ω)	I^0 (mA)	I^s (mA)	t(Li$^+$)
2PEO-*ta*-POSS	10	60.7	59.5	0.0471	0.0108	0.17
4PEO-*ta*-POSS	10	37.3	40.8	0.0468	0.0161	0.30
6PEO-*ta*-POSS	10	46.2	41.2	0.0645	0.0168	0.20
4PEO-*amine*-POSS	10	23.7	26.4	0.0839	0.0106	0.11

Table S3 Fitting parameters of the equivalent circuit models of fresh Li/SPE/PBQS cells from Figure S10.

SPEs	R_e (Ω)	R_1 (Ω)	CPE_1 (μF)	W (Ω)
4PEO-*amino*-POSS	58.0	40.1	7.0	65.7
4PEO-*ta*-POSS	110.3	72.1	5.2	1354

Table S4 Fitting parameters of the equivalent circuit models of cycled Li/SPE/PBQS cells from Figure S10.

SPEs	R_e (Ω)	R_1 (Ω)	CPE_1 (μF)	R_2 (Ω)	CPE_2 (mF)
4PEO-*amino*-POSS	213.4	30.8	3.7	208.1	4.8
4PEO-*ta*-POSS	532.3	444.9	18	1576	0.7

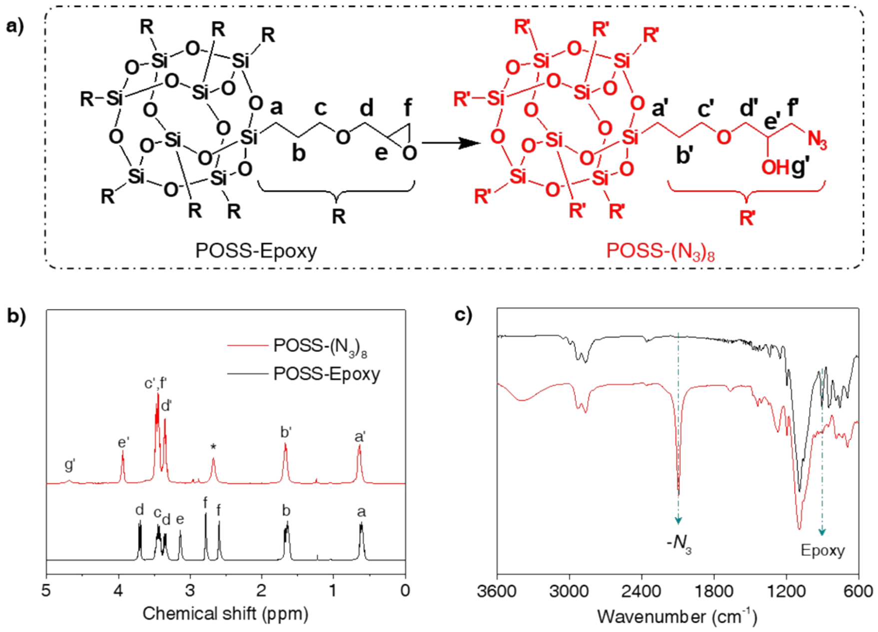

Figure S1. (a) Synthesis route and chemical structures of POSS-epoxy and POSS-$(N_3)_8$, (b) 1H NMR spectra and (c) FT-IR spectra of POSS-epoxy and POSS-$(N_3)_8$.

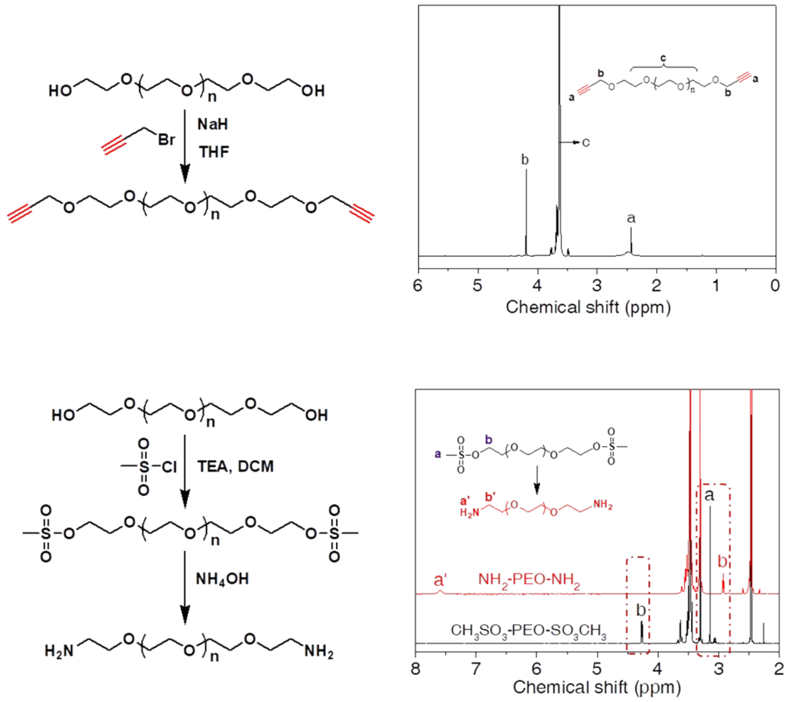

Figure S2. Synthesis route and ^{1}H NMR spectra of (a) PEO-dialkynyl and (b) PEO-diamino.

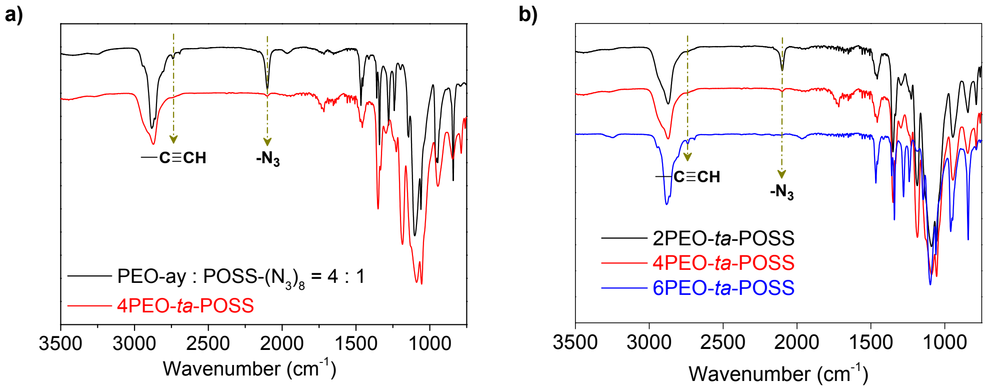

Figure S3. FT-IR spectra of a) the precursor of 4PEO-*ta*-POSS and 4PEO-*ta*-POSS, b) the crosslinked polymer electrolytes.

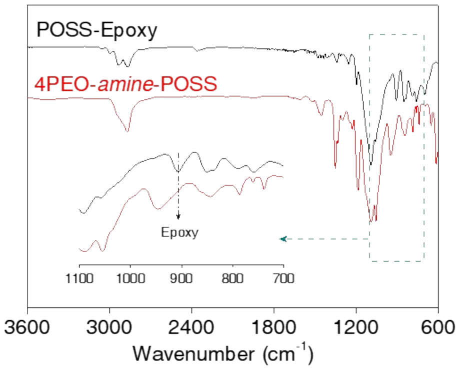

Figure S4. FT-IR spectra of POSS-epoxy and 4PEO-*amine*-POSS crosslinked polymer electrolytes.

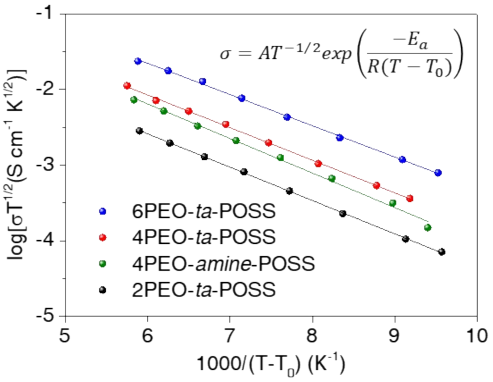

Figure S5. Ionic conductivities of PEO-POSS SPEs fitted using the VTF equation shown in the inset. Fitting parameters are listed in Table S1.

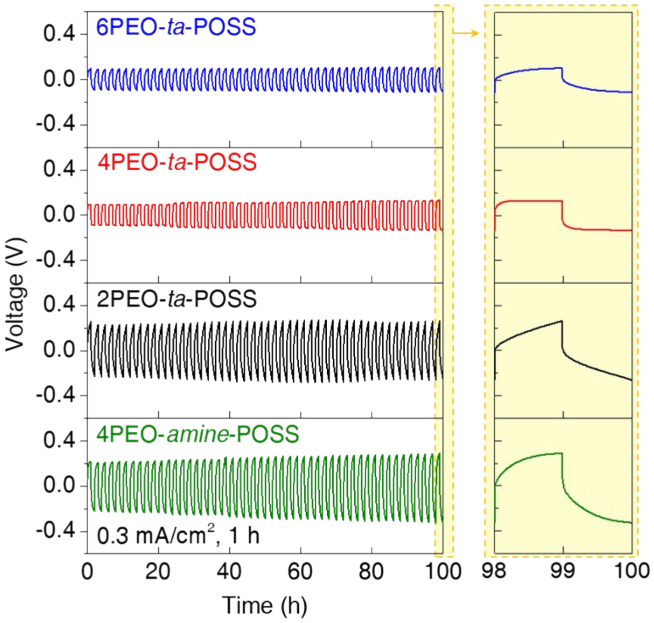

Figure S6. Galvanostatic cycling curves of Li|PEO-POSS SPE|Li cells at current densities of 0.3 mA cm^{-2} at 90 °C.

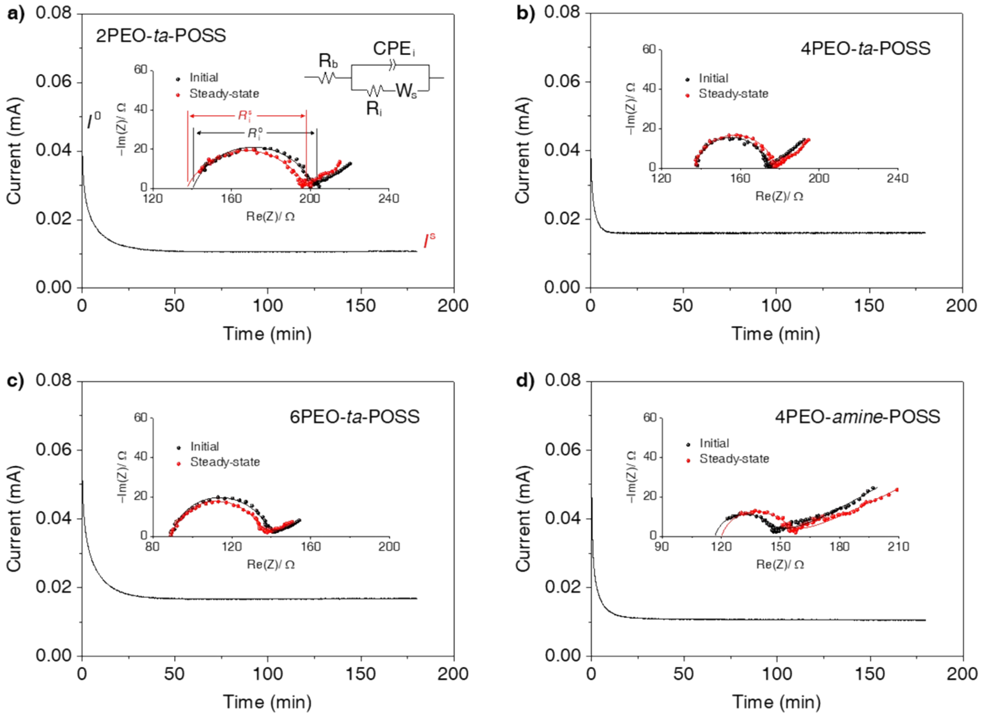

Figure S7. Li$^+$ transference number measurements using Bruce-Vincent method. Chronoamperometry of Li|PEO-POSS SPE|Li symmetric cells. The inserts show AC impedance spectra at the initial and steady state. The parameters are listed in Table S2.

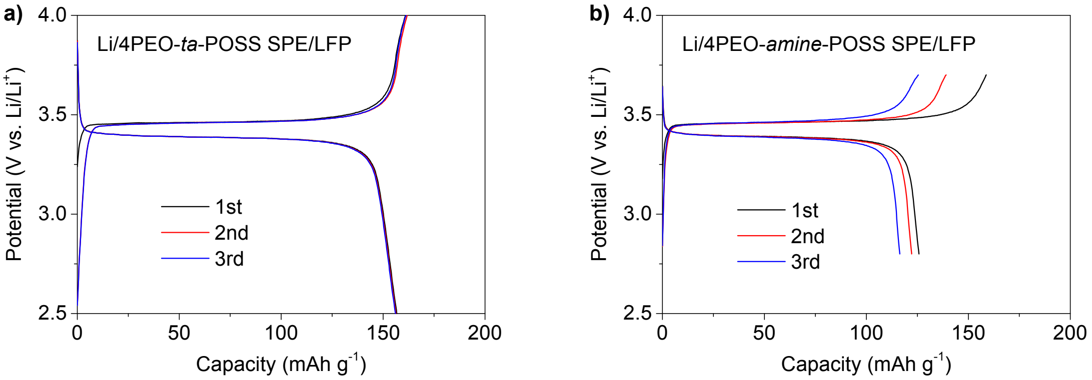

Figure S8. The 1st, 2nd and 3rd voltage profiles of a Li/PEO-POSS SPE/$LiFePO_4$ cells at 90 °C using (a) 4PEO-*ta*-POSS and (b) 4PEO-*amine*-POSS electrolytes at 0.2C (1C = 170 mA g^{-1}).

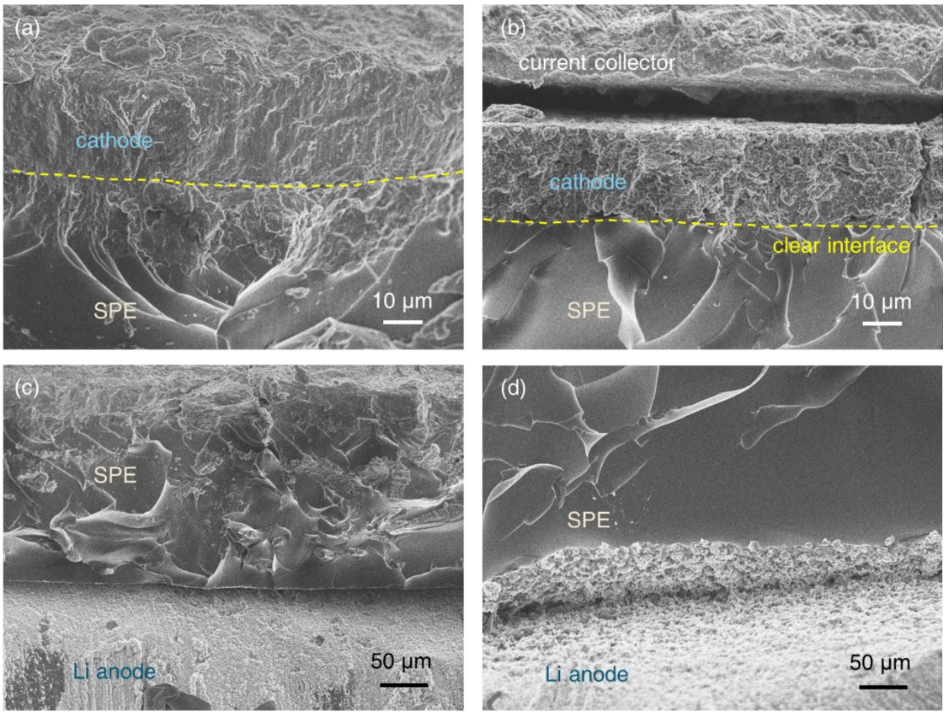

Figure S9. SEM images of (a, c) cycled Li/4PEO-amino-POSS SPE/PBQS cell and (b, d) Li/4PEO-ta-POSS SPE/PBQS cell.

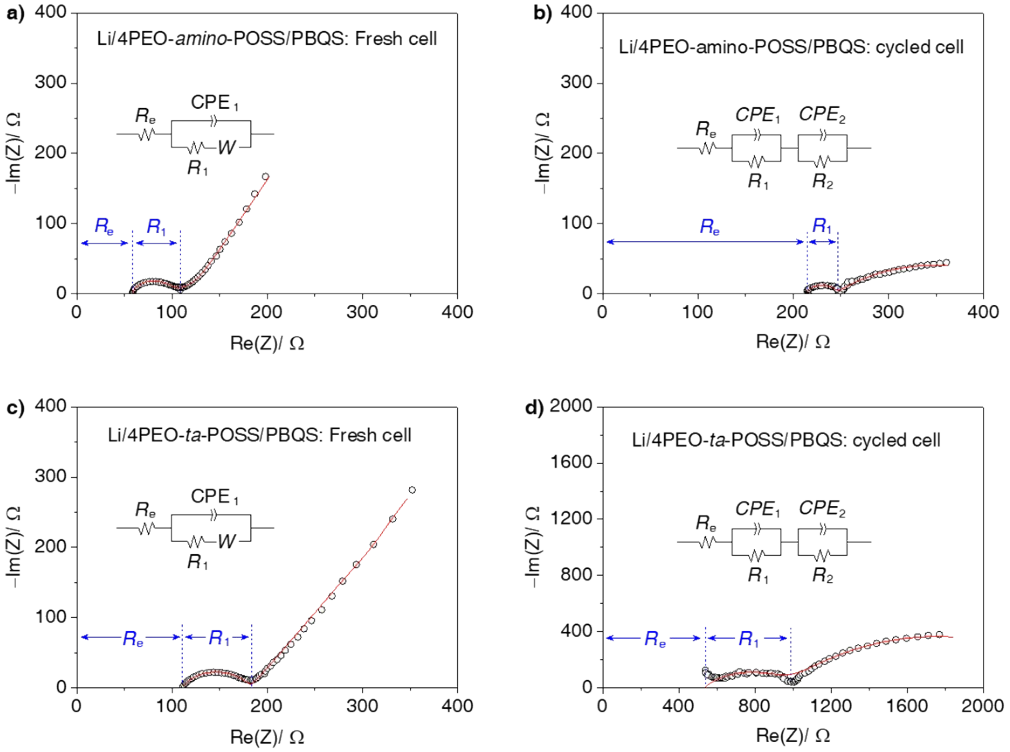

Figure S10. Nyquist plots of fresh Li/4PEO-*amino*-POSS SPE/PBQS cell (a) and Li/4PEO-*ta*-POSS SPE/PBQS cell (b). Nyquist plots of Li/4PEO-*amino*-POSS SPE/PBQS cell (c) and Li/4PEO-*ta*-POSS SPE/PBQS cell (d) after 300 cycles.

References

[1] K. M. Diederichsen, H. G. Buss, B. D. McCloskey, *Macromolecules* **2017**, 50, 3831-3840.

[2] J. Evans, C. A. Vincent, P. G.Bruce, *Polymer* **1987**, 28, 2324-2328.