Supporting Information

A smart lithiophilic polymer filler in gel polymer electrolyte enables stable and dendrite-free Li metal anode

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1. Experimental Section

Synthesis of PQ Filler. Similar to a previous work,[s1] the PQ was synthesized via a molten-salt polycondensation method with PMDA and AQ as the raw materials and anhydrous $ZnCl_2$ as the catalyst. After mixing at the molar ratio of 1:1:1, the PMDA+AQ+$ZnCl_2$ mixture was ground for several minutes in an Ar-filled glovebox, then transferred to a small glass bottle, sealed and calcined at 330 °C for 12 h. After the calcinations, 50 mL of 10 wt.% HCl was used to remove the $ZnCl_2$ catalyst. The as-obtained primary product was then ground in the mortar and wished by deionized water, ethanol and toluene in sequence for 24 h, respectively, and further high-energy ball milled at 400 rpm for 2 h. After drying in vacuum at 100 °C for 12 h, the PQ filler was obtained and stored for later use.

Characterizations of PQ Filler. ^{13}C cross-polarization/magic angle spinning solid-state nuclear magnetic resonance (^{13}C CP/MAS SSNMR) spectrum was performed on a Bruker Avance 4000D spectrometer with a 7-mm double-resonance probe. Fourier transform infrared (FT-IR) spectra (Nicolet 380FT-IR Spectrometer, Thermo Nicolet, America) and Raman spectroscopy (HR800, JOBIN YVON, France) were used to identify the structural variations in the samples. X-ray diffraction (XRD, Rigaku Smart Lab diffractometer) spectra were performed to investigate the phase structure of the sample. X-ray photoelectron spectroscopy (XPS, PHI5000) was used to characterize the chemical compositions of the sample. The morphology and energy dispersive X-ray spectroscopy (EDX) of the sample were collected by transmission electron microscopy (TEM, Tecnai G2 F30 S-Twin). The nitrogen adsorption-desorption isothermwas studied by BELSORP II at 77 K.

Fabrication of PQPU Membranes. To prepare PT composite membranes, TPU powder was first dissolved in N-Methyl-2-pyrrolidone (NMP) (1/10, w/w) at 70 °C to form a sheer solution, the as-prepared PQ filler (three different PQ filler mass percentages of 30%, 50% and 80% were tried) and the above solution was then mixed to form a homogeneous slurry under ultrasonic dispersion for sufficient time. The slurry was casted onto a PTFE film and subsequently dried at 70 °C in an oven overnight to form PQPU membranes. The TPU membrane was prepared in the same manner, but without PQ filler.

Characterization of PQPU Membranes. The thermal stability was evaluated by Thermogravimetric analysis (TGANETZSCH STA 449 F3) in air. The surface and cross-sectional morphology of the as-prepared membranes were observed by field-

emission scanning electron microscopy (FE-SEM, Hitachi S-4800). Phase structure of membranes was examined by XRD. The mechanical strength of the polymer electrolyte membranes was tested on a universal testing machine (CMT6103, MTS Systems Corporation). Dimensions of the membranes to be measured are 1 cm×4 cm×150 μm (W×L×D), and the rate of extension was kept at 40 mm min^{-1}.

Electrochemical Measurements. PQPU and TPU electrolyte membranes were formed by immerging as-prepared PQPU and TPU membranes in 1 M LiPF6 electrolyte (EC/DMC, 1:1, w/w). Three different PQPUs were namely PQPU with 30% PQ filler, PQPU with 50% PQ filler and PQPU with 80% PQ filler, respectively. The Li-ion conductivity of the prepared electrolyte membranes were measured by AC impedance based on the stainless steel (SS) symmetrical cell with the configuration of SS/GPE/SS. The measurement was conducted at 20-90 °C, and the applied frequency was changed from 100 kHz to 100 mHz. The Li-ion conductivity (σ) of GPEs was calculated based on the equation as follows:

$$\sigma = \frac{D}{R_b \times A} \quad (1)$$

where D is the thickness of the membrane, A is real contact area between membrane and blocking electrode, and R_b is the bulk resistance of GPEs.

The transference number of lithium ion was achieved by the following Bruce-Vincent-Evans Equation:

$$t_{Li+} = \frac{I_s(\Delta V - I_o R_o)}{I_o(\Delta V - I_s R_s)} \quad (2)$$

ΔV is the constant potential step of 20 mV, I0 and Is are the initial and the steady-state currents, and R_0 and R_s are the interface resistance before and after polarization. All the above measurements were performed on a Princeton 2273 electrochemical workstation.
The Li plating/striping behavior was investigated by using the Li symmetrical cells. CR2025-type coin cells with the configuration of NCM622/GPE/Li were constructed to test the electrochemical performance of the electrolyte membrane in single cell. The cathode was prepared as follows: NCM622, Super P and PVDF (polyvinylidene fluoride) were mixed at the weight ratio of 8:1:1 in a mortar and ground carefully. After adding NMP into the mixture, the slurry was coated onto an Al foil and dried at 100 °C in vacuum box. The assembly process of coin cells was conducted in an argon-filled glovebox and the active material weight of cathode is approximately 3 mg cm^{-2}. The

performance of all the cells was evaluated by a computer-controlled galvanostat (LANDet, Wuhan) under a galvanostatic mode at room temperature

2. Supplemental Figures and Captions

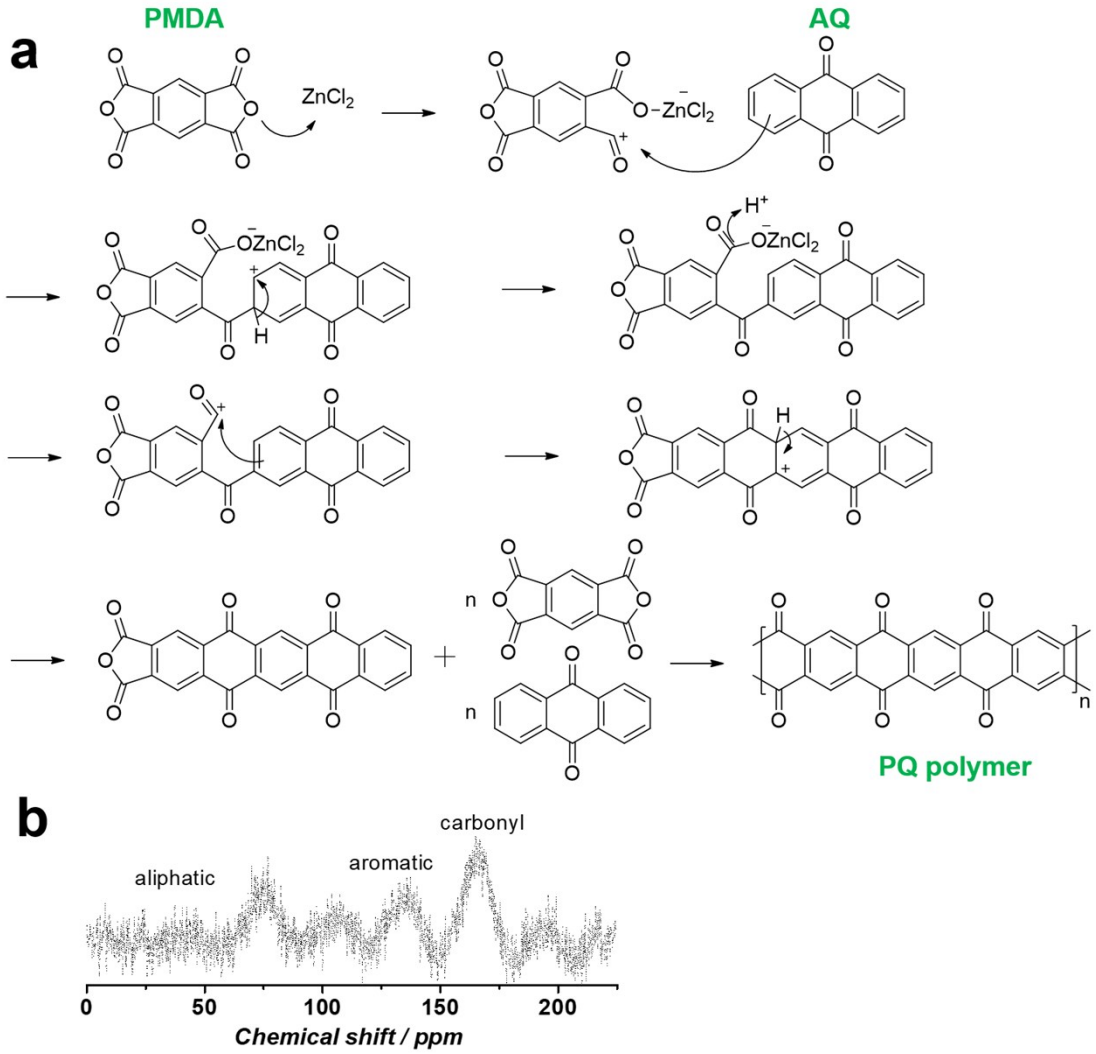

Figure S1. (a) Synthesis process and Friedel-crafts reaction mechanism of the PQ filler. (b) The ^{13}C CP/MAS NMR spectrum of the synthesized PQ filler.

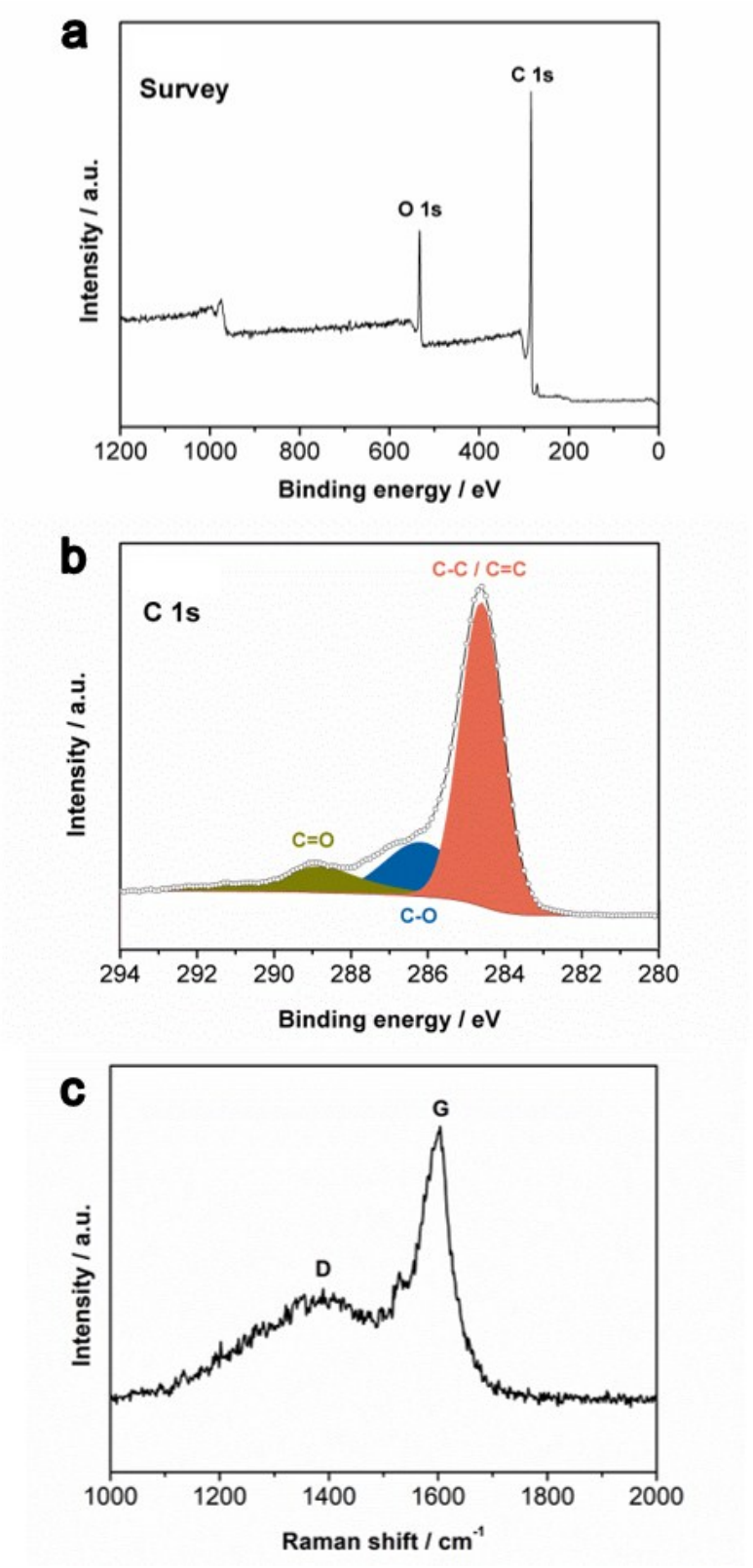

Figure S2. XPS survey spectrum (a) and high-resolution C 1s XPS spectrum (b) of the PQ filler. (c) Raman spectrum of the PQ filler.

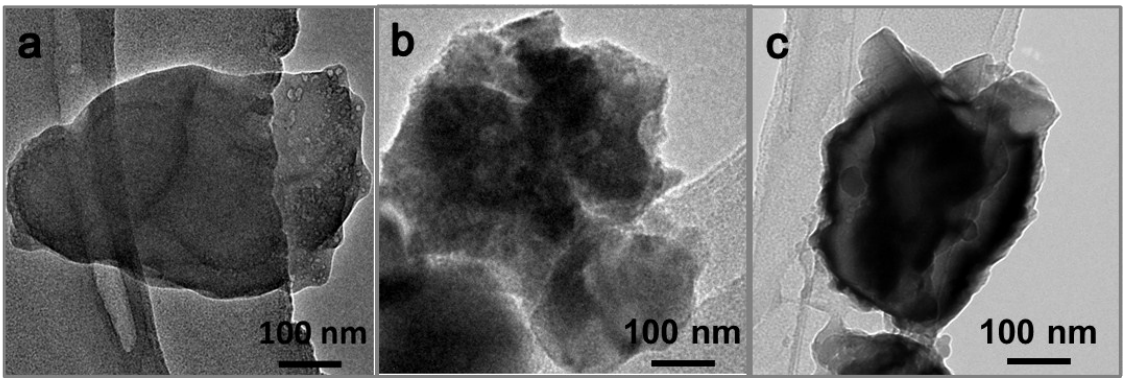

Figure S3. TEM images of the morphology of the as-prepared PQ fillers.

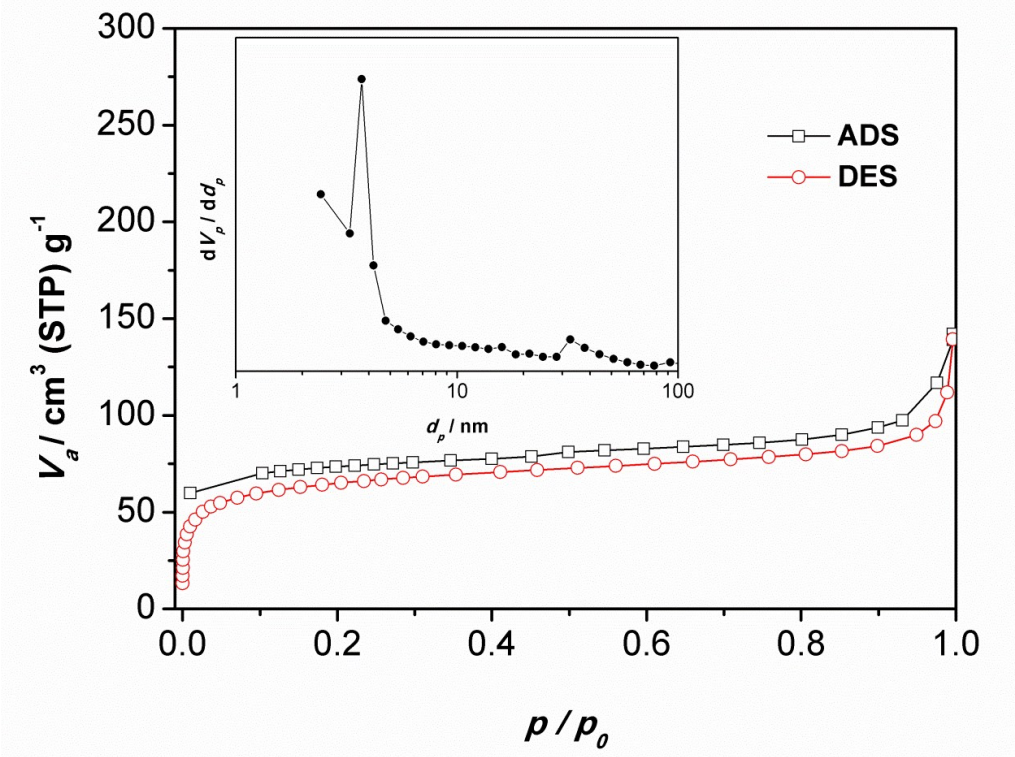

Figure S4. Nitrogen adsorption-desorption isotherm of the PQ filler. Inset is the pore size distribution of the PQ filler.

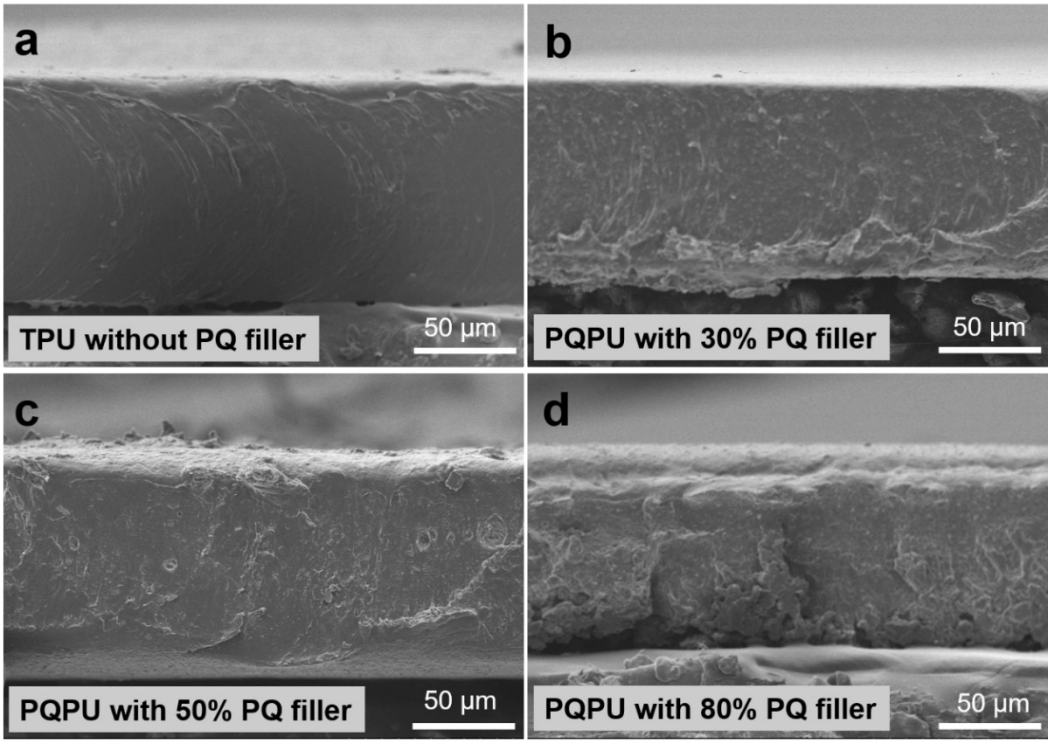

Figure S5. SEM images recorded at the cross section of (a) TPU without PQ filler, (b) PQPU with 30% PQ filler, (c) PQPU with 50% PQ filler, and (d) PQPU with 80% PQ filler, respectively.

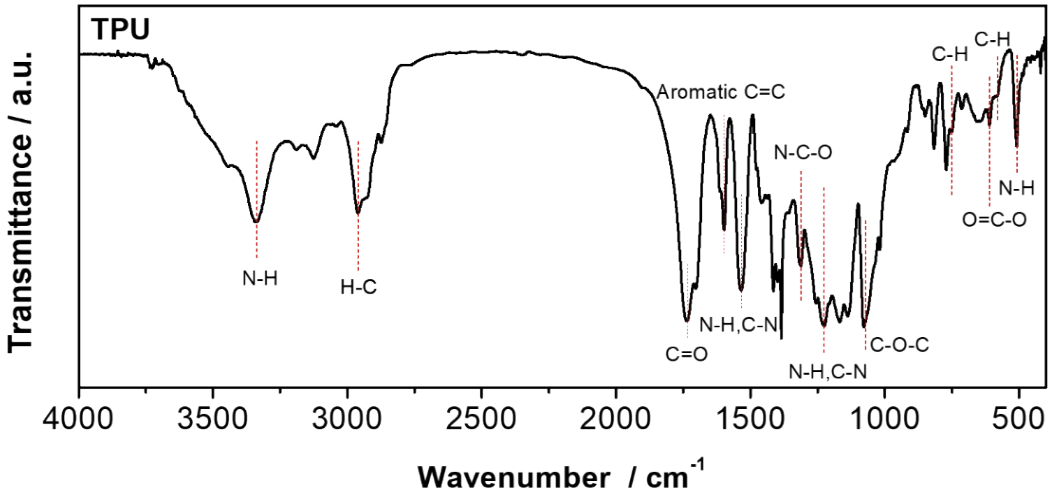

Figure S6. FT-IR spectrum of the TPU.

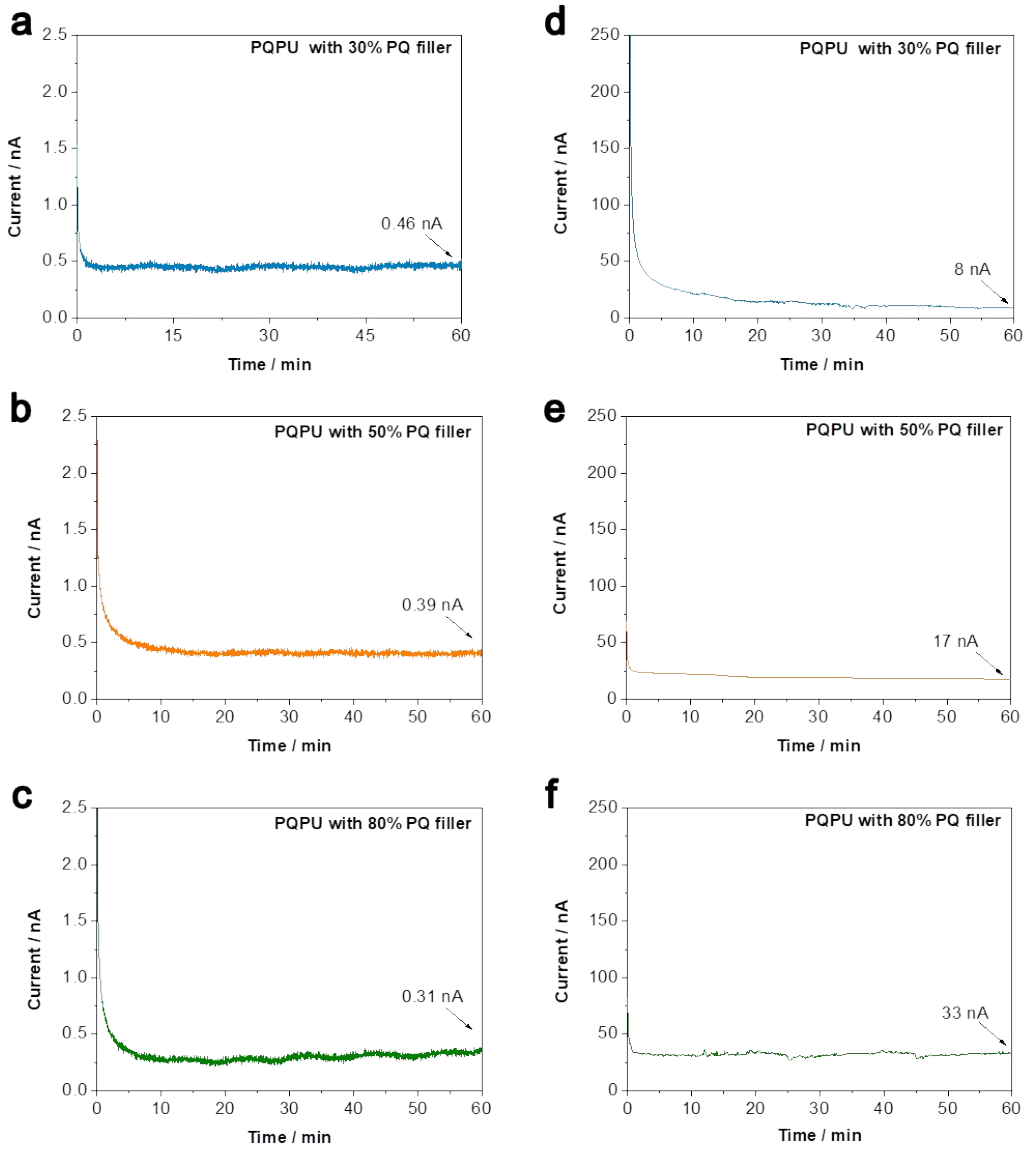

Figure S7. Potentiostatic polarization curves of PQPUs with different amount of PQ fillers (ie., 30%, 50%, 80%) before (a,b,c) and after (d,e,f) gelating process, respectively. The tests were carried out at room temperature with the applied DC voltage of 4.5 V.

The electronic conductivity can be calculated by the following formula:

$$\sigma_e = \frac{d \times I}{A \times U}$$

where "σ_e" refers to the electronic conductivity, "d" refers to the membrane thickness, "I" refers to the steady-state current, "A" refers to the contact area between the electrolyte membrane and the blocking electrode, and "U" refers to the applied DC voltage.

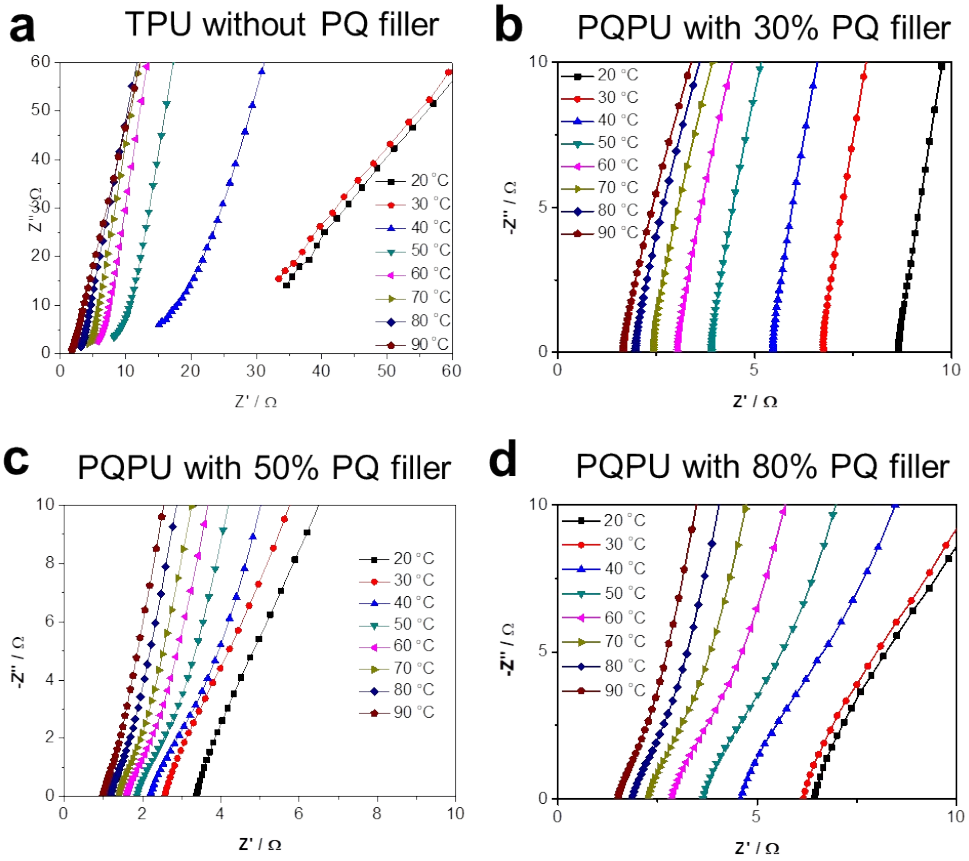

Figure S8. Temperature-dependent AC impedance spectra of (a) TPU without PQ filler, (b) PQPU with 30% PQ filler, (c) PQPU with 50% PQ filler, and (d) PQPU with 80% PQ filler.

Table S1 Ionic conductivity of the GPE samples at different temperatures.

Temperature (°C)		**20**	**30**	**40**	**50**	**60**	**70**	**80**	**90**
Ionic conductivity (mS cm^{-1})	TPU without PQ filler	0.18	0.2	0.43	0.79	1.17	1.49	2.11	3.71
	PQPU with 30% PQ filler	1.75	2.09	2.82	3.54	4.53	5.67	6.91	8.52
	PQPU with 50% PQ filler	3.78	4.95	6.05	6.85	8.01	9.25	10.7	12.8
	PQPU with 80% PQ filler	1.9	2.47	3.05	4.23	5.45	6.88	8.41	9.98

Table S2. Room temperature ion conductivities and Li-ion transfer number of various composite gel polymer electrolytes.

Gel polymer electrolyte	Ion conductivity (S cm^{-1})	Li-ion transfer number	Ref.
PL60TF-GPE	1.84×10^{-3}, 20 °C	0.563	S2
PDEIm/P(VDF-HFP)-GPE	1.78×10^{-3}, 25 °C	0.42	S3
Cellulose/PEG-GPE	3.31×10^{-3}, 25 °C	0.63	S4
PPSE15-GPE	3.78×10^{-4}, 25 °C	0.62	S5
G-PPC-GPE	1.64×10^{-4}, 25 °C	0.83	S6
PQPU-GPE	3.78×10^{-3}, 25 °C	0.74	This work

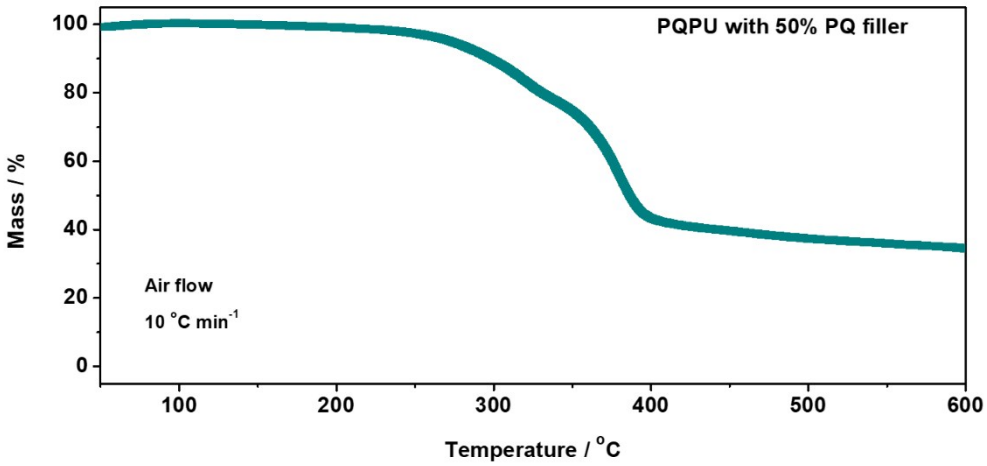

Figure S9. TGA curve of the PQPU with 50% PQ filler.

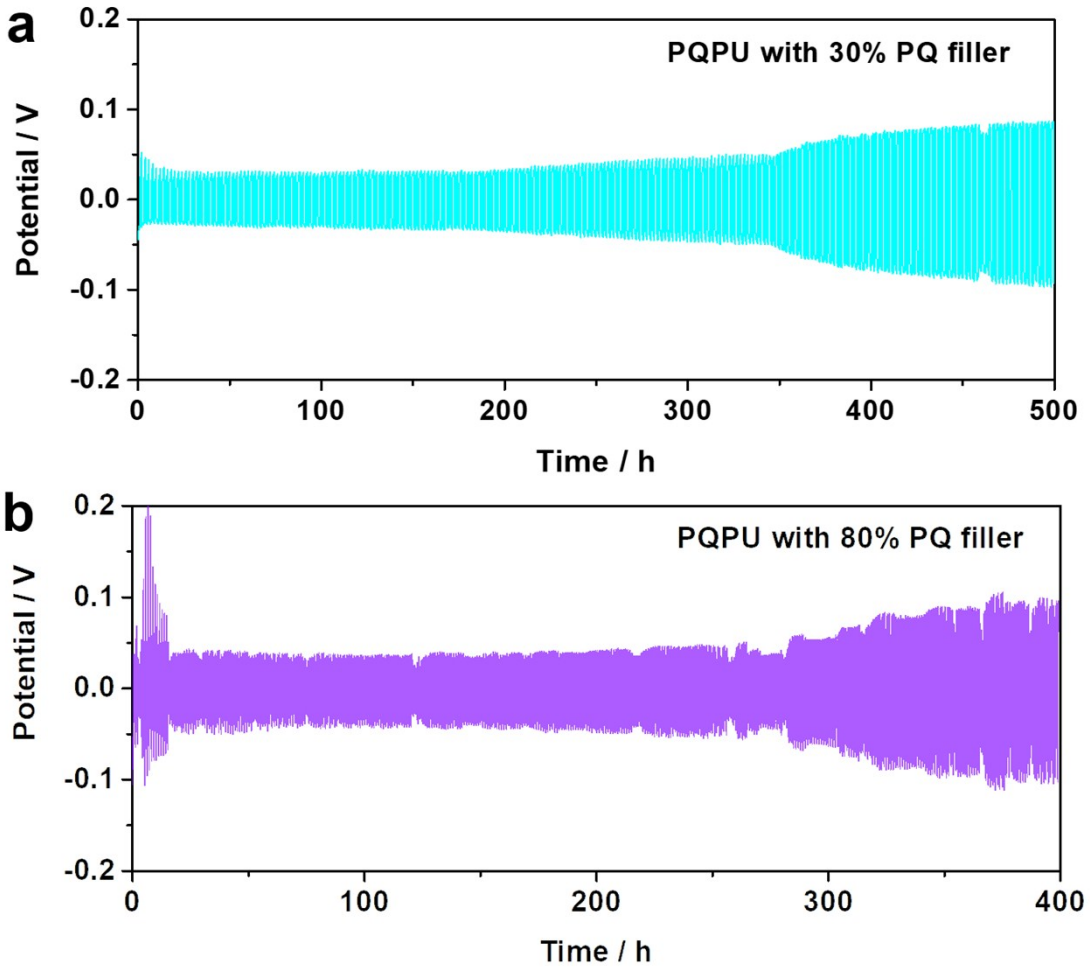

Figure S10. Comparison of the cycling stability of the Li-Li symmetric cells at 0.1 mA cm^{-2} using (a) PQPU with 30% PQ filler and (b) PQPU with 80% PQ filler.

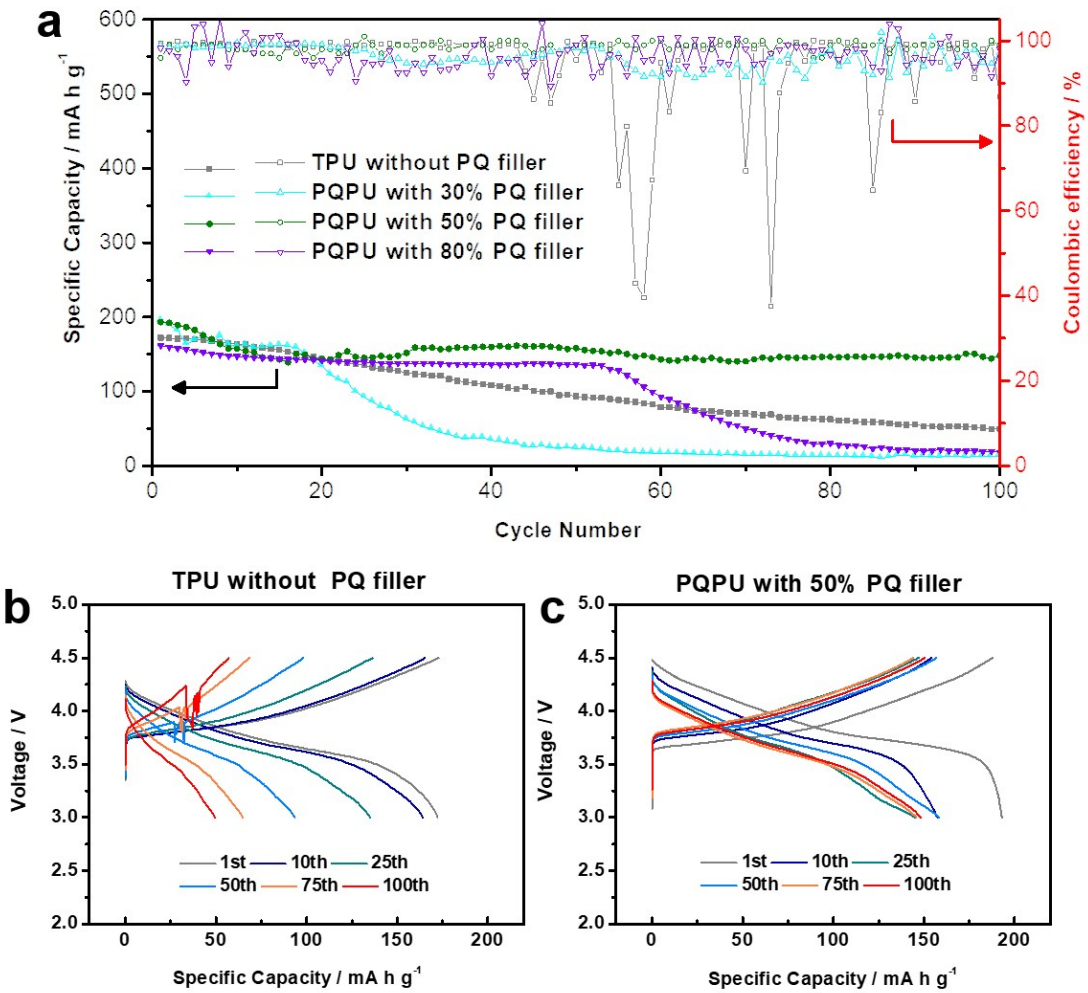

Figure S11. (a) Comparison of the cycling performances of the NCM622-Li cells with different gel polymer electrolytes tested at 0.5 C. The corresponding charge- discharge profiles of 1st, 10th, 25th, 50th, 75th, and 100th cycles of the cells with (b) the TPU without PQ filler and (c) the PQPU with 50% PQ filler, respectively.

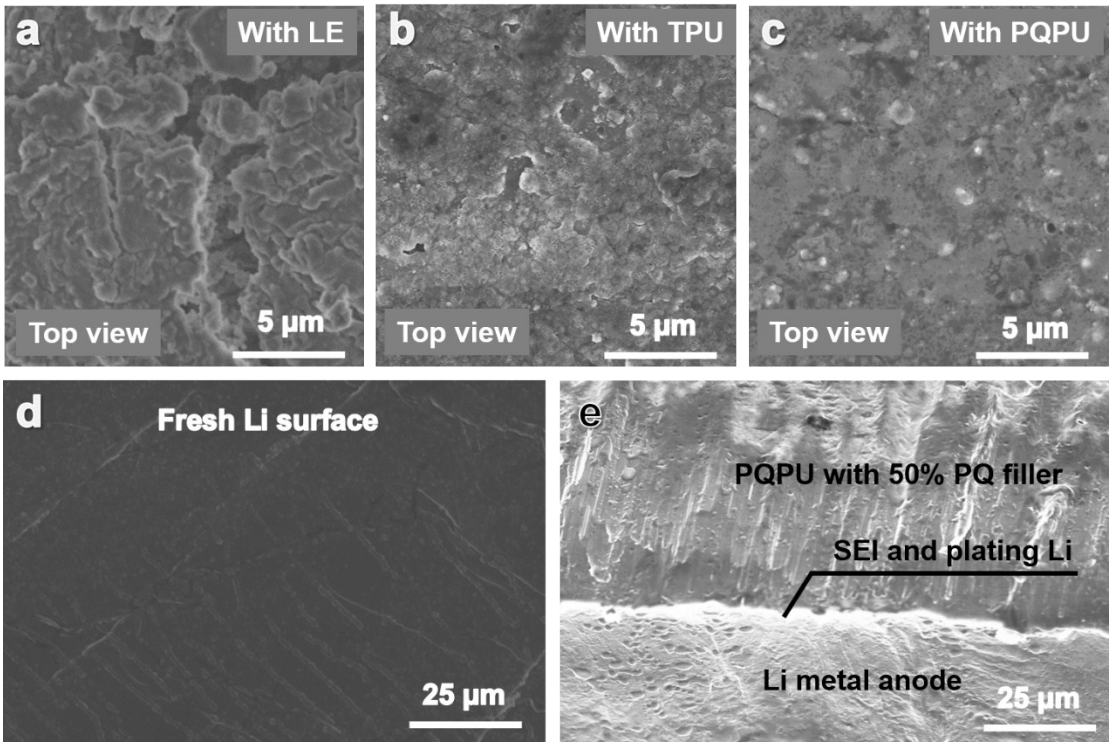

Figure S12. SEM images of the surface of Li metal anodes after being cycled for 100h in symmetric cells of (a) Li/LE/Li and (b) Li/TPU without PQ filler/Li, and 300h in the symmetric cell of (c) Li/PQPU with 50% PQ filler/Li. (d) Top-view SEM image of the flesh Li metal anode. (e) Cross-section SEM image of the Li metal anode disassembled from Li/PQPU with 50% PQ filler/Li cell after being cycled for 300 h.

Reference

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