

## Supporting Information

# **A Lithiated Organic Nanofiber-Reinforced Composite Polymer Electrolyte Enabling Li-ion Conduction Highways for Solid-State Lithium Metal Batteries**

Liying Tian<sup>a</sup>, Ying Liu<sup>b</sup>, Zhe Su<sup>a</sup>, Yu Cao<sup>a</sup>, Wanyu Zhang<sup>a</sup>, Shan Yi<sup>a</sup>, Yayun Zhang<sup>a</sup>, Bo Niu<sup>a</sup>, Panpan Dong<sup>\*c</sup>, and Donghui Long<sup>\*a</sup>

<sup>a</sup> Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai, 200237, China

<sup>b</sup> Key Laboratory for Advanced Materials, Center for Computational Chemistry and Research Institute of Industrial Catalysis, School of Chemistry & Molecular Engineering, East China University of Science and Technology, Shanghai 200237, China

<sup>c</sup> School of Mechanical and Materials Engineering, Washington State University, Pullman, Washington 99164, United States

---

\* Corresponding author:

E-mail: longdh@mail.ecust.edu.cn (Donghui Long); panpan.dong@wsu.edu (Panpan Dong).

## **Experimental Section**

### **1. Preparation of LOF**

To prepare LOF, three major steps including electrospinning, grafting reaction, and dynamic adsorption process are conducted as follows:

(1) Electrospinning. To obtain the electrospinning solution, 2 g of PAN (M<sub>w</sub> ~150,000) was dissolved in 18 g of DMF with stirring for 12 hours at 50 °C. During electrospinning, a high voltage of 13 kV was employed between the needle and collector with the distance of 15 cm. After electrospinning for 5 hours, the PAN membrane was peeled off from the drum collector and kept in a vacuum oven at 50 °C for 6 hours to remove the DMF residue. The free-standing nanofiber membrane was then pressed under proper temperature and pressure to achieve 80% porosity before further use.

(2) Grafting reaction. 120 mg of PAN fibers were introduced into a 50 mL flask with 40 mL of 10 mg/mL branched polyethylenimine (bPEI) ethylene glycol solution. Next, the flask was placed into an oil bath and the mixture was stirred under reflux at 140 °C for 8 hours. The obtained bPEI-grafted PAN fibers (bPEI-PAN) were then collected, subsequently washed with ethanol and deionized water, and finally dried at room temperature and 50 °C for 6 hours, respectively.

(3) Kinetic adsorption process. LiI ethanol solution with a concentration of 0.5 mol/L was pre-prepared. Next, a piece of bPEI-PAN was soaked into LiI/ethanol solution under stirring for 6 hours and after that, dried at 60 °C for 12 hours. The lithiated organic nanofiber (LOF) membrane was finally obtained.

### **2. Preparation of composite polymer electrolyte supported by LOF-CPE**

#### **2.1 Preparation of LOF-CPE**

PEO-based solid polymer electrolyte (named as SPE) membrane was firstly prepared with a thickness of  $\sim 30$   $\mu\text{m}$ , in which the PEO polymer and LiTFSI ( $[\text{EO}]/[\text{Li}^+]=16:1$ , molar ratio) were added into acetonitrile under stirring for 6 hours. The obtained uniform mixture was poured into a Teflon dish and dried under vacuum at  $50$   $^\circ\text{C}$  for 24 hours. To prepare PEO/LiTFSI/LiI electrolyte (named as SPE-LiI), PEO, LiTFSI, and LiI ( $16:1:1/7$ , molar ratio) were added into acetonitrile and other steps are the same as that of SPE. Then, the LOF was sandwiched by two PEO membranes and this three-layer precursor was placed between two steel plates. Next, the precursor was heated up under vacuum followed by the detailed temperature ramping procedure as below: holding at  $50$   $^\circ\text{C}$  for 30 min; heat up from  $50$   $^\circ\text{C}$  to  $185$   $^\circ\text{C}$  for 100 min; holding at  $185$   $^\circ\text{C}$  for 360 min; then quenching back to room temperature. The obtained LOF-CPE membrane was dried at  $60$   $^\circ\text{C}$  for 12 hours under vacuum and stored into an argon-filled glove box before use. In addition, the CPE supported by organic framework of bPEI-PAN (GOF-CPE) was prepared using the same method. And GOF/LiI-CPE was also used the same method with the replacement SPE with SPE-LiI

## 2.2 Preparation of LOF-CPE-CS

PEO and LiTFSI ( $[\text{EO}]/[\text{Li}^+]=16:1$ , molar ratio) were firstly dissolved into acetonitrile with a concentration of 5wt% PEO. The mixture was mechanically stirred at  $60$   $^\circ\text{C}$  for 12 hours, then dropped onto a LOF and dried at  $60$   $^\circ\text{C}$  for 24 hours. The well-prepared LOF-CPE-CS was stored at glove box for further analysis.

## 3. Material characterization

The scanning electron microscope (SEM, Nova NanoSEM 450) was applied to observe morphologies of nanofibers, polymer electrolytes, and lithium deposition of anode

surfaces. X-ray photoelectron spectrometer (XPS, ESCALAB 250Xi) was conducted to evaluate the surface chemical state. Fourier transform infrared spectrum (FTIR, Spectrum 10) was carried out from 4000  $\text{cm}^{-1}$  to 500  $\text{cm}^{-1}$ . The melting and glass transition temperatures were measured by differential scanning calorimeter (DSC, DSC 8500) with the range from  $-75$   $^{\circ}\text{C}$  to  $100$   $^{\circ}\text{C}$  at the heating rate of  $10$   $^{\circ}\text{C}/\text{min}$ . Thermogravimetric analysis (TGA, TGA 8000) was conducted to test the decomposition temperature under air atmosphere, in which the heating range and rate were set to  $60$   $^{\circ}\text{C}$ – $800$   $^{\circ}\text{C}$  and  $5$   $^{\circ}\text{C}/\text{min}$ , respectively. The crystallinity of polymer electrolyte membrane was characterized by X-ray diffraction (XRD, D/max2550VB/PC). The universal testing machine (DMA Q800) was used to measure the mechanical properties of CPEs.

#### 4. DFT calculations

All the spin-polarized calculations were performed using density functional theory (DFT) in the Ab-initio Simulation Package (VASP) code<sup>1, 2</sup>. The project augmented wave method (PAW) was used throughout for the theoretical prediction of the energetics. The exchange-correlation function was represented by generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE). The valence electronic states were expanded in plane basis sets with energy cut-off at  $450$  eV<sup>3</sup>. To avoid the influence from pseudo-atom, the polymer chain was set at a square simulation box with  $25$   $\text{\AA}$  in length and thus only one K-point was utilized by Gaussian smearing. The geometry convergence criterion was set as  $0.05$  eV/ $\text{\AA}$ . To well describe their surface energies, the DFT-D3 method with the van der Waals dispersion effect included was used<sup>4</sup>. The binding energy ( $E_b$ ) was calculated via the equation:

$$E_b = E_{\text{polymer}} + E_{\text{Li}} - E_{\text{polymer-Li}}$$

where  $E_{polymer}$ ,  $E_{Li}$ , and  $E_{polymer-Li}$  refers to the energy of polymer,  $Li^+$  ion, polymer-Li system, respectively.

## 5. Experiment for calculating porosity of PAN

The bulk density ( $\rho_1$ ) of PAN is 1.184 g/cm<sup>3</sup>. PAN mat was punched into circular disks (d=19 mm) and then measured the thickness and mass of disks.

The density of the disk was first calculated using the following equation:

$$\rho_2 = \frac{m_1}{\pi \times \left(\frac{d}{2}\right)^2 \times h}$$

The porosity was thereby calculated as follows:

$$\varepsilon = \frac{\frac{1}{\rho_2} - \frac{1}{\rho_1}}{\frac{1}{\rho_2}}$$

Where  $\rho_2$  (g/cm<sup>3</sup>) is the density of PAN nanofiber mat,  $m_1$  (g) and  $h$  ( $\mu$ m) is the weight and thickness of one circular disk, respectively, and  $\varepsilon$  is the porosity of network.

## 6. Adsorption experiment of metal ions

Circular disks with a diameter of 19 mm were obtained via punching into bPEI-PAN membrane, weighed up as  $W_1$  (g), then placed them into LiI ethanol solutions with the concentration of 500 mg/L. The disk was taken out at various time, dried at 60 °C for an hour, and weighed up as  $W_2$ . The adsorption capacity ( $q$ , mg/g) was calculated by the following equation:

$$q = \frac{(W_2 - W_1) \times 1000}{W_1}$$

## 7. $Li^+$ adsorption capacity

A piece of circular PAN is ca. 5mg, and its weight enhances ca. 20wt% after graft reaction. Its height is ca. 80  $\mu\text{m}$  and its diameter is 19 mm, and thereby its porosity is calculated ca. 80%. The density of PEO/LiTFSI with a molar ratio of 16:1 (EO:Li<sup>+</sup>) is ca. 1.06 g/cm<sup>3</sup>. The molar mass of repeat unit of bPEI is 471 mg/mmol. One repeat unit of bPEI molecular could adsorb four Li<sup>+</sup> according to the DFT results. And we could calculate the capacity of Li<sup>+</sup> on bPEI-PAN in the following equation:

$$\text{Capacity (Li}^+) = \frac{5 \text{ mg} \times 20 \text{ wt}\%}{471 \text{ mg/mmol}} \times 4 = 8.5 \times 10^{-3} \text{ mmol}$$

PEO/LiTFSI occupies 80% of volume in bPEI-PAN membrane, which the capacity of Li<sup>+</sup> in PEO/LiTFSI is also calculated:

$$\begin{aligned} \text{Capacity (Li}^+) &= \frac{3.14 \times \left(\frac{1.9 \text{ cm}}{2}\right)^2 \times (80 \times 10^{-4}) \text{ cm} \times 80\% \text{ porosity} \times (1.06 \times 10^3 \text{ g/cm}^3)}{287 \text{ mg/mmol} + (16 \times 44) \text{ mg/mmol}} \\ &= 1.9 \times 10^{-2} \text{ mmol} \end{aligned}$$

## 8. Electrochemical measurements

Electrochemical impedance spectroscopy (EIS) was conducted to measure ionic conductivity with the battery configuration of sandwiching composite polymer electrolyte between two stainless steel electrodes. The testing temperature and frequency were set from 20 °C to 80 °C, and 1MHz to 10 mHz, respectively. The ionic conductivity ( $\sigma$ ) can be calculated as the following equation:

$$\sigma = \frac{L}{R_b \cdot S}$$

where  $R_b$  and  $L$  refers to the bulk resistance and thickness of CPE, respectively, and  $S$  is the area of electrolyte contacting with electrode. Linear sweep voltammetry (LSV) was

applied to evaluate electrochemical stability window at a sweep rate of 0.5 mV/s in the voltage range of 0–6 V vs. Li/Li<sup>+</sup>. The Li<sup>+</sup> transference number ( $t_{Li^+}$ ) was measured using Li|CPE|Li symmetric battery via the combination method of direct current (DC) polarization/alternating current (AC) impedance. The following equation was utilized to deduce the  $t_{Li^+}$  value:

$$t_{Li^+} = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)}$$

where  $\Delta V$  is represented as polarization voltage of 10 mV,  $I_0$  and  $I_s$  are the initial and steady currents,  $R_0$  and  $R_s$  are the impedance before and after DC polarization, respectively. The activation energy below melting temperature was calculated by Arrhenius equation as follows,

$$\sigma = \frac{\sigma_0}{T} \exp\left(-\frac{E_a}{RT}\right)$$

And the activation energy above melting temperature was calculated by Vogel-Tamman-Fulcher (VTF) equation as follows,

$$\sigma = \frac{\sigma_0}{T^2} \exp\left(-\frac{E_a}{R(T - T_0)}\right)$$

where  $T_0$  is a temperature that is ~50 K below glass transition temperature ( $T_g$ ).

Lithium symmetric battery was assembled to test the Li plating/stripping performances at the current density of 0.2 mA/cm<sup>2</sup>. LiFePO<sub>4</sub>|Li solid-state battery was applied to measure long-term cycling stability and rate performances at the voltage range of 2.8–4.2V vs. Li/Li<sup>+</sup>. To prepare cathode material, LiFePO<sub>4</sub>, super C, and PVDF at a weight ratio of 8:1:1

were dispersed into NMP solvent with stirring for 12 hours, then the mixture was cast onto a aluminum foil and dried at 60 °C for 24 hours. After that, the cathode material is punched into disks with 12mm in diameter and the areal loading of active material is around 2 mg/cm<sup>2</sup>.

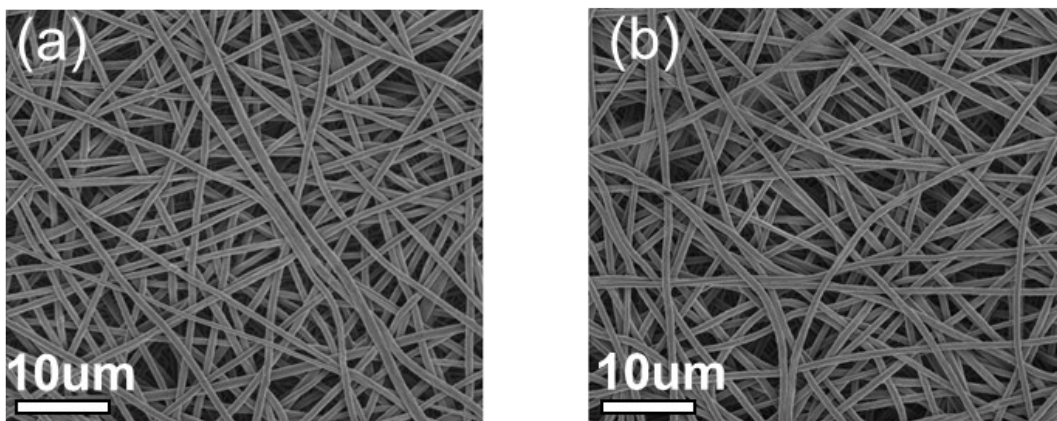


Fig. S1. SEM images of (a) PAN and (b) bPEI-PAN.



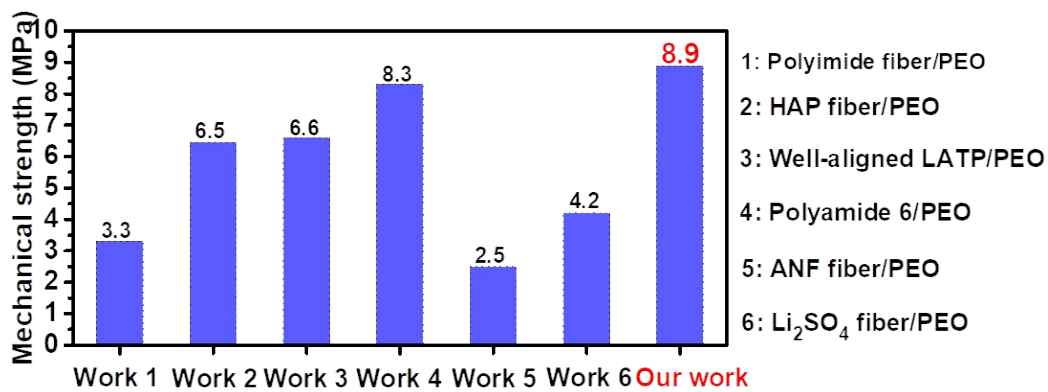


Fig. S2. A comparison of mechanical strength using casting solution method from representative works and our work.

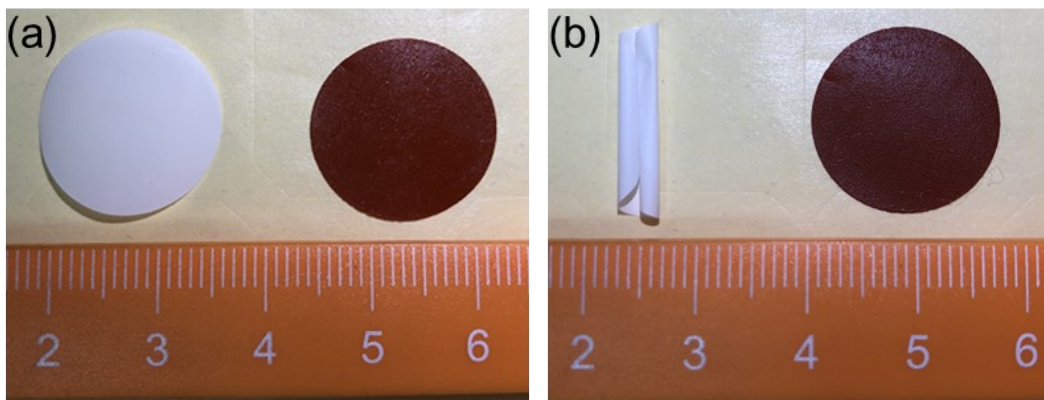


Fig. S3. Digital photos of Celgard 2500 (white) and LOF-CPE (colored) (a) before and (b) after heated at 120 °C.

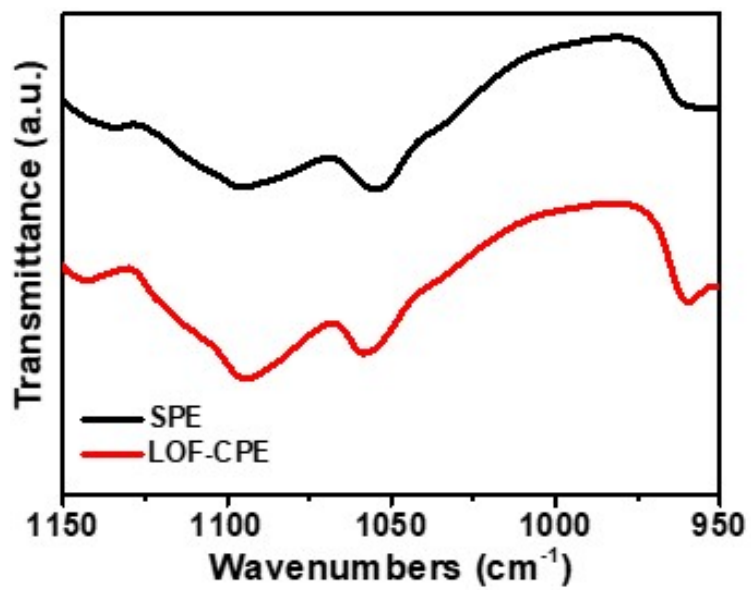


Fig. S4. FTIR spectra of illustration changes of  $\text{-C-O-C-}$  in SPE and LOF-CPE.

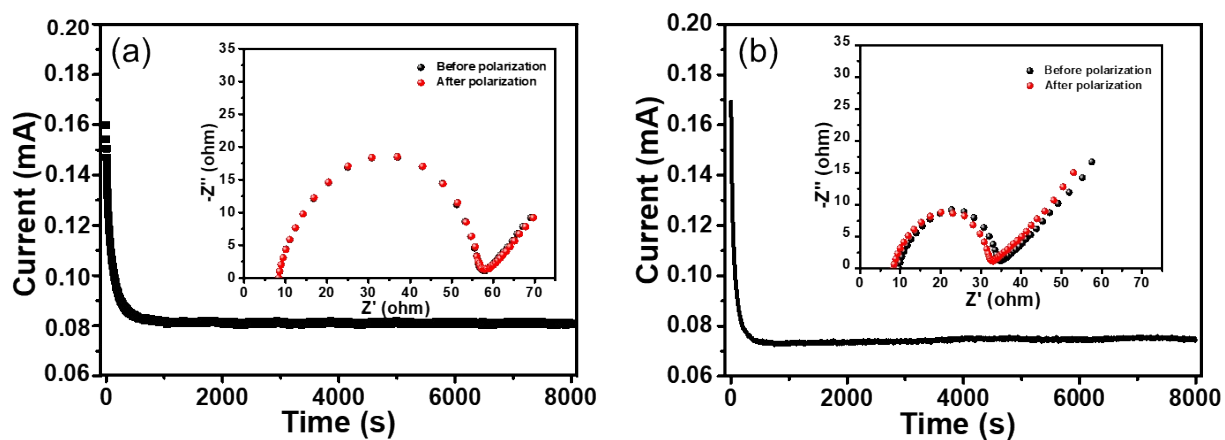


Fig. S5. The chronoamperometry plots of symmetric battery with (a) SPE and (b) GOF-CPE under the polarization voltage of 10 mV. Insert plots are EIS results before and after polarization, respectively.

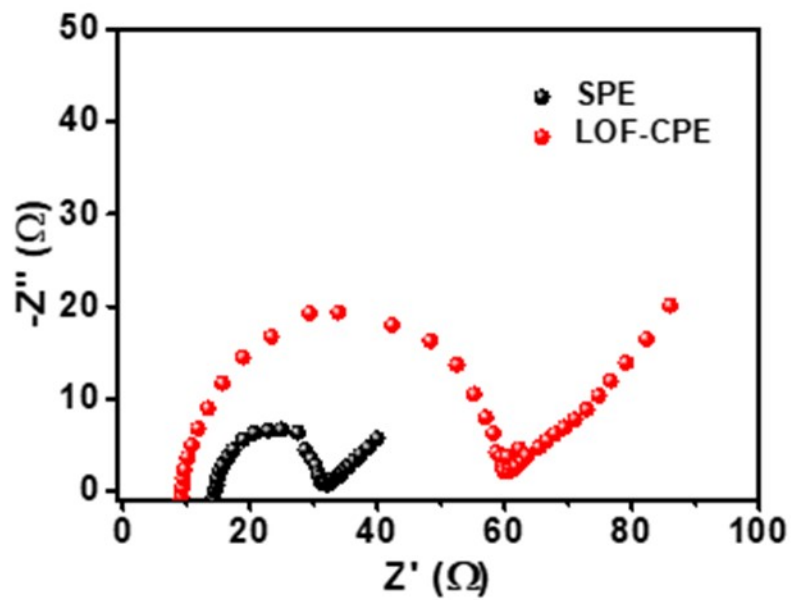


Fig.S6. The Nyquist plots of lithium symmetric batteries with SPE and LOF-CPE

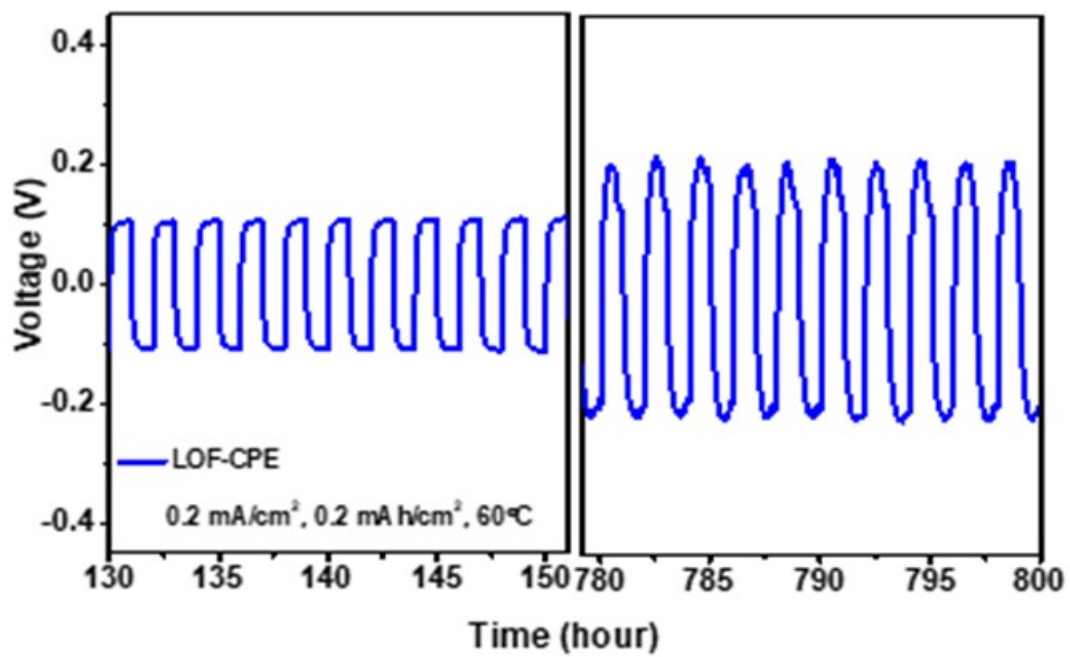


Fig.S7. The zoomed-in voltage profile of lithium symmetric battery with LOF-CPE

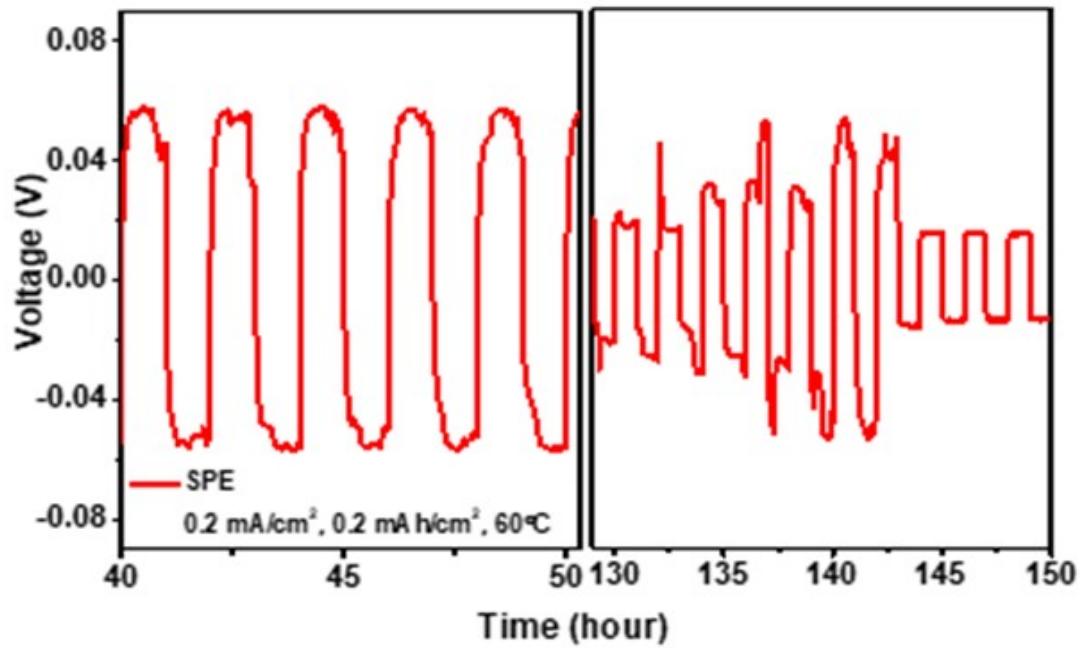


Fig. S8. The zoomed-in voltage profile of lithium symmetric battery with SPE.

Table S1. The porosity of circular disks of PAN nanofiber with a diameter of 19 mm.

Sample	A	B	C	D	E	F
Weight/mg	4.50	4.52	3.83	4.61	4.69	4.49
Height/ $\mu\text{m}$	75	67	63	77	68	70
Density/ $\text{g}\cdot\text{cm}^{-3}$	0.212	0.238	0.215	0.211	0.243	0.226
Porosity/%	82.10	79.89	81.88	82.16	79.44	80.88



Table S2. Mechanical properties of LOF-CPE and LOF-CPE-CS

Electrolyte	Tensile strength (MPa)	Young's modulus (MPa)
LOF-CPE	8.9	111.4
LOF-CPE-CS	7.0	65.9

Table S3. Thermal properties of SPE, GOF-CPE and LOF-CPE.

Electrolyte	$T_g$ (°C)	$T_m$ (°C)	$H_m$ (J/g)	$X_c$ (%)
SPE	-37.9	51.2	60.9	30.1
GOF-CPE	-40.0	49.3	45.1	22.2
LOF-CPE	-42.0	48.9	36.7	18.1

Table S4. Kinetic parameters for Li<sup>+</sup> ion adsorption.

<b>Models</b>	Pseudo-first-order Model			Pseudo-second-order Model		
<b>Parameter</b>	q <sub>e</sub>	k <sub>1</sub>	R <sup>2</sup>	q <sub>e</sub>	k <sub>2</sub>	R <sup>2</sup>
<b>Value</b>	112.2 3	4.36×10 <sup>-3</sup>	0.8556	158.23	8.98×10 <sup>-5</sup>	0.9904

<b>Models</b>	Webber-Morris Model					
<b>Parameter</b>	k <sub>d1</sub>	R <sup>2</sup> <sub>1</sub>	k <sub>d2</sub>	R <sup>2</sup> <sub>2</sub>	k <sub>d3</sub>	R <sup>2</sup> <sub>3</sub>
<b>Value</b>	8.85	0.9608	7.22	0.5277	3.17	0.6660

Espe

cially, the original data of adsorption experiment are shown in Table S5 as below, which could be calculated and fitted by different kinetic adsorption models.

Models	Equation	Description
Pseudo-first-order Model	$\ln(q_e - q_t) = \ln q_e - k_1 t$	Adsorption process was controlled by diffusion.

Table S5. Adsorption capacity of bPEI-PAN at different times.

Adsorption											
time (min)	15	30	40	50	100	120	150	180	210	240	420
Capacity (mg/g)	30	49	53	59	101	95	113	118	112	128	134

---

Pseudo-second-order Model	$\frac{t}{q_t} = \frac{1}{k_2 \times q_e^2} + \frac{t}{q_e}$	Adsorption process was controlled by chemical adsorption via sharing electron pairs between adsorbent and adsorbate.
Webber-Morris Model	$q_t = k_{td}t^{1/2}$	Adsorption process was controlled by internal diffusion of adsorbent.

---

Table S6. Three different adsorption kinetic models.

## Reference

1. G. Kresse and J. Hafner, *Journal of Physics: Condensed Matter*, 1994, **6**, 8245.
2. G. Kresse and J. Furthmüller, *Computational Materials Science*, 1996, **6**, 15-50.

3. G. Kresse and D. Joubert, *Physical review b*, 1999, **59**, 1758.
4. S. Grimme, S. Ehrlich and L. Goerigk, *Journal of computational chemistry*, 2011, **32**, 1456-1465.