

## Supplementary material

### 3D Fiber Skeleton Reinforced PEO -Based Polymer Electrolyte for High Rate and Ultra-Long Cycle All-Solid-State Battery

#### Experimental Methods

##### 1. Preparation of LS -AEF

The fruit of the plant loofah was grown and matured under normal conditions. After natural air-drying or drying, the impurity surface, skin, and the loofah seeds inside the pores were removed, and the cylindrical loofah sponge was obtained. The cylindrical loofah was prepared by cutting it with clean scissors to obtain cuboid-shaped loofah with a range of lengths and heights. After rinsing the cube-shaped loofah, it was then soaked in steamed water. It was stirred with an electric mixer for half an hour to one hour and then put it in a blast drying oven at 100 °C. The dried small pieces of loofah were sealed, dried, and saved. A small piece of loofah for drying was weighed, and the small piece of dry loofah was put into a mixed solution of N, N, dimethylformamide and epichlorohydrin and stirred in a heated water bath. Then, pyridine was added. The solution was used as a catalyst. Heating and stirring in a water bath continued, and finally, a 33 % mass concentration of dimethylamine aqueous solution was added. Heating in a water bath continued to obtain the grafted loofah fiber. The grafted loofah was transferred to a funnel, cooled to room temperature, rinsed with 0.1 M sodium hydroxide and hydrochloric acid solution twice, then transferred to a glass beaker. It was poured into an ethanol water bath and heated and stirred vigorously.

##### 2. Preparation of PEO@ LS-AEF SPEs

The PEO-based solid electrolyte was prepared by a solution casting method. For convenience, the thickness of the solid electrolyte is kept at about 120 μm. PEO (Aladdin Inc. Mw = 600,000) was dried for 24 h at 60 °C under vacuum conditions and stored in an argon-filled glove-box (with H<sub>2</sub>O and O<sub>2</sub> contents below 0.1 ppm) before use. In order to prepare the PEO@5%LS-AEF composite polymer electrolyte, 0.7 g PEO and 0.25 g LiTFSI were dissolved in acetonitrile and stirred at room temperature for 24 h to form a homogeneous solution A. 0.05 g LS-AEF was added into 5 ml acetonitrile solution to obtain solution B. The two solutions A and B were mixed evenly and stirred for 24 h at room temperature. Then the slurry was cast into a polytetrafluoroethylene mold and then placed in a vacuum drying dish at room temperature to dry for 24 h to remove most of the acetonitrile solvent. Then, vacuum drying was continued at 60 °C for 24 h to completely evaporate the acetonitrile solvent. All the above steps were carried out in a glove box filled with Ar gas and in order to explore the optimal ratio of LS-AEF added to the PEO polymer electrolyte. Polymer

electrolytes with different amounts of LS-AEF (such as 7 %, 5 %, 3 %, 0 %) were also prepared. Obtained by assembled battery test performance, the battery performance is best when the addition amount is 5 %. All synthesized membranes were stored in an argon-filled glove-box.

### 3. Characterization

A polarizing microscope is used to characterize the morphology of LS and LS@PEO SPEs. X-ray powder diffraction (XRD, Rigaku Ultima IV) was employed to characterize the structure of the PEO, LiTFSI, and the PEO@5%LS-AEF SPEs membranes within a diffraction angle ( $2\theta$ ) range from  $10^\circ$  to  $70^\circ$  at a scan rate of  $1^\circ \text{ min}^{-1}$  at room temperature. Differential scanning calorimetry (DSC, NETZSCH DSC 200F3) analyses were performed from  $-80^\circ \text{ C}$  to  $140^\circ \text{ C}$  to investigate material phase transitions during heating. Fourier transform infrared (FTIR, Bruker VERTEX 70V FTIR Spectrometer) spectra of LS, LS-AEF, and LS-AEF-TFS were recorded between  $400$  and  $4000 \text{ cm}^{-1}$  by the KBr compression method. Raman spectra (WITecalpha 300R) were collected using a 100X lens on a confocal Raman system with a laser wavelength of  $532 \text{ nm}$ . Tensile strength samples were stretched at a rate of  $5 \text{ mm} \cdot \text{min}^{-1}$  with a gage length of  $20 \text{ mm}$  on an electronic tensile machine (CMT6503, MTS) with a  $50 \text{ N}$  sensor to evaluate the mechanical performance.

### 4. Electrochemical tests

The ionic conductivity of PEO SPEs and PEO@5%LS-AEF SPEs was tested by AC impedance. The prepared polymer electrolyte was sandwiched between two stainless steel electrodes, the frequency was maintained between  $10^6$  and  $10^{-2} \text{ Hz}$ , and the temperature was increased from  $30$  to  $80^\circ \text{ C}$ . The ionic conductivity of SPE was calculated using the following formula:

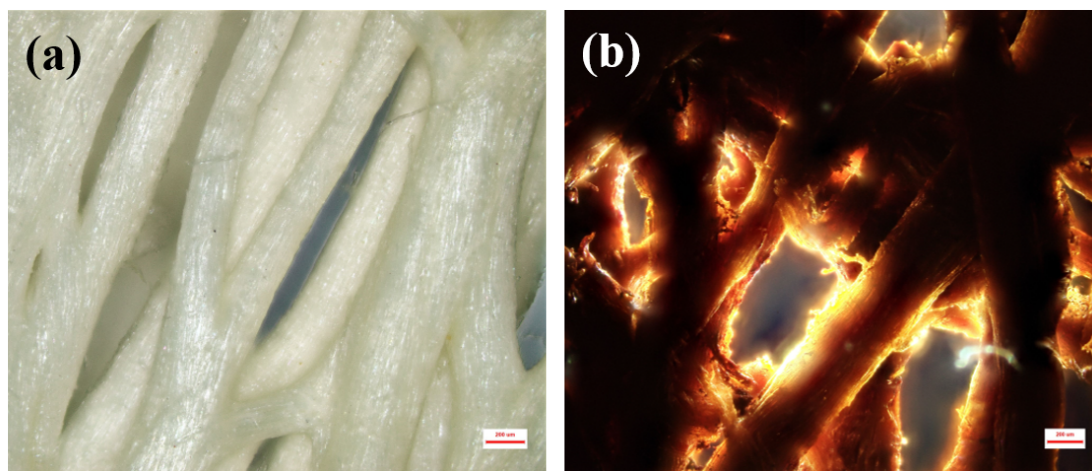
$$\sigma = \frac{L}{RS}$$

where  $L$ ,  $R$ , and  $S$  are SPE thickness, bulk resistance, and area, respectively. Linear sweep voltammetry (LSV) of 5% PEO@5%LS-AEF SPEs and PEO SPEs was conducted using impedance spectroscopy at a scan rate of  $10 \text{ mVs}^{-1}$  on devices prepared with Li/ PEO@5%LS-AEF SPEs /stainless steel, CR2032 coin cells. Li + transference numbers in SPEs were calculated using the Bruce-Vincent-Evans equation:

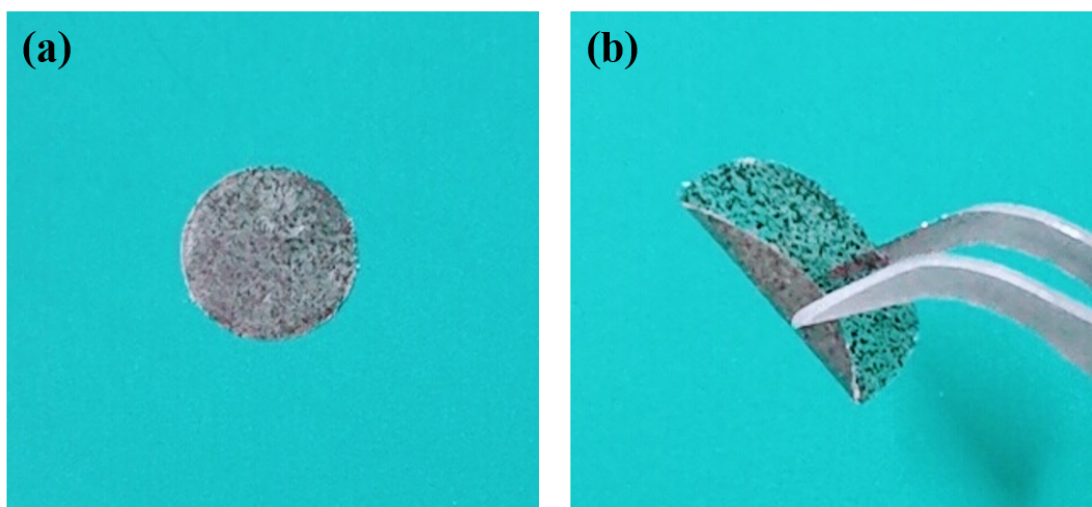
$$t_{\text{Li}^+} = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)}$$

$\Delta V$  is the polarization voltage and was equal to operating voltage ( $\Delta V = 0.01 \text{ V}$ ).  $I_0$  is the initial current, the interfacial resistance before polarization is  $R_0$ , the steady state current is  $I_s$ , and  $R_s$  is the electrolyte and electrode interfacial resistance after applying the  $\Delta V$  voltage for 3 h. In order to test battery performance,  $\text{LiFePO}_4$ , polyvinylidene fluoride (PVDF), and acetylene black were scattered in N-methyl-2-pyrrolidone (NMP) at a weight ratio of 7:2:1. The resulting slurry was then cast onto an aluminum foil and dried under vacuum for more than 12 h at  $80^\circ \text{ C}$ . In this experiment, the cathode active material mass was  $2.5 \pm 0.1 \text{ mg} \cdot \text{cm}^{-2}$ , and charge/discharge performances were tested

with LAND battery testing systems and coin-type cells (CR2032) at 30 °C and 160 °C, respectively. The cut-off voltage range for the Li-LFP battery testing is 2.7–3.8 V.



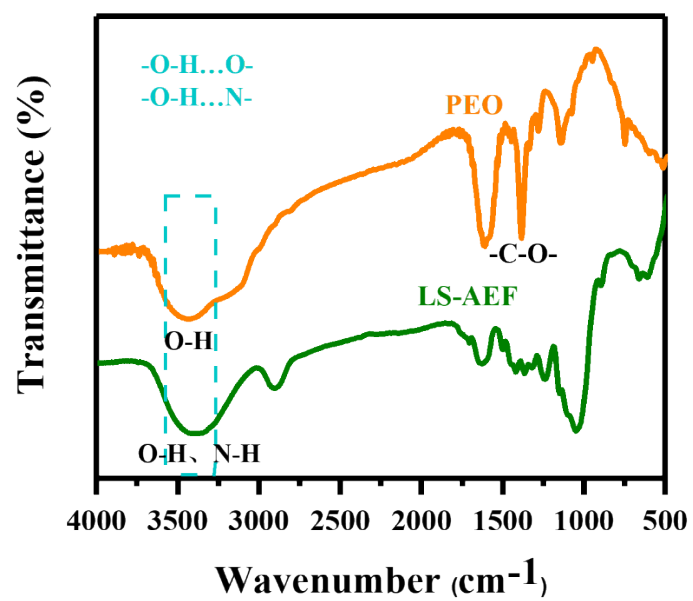
**Figure S1.** The polarized light micrograph of the LS fiber before(a) and after(b) functionalization



**Figure S2.** The optical photos of PEO@LS-AEF SPE.



**Figure S3.** The optical photos of PEO SPE.



**Figure S4.** FTIR spectra of PEO and LS-AEF

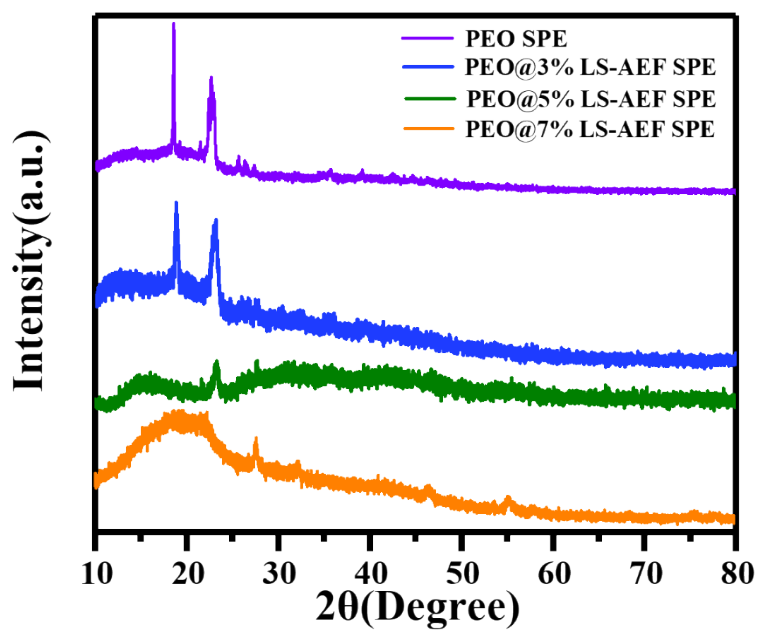


Figure S5. XRD of LS-AEF polymer electrolyte with different content.

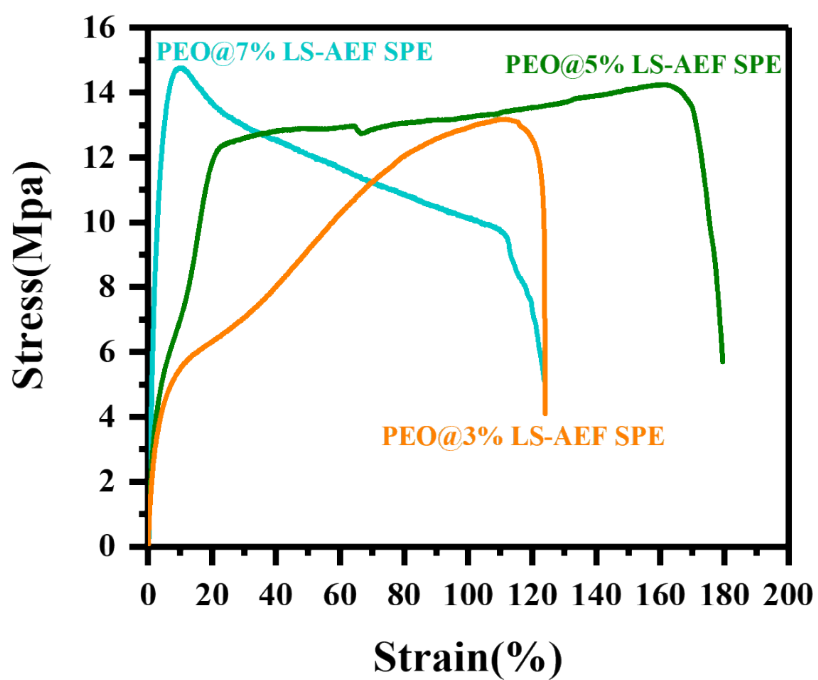


Figure S6. Stress-strain curves of hybrid SPEs with various LS-AEF ratios.

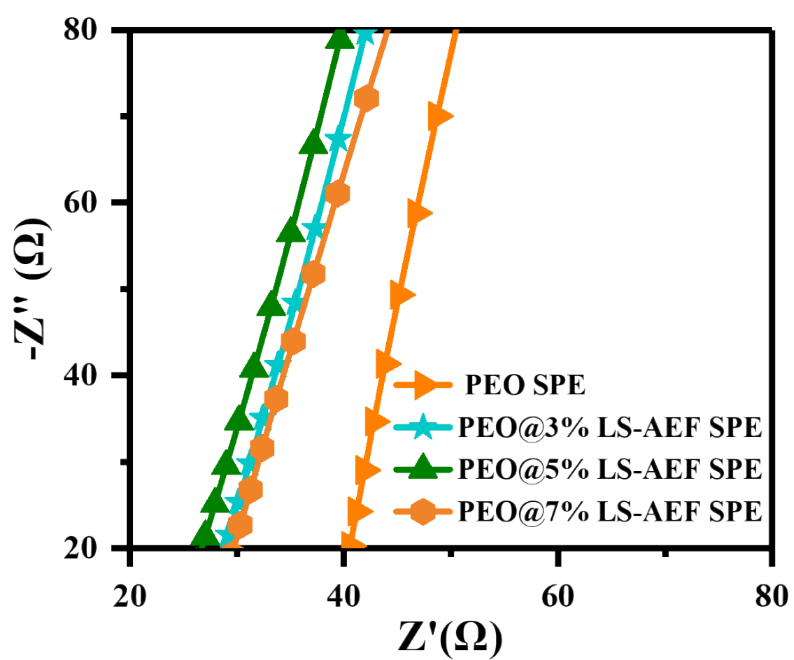


Figure S7. Impedance of LS-AEF polymer electrolyte with different content at 60 °C.

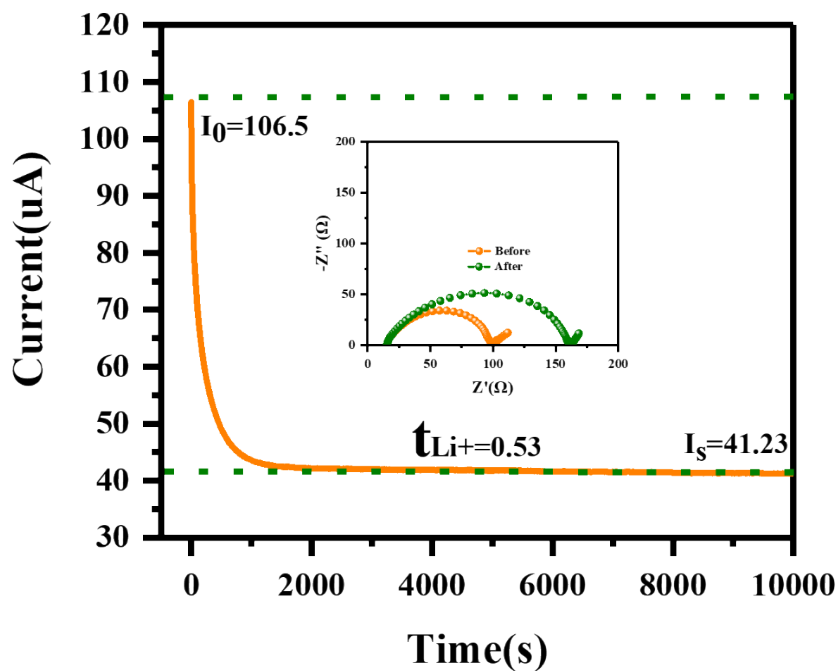
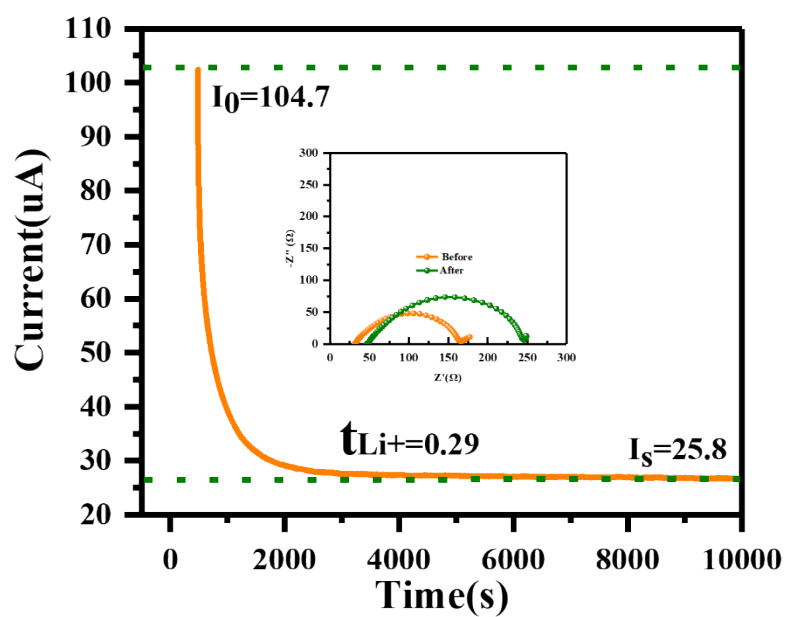
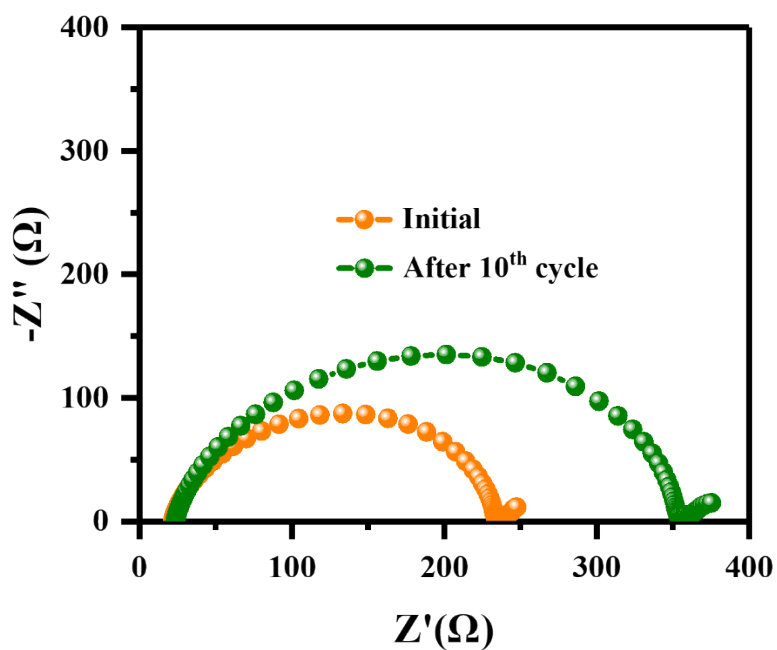


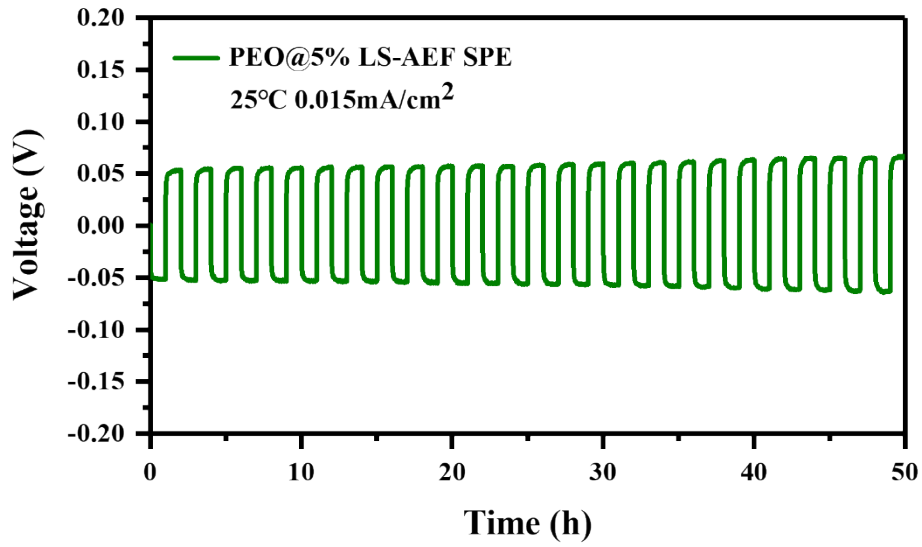
Figure S8. Chronoamperometry profiles and impedance spectra (inset) before and after polarization for symmetric Li/PEO@5%LS SPEs/Li cells.



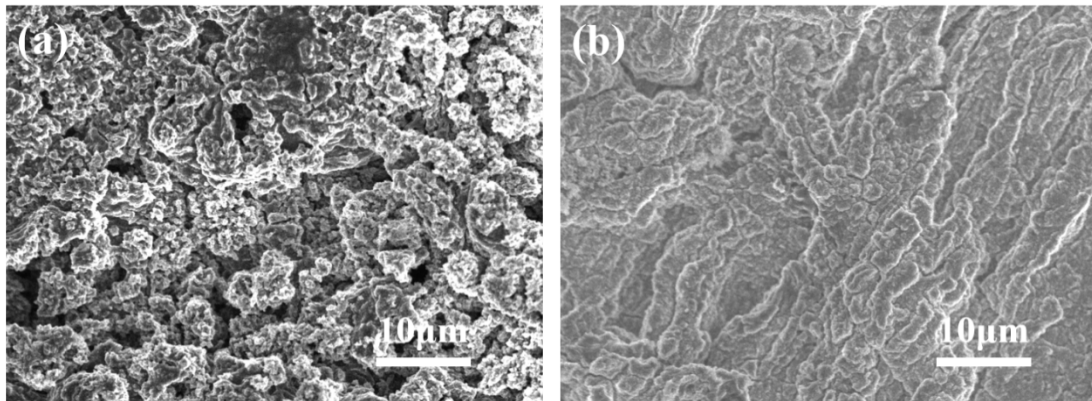
**Figure S9.** Chronoamperometry profiles and impedance spectra (inset) before and after polarization for symmetric Li/PEO SPEs/Li cells.



**Figure S10.** Impedance spectra of the Li/PEO@5%LS-AEF SPE/LFP battery before and after 10 cycles



**Figure S11.** Voltage–time profiles of Li metal plating/stripping as a function of cycle number at 0.015 mA cm<sup>-2</sup> and 25 °C.



**Figure S12.** SEM images of Li metal after plating/stripping cycles in PEO SPE (a) and PEO@5%LS-AEF SPE (b).



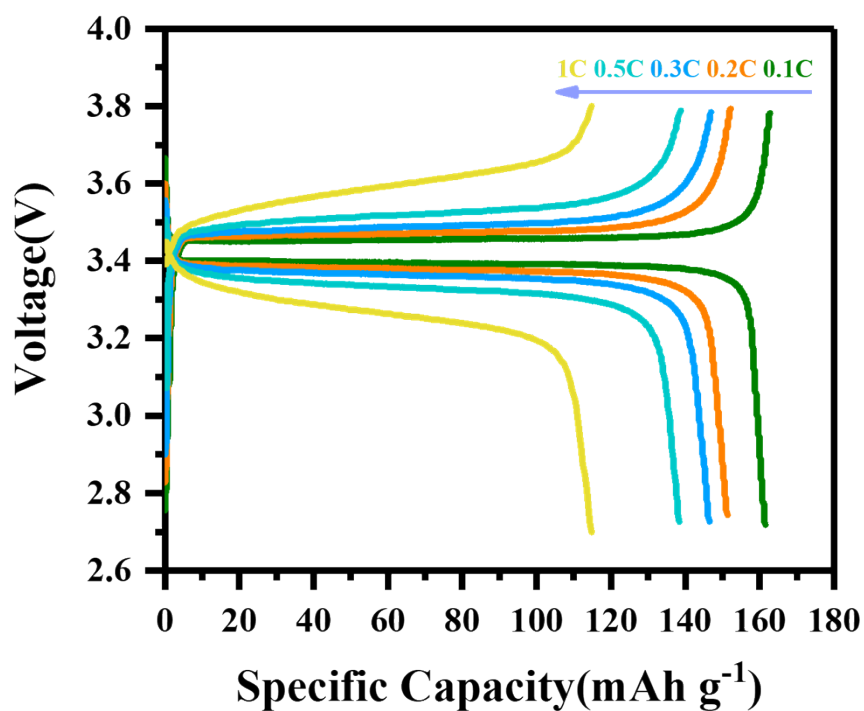


Figure S13. Charge-discharge curves of the Li/PEO@5%LS-AEF SPE/LFP cell at 0.1-1 C.

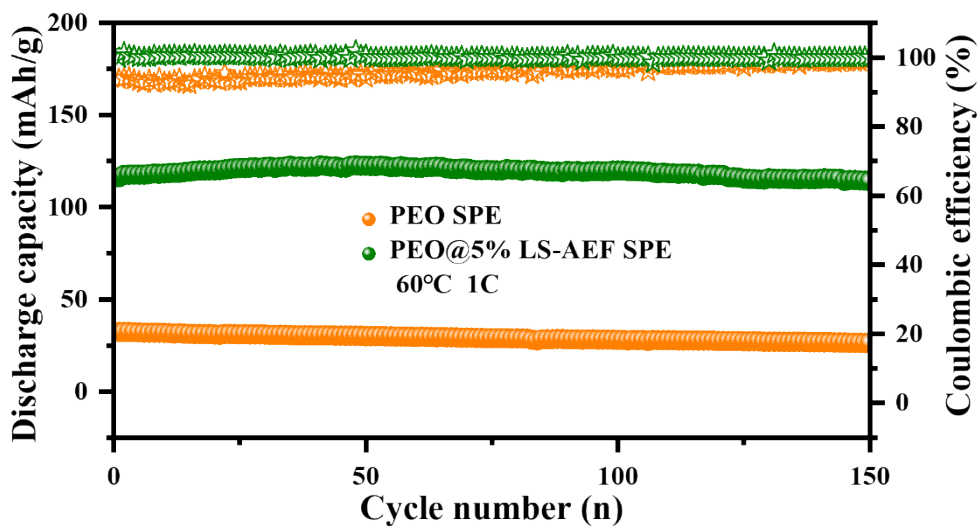
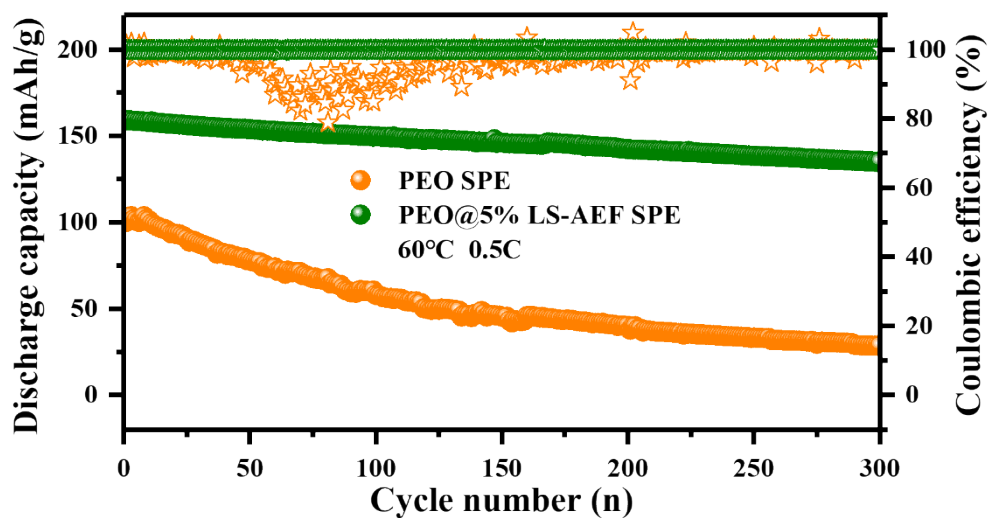
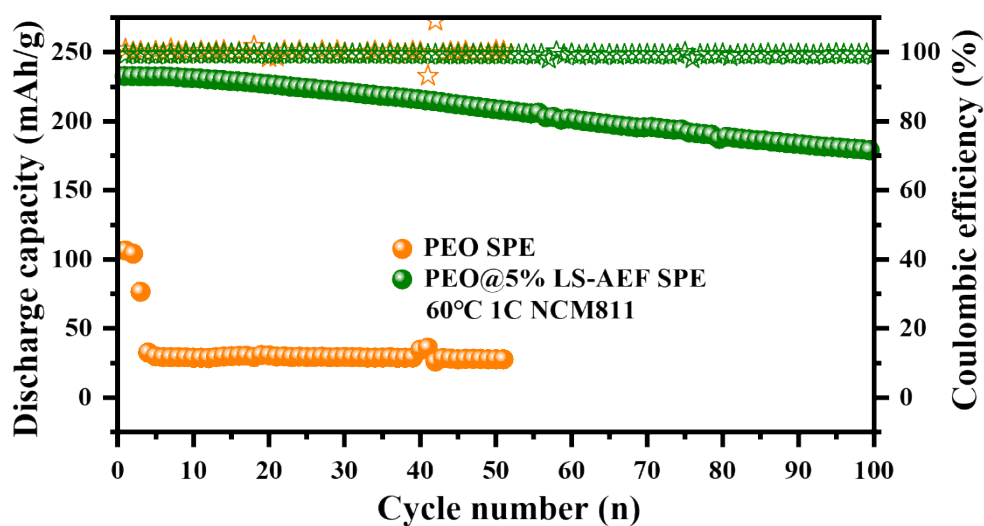


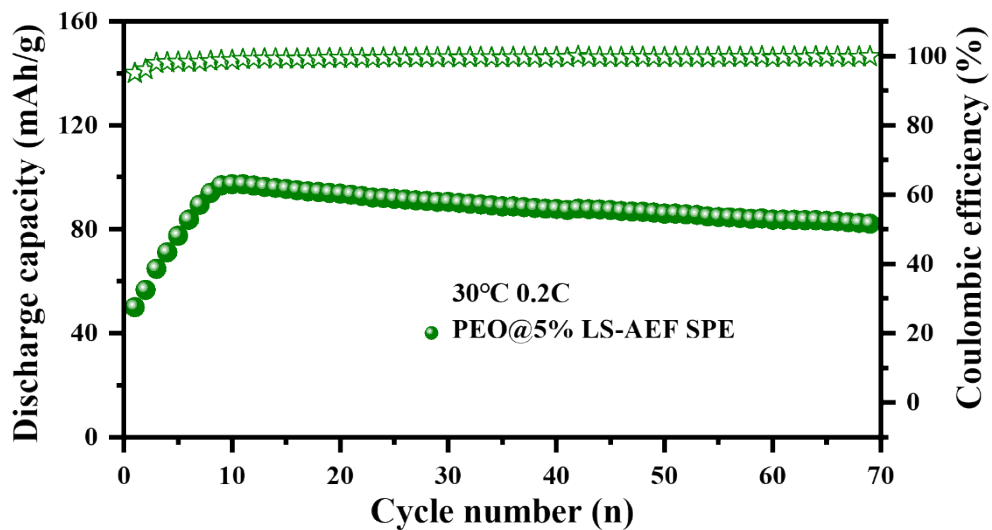
Figure S14. Cycle performance of LFP/SPEs/Li cells using PEO SPEs and PEO@5%LS-AEF SPEs at 1 C (60 °C).



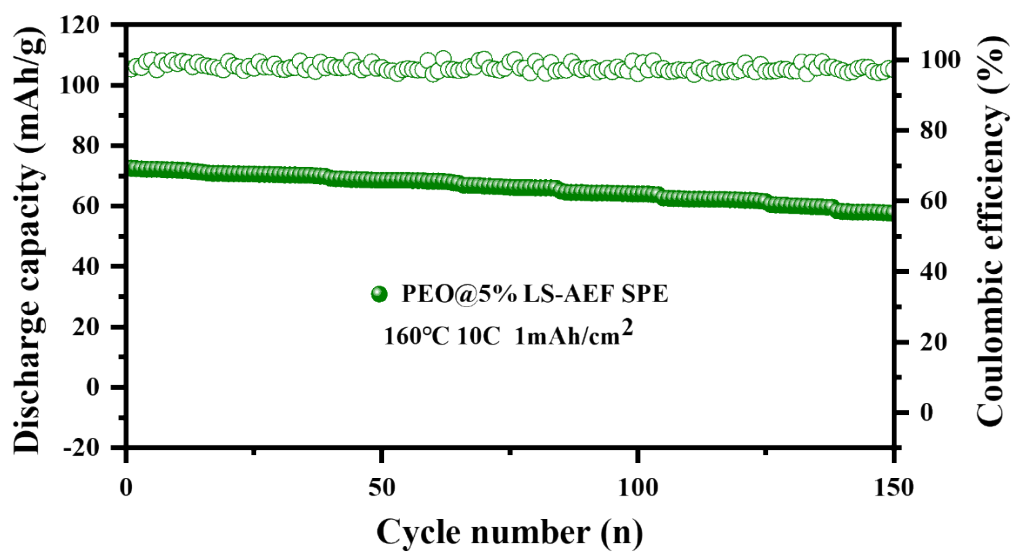
**Figure S15.** Cycle performance of LFP/SPEs/Li cells using PEO SPEs and PEO@5%LS-AEF SPEs at 0.5 C (60 °C).



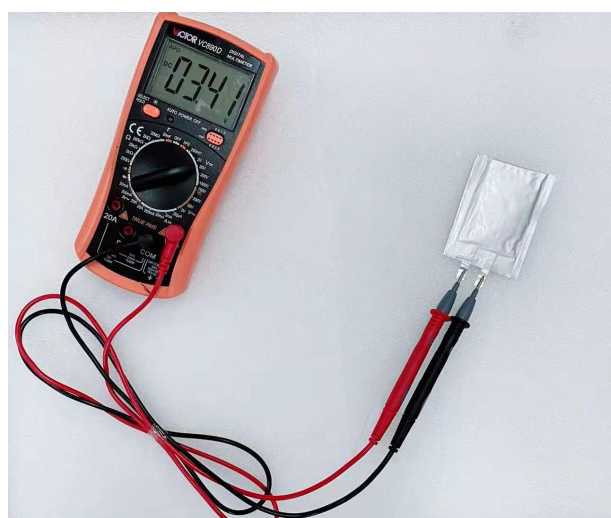
**Figure S16.** Cycle performance of NCM811/SPEs/Li cells using PEO SPEs and PEO@5% LS-AEF SPEs at 1 C (60 °C).



**Figure S17.** Cycle performance of LFP/SPEs/Li cells using PEO SPEs and PEO@5%LS-AEF SPEs at 0.2 C (30 °C).



**Figure S18.** Cycling performance of the LFP/PEO@5%LS-AEF SPE/Li battery at 160 °C and 10 C (cathode loading: 1.0 mAh cm<sup>-2</sup>).



**Figure S19.** Optical photo of soft pack battery voltage.

**Table S20.** The electrochemical performance of Soft pack batteries using different solid electrolytes.

Solid electrolytes	Working temperature	Discharge capacities	Number of cycles	Ref.
PEO-LGPS-LiTFSI	60 °C	/	/	17
PEO-LAGP-LiClO <sub>4</sub>	55 °C	/	/	25
PEO-MnO <sub>2</sub> -LiTFSI	60 °C	/	/	26
PTFE-LLZTO-SN	60 °C	/	/	31
PEO-Mg <sub>2</sub> B <sub>2</sub> O <sub>5</sub> nanowire-LiTFSI	50 °C	100 mAh.g <sup>-1</sup> (1 C)	40	36
BC-GPES	25 °C	/	/	52
PEO-LS-AEF -LiTFSI	60 °C	135 mAh.g <sup>-1</sup> (0.2 A/g)	1000	<b>This work</b>
	30°C-150 °C	120 mAh.g <sup>-1</sup> (1 C)	100	