Supporting Information

Precise Regulation of Hydrogen Bond Network for Rapid Ion Transport in PEO-Based Composite Solid Electrolytes

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Experimental Section

Materials

All battery-related materials, including carbon-coated aluminum foil, Super P LI carbon black, CR2025 coin cell cases, $LiFePO_4$ (LFP) cathode material, and lithium disks for coin cells (diameter: 14 mm, thickness: 300 μm), were purchased from Shenzhen Kejingstar (MTI) Technology Co., Ltd. The commercial liquid electrolyte (LE) was 1 mol L^{-1} lithium bistrifluoromethane sulfonamide (LiTFSI) salt in 1,3-dioxolane/1,2-dimethoxyethane (1:1, v/v) with 2 wt% $LiNO_3$, which was purchased from Duoduo chemical company in Suzhou. All other reagents used in this work were purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China) and employed as received, without any additional purification.

Preparation of LLZO nanofibers

A trace amount of aluminum-doped $Li_{6.4}La_3Zr_2Al_{0.2}O_{12}$ (LLZO) inorganic ceramic nanofibers were fabricated using electrospinning and solid-state sintering methods. First, polyvinylpyrrolidone (PVP) was dissolved in *N,N*-dimethylformamide (DMF) to prepare a 10 wt% solution, which was stirred for 1 h. Subsequently, lithium nitrate ($LiNO_3$), lanthanum nitrate hexahydrate ($La(NO_3)_3 \cdot 6H_2O$), zirconium n-propoxide ($C_{12}H_{28}O_4Zr$), aluminum nitrate nonahydrate $Al(NO_3)_3 \cdot 9(H_2O)$, and acetic acid were added to the PVP solution in a stoichiometric ratio, followed by continuous stirring for 12 h until a homogeneous, light-yellow transparent spinning solution was obtained.

To ensure a stable electrospinning process, the temperature was maintained at 25-28 °C, and the humidity was controlled within 40-45%. The prepared solution was then loaded into a 10 mL syringe, with a needle-to-collector distance of approximately 15 cm, an injection rate of 0.08 mm min^{-1}, and an applied voltage of 14 kV. A white, flexible nanofiber membrane was successfully obtained. The membrane was subsequently sintered in a tube furnace under an air atmosphere at 750 °C for 2.5 h, yielding the final LLZO ceramic nanofibers.

Since LLZO fibers do not form a self-supporting membrane after sintering, the obtained fibers were ground in an agate mortar for 0.5 h to obtain a fine powder, which was then stored in a desiccator for further use.

Preparation of AEAPTMS surface-modified LLZO nanofibers

AEAPTMS (1 mL), acetic acid (1 mL), deionized water (2 mL), and ethanol (36 mL) were added to a beaker and left undisturbed for 1 h to obtain a silane precursor solution. Subsequently, LLZO powder (1.4 g) was introduced into the precursor solution, maintaining an AEAPTMS-to-LLZO mass ratio of approximately 5:7. The mixture was stirred at 70 °C in an oil bath for 4 h to facilitate the silanization reaction. After the modification process, the obtained A@LLZO (5:7) powder was washed three times with ethanol via centrifugation to remove the residual reactants. Finally, the purified powder was dried in a vacuum oven at 60 °C for 12 h. Using the same procedure, A@LLZO (5:9), A@LLZO (5:5), and P@LLZO (5:7) were prepared.

Preparation of CSEs

To fabricate the A@LLZO (5:7)-PEO composite electrolyte, poly(ethylene oxide) (PEO) and LiTFSI were dissolved in acetonitrile at a mass ratio of 5:1 and stirred at 50 °C for 12 h, resulting in a polymer concentration of 5 wt%. Subsequently, A@LLZO (5:7) (10 wt% relative to the total mass of PEO and A@LLZO (5:7)) was added to the solution and thoroughly mixed to form a uniform slurry. The slurry was then cast onto a polytetrafluoroethylene plate and dried under vacuum at 40 °C for 24 h, yielding the final A@LLZO (5:7)-PEO electrolyte membrane.

Following the same methodology, PEO, LLZO-PEO, A@LLZO (5:9)-PEO, A@LLZO (5:5)-PEO, and T@LLZO (5:7)-PEO electrolytes were also prepared for comparative analysis.

Materials Characterization

The morphology and lattice structure of LLZO nanofibers were characterized using transmission electron microscopy (TEM, JEM-2100). SEM images of all samples were captured by JEOL JSM 7500F. The XRD patterns were characterized by Bruke D8 Advance using a Cu-K_α source ($\lambda = 1.54$ Å). FTIR spectra were characterized through Perkin Elmer Spectrum BX II (equipped with ATR accessory). XPS spectra were obtained with an Escalab 250Xi system. DSC curves were investigated via PerkinElmer DSC 4000 at a fixed heating or cooling rate of 2 °C min^{-1}. The stress-strain tests were conducted on an electromechanical test system (SANS UTM2102) at a stretching speed of 5 mm min^{-1}.

Electrochemical Measurements

All the cells were assembled in a glovebox filled with Ar ($H_2O < 0.1$ ppm, $O_2 < 0.1$ ppm) and sealed in CR2025 coin cell cases or aluminum-plastic films. Electrochemical impedance spectroscopy (EIS), chronoamperometry (CA) and linear sweep voltammetry (LSV) tests were carried out using a DH7000 electrochemical workstation (Jiangsu Donghua Analytical Instrument Co., Ltd.). For all EIS measurements, the frequency range was set from 1 Hz to 1 MHz, with an applied amplitude of 10 mV. The ionic conductivities (σ) of different electrolytes were characterized through EIS measurements on a cell configuration of stainless steel (SS) || electrolyte || SS and calculated by the following equation:[1]

$$\sigma = \frac{L}{R \times S}\#(1)$$

where L (cm) represents the thickness of the electrolyte (~100 μm), R (Ω) is the bulk resistance, and S (cm^2) denotes the contact area between the SS and the electrolyte. The temperature-dependent ionic conductivity was fitted with the Arrhenius equation to calculate the activation energy (E_a) of the electrolyte:[2]

$$\sigma = A \times exp(\frac{E_a}{k_b \times T})\#(2)$$

where A stands for the pre-exponential factor, k_b stands for the Boltzmann constant, and T stands for the absolute temperature. CA tests were conducted by applying a constant voltage of 10 mV to the cell and recording the corresponding current as it gradually stabilized. The t_{Li+} was calculated using the following equation:

$$t_{Li^+} = \frac{I_{ss}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{ss} R_{ss})} \#(3)$$

where I_0 and I_{ss} represent the initial current and steady-state current, respectively. R_0 and R_{ss} correspond to the initial and steady-state bulk resistances, which were extracted from EIS fitting. By integrating the impedance variations and current relaxation behavior, an accurate transference number was obtained. LSV curves of different electrolytes were recorded using a cell configuration of Li || electrolyte || SS over a voltage range of 2.5 V to 6 V with a scan rate of 0.1 mV s^{-1}. Galvanostatic charge/discharge tests for all Li || electrolyte || Li symmetric cells and Li || electrolyte || LFP full cells were tested at 60 °C based on a NEWARE battery testing system (MIHW-200-160CH-B, Shenzhen Neware Electronics Co., Ltd).

During the assembly of Li || electrolyte || LFP, 5 μL of LE were injected at the interface between the electrolyte and the cathode, respectively, to enhance the electrochemical performance. For the cathode preparation, LFP powder, Super P LI carbon black, and PEO were mixed in a weight ratio of 7:2:1 in1-methyl-2-pyrrolidone. The resulting slurry was coated onto a carbon-coated aluminum foil, followed by drying at 80 °C in a vacuum oven overnight. The coated foil was then punched into 12 mm disks with a mass loading of 1.5-1.8 mg cm^{-2}.

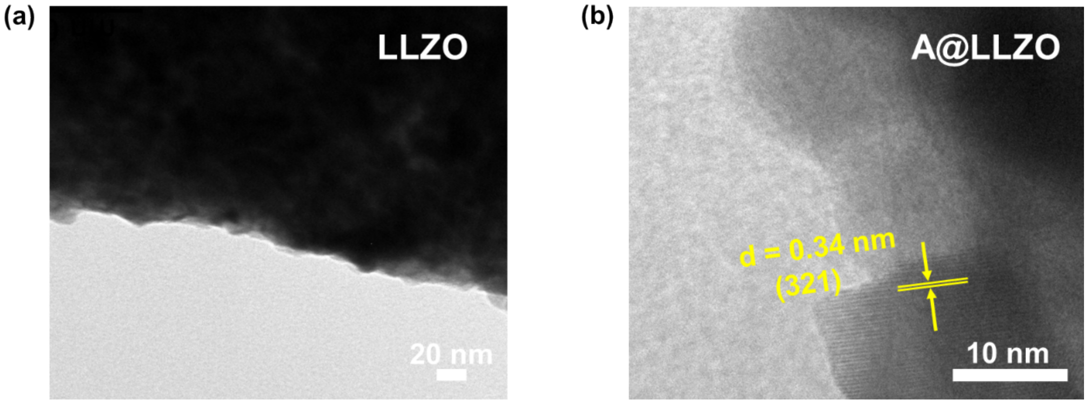

Fig. S1 TEM images of (a) LLZO and (b) A@LLZO.

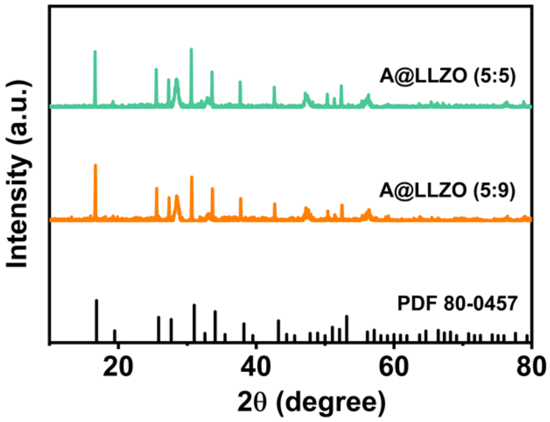

Fig. S2 XRD patterns of A@LLZO (5:5) and A@LLZO (5:9).

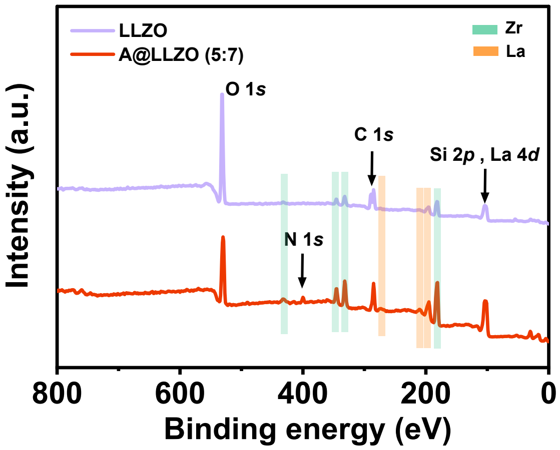

Fig. S3 The Full XPS spectra of LLZO and A@LLZO (5:7).

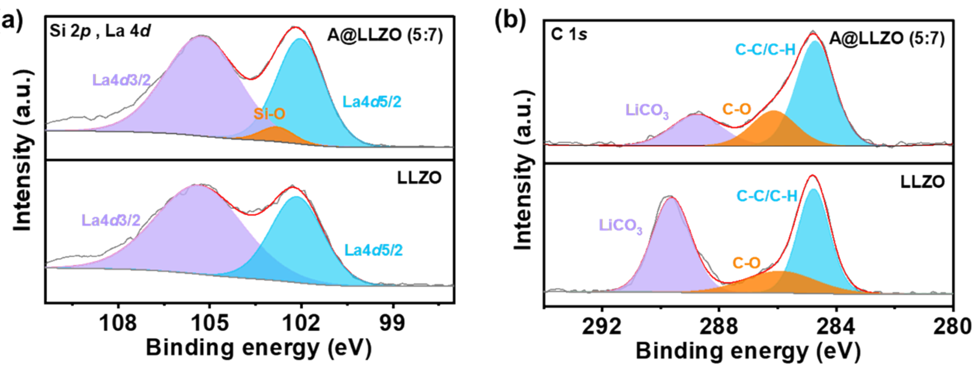

Fig. S4 XPS spectra of (a) Si 2p, La 4d and (b) C 1s for the pristine LLZO and A@LLZO (5:7).

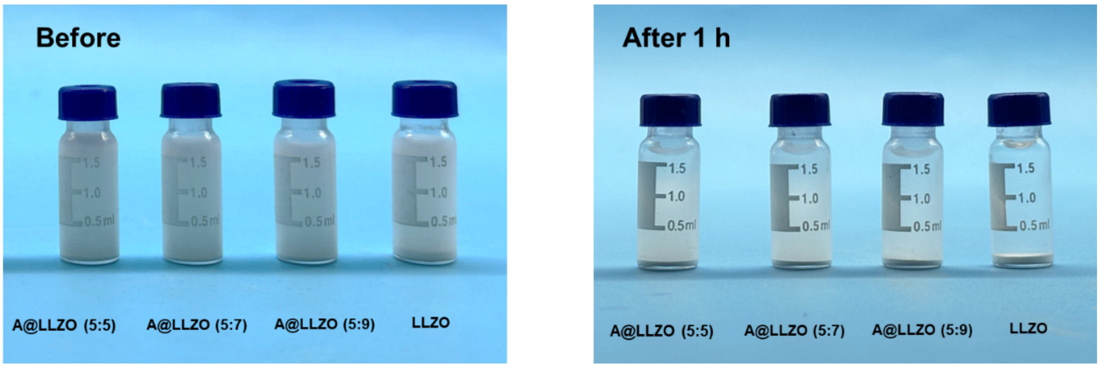

Fig. S5 Clarification experiments of different nanofibers in the acetonitrile solution.

Fig. S6 Variation of the contact angle with time for the pristine LLZO.

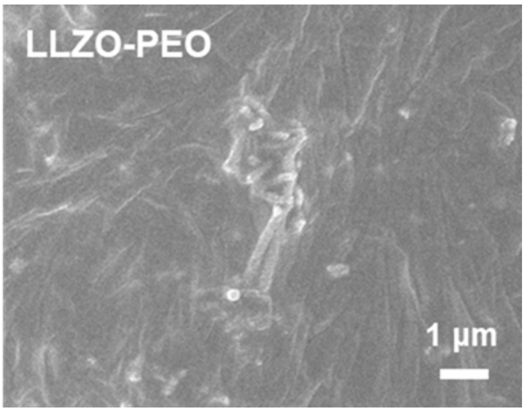

Fig. S7 The SEM image of the LLZO-PEO electrolyte.

Fig. S8 The photograph showing the thickness of A@LLZO (5:7)-PEO measured by the thickness gauge.

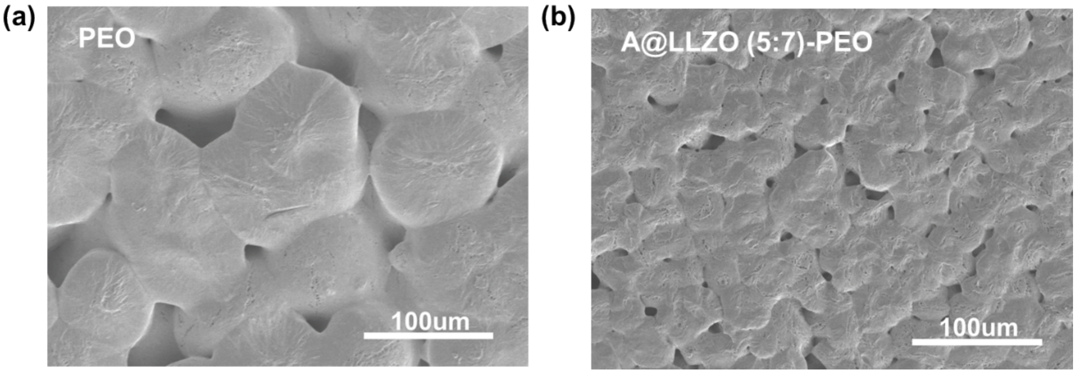

Fig. S9 SEM images of (a) PEO and (b) A@LLZO (5:7)-PEO electrolytes.

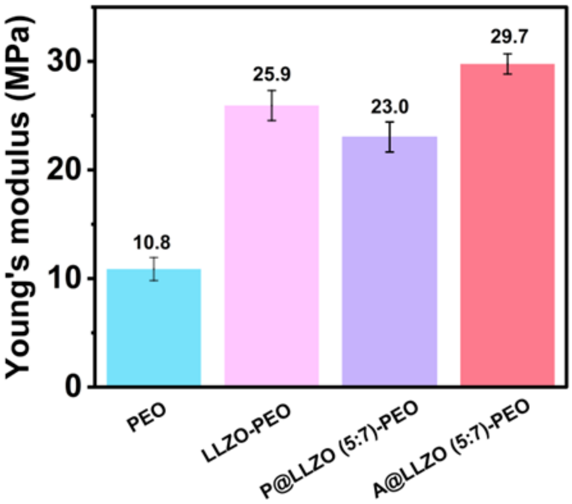

Fig. S10 Young's modulus histograms of different CSEs.

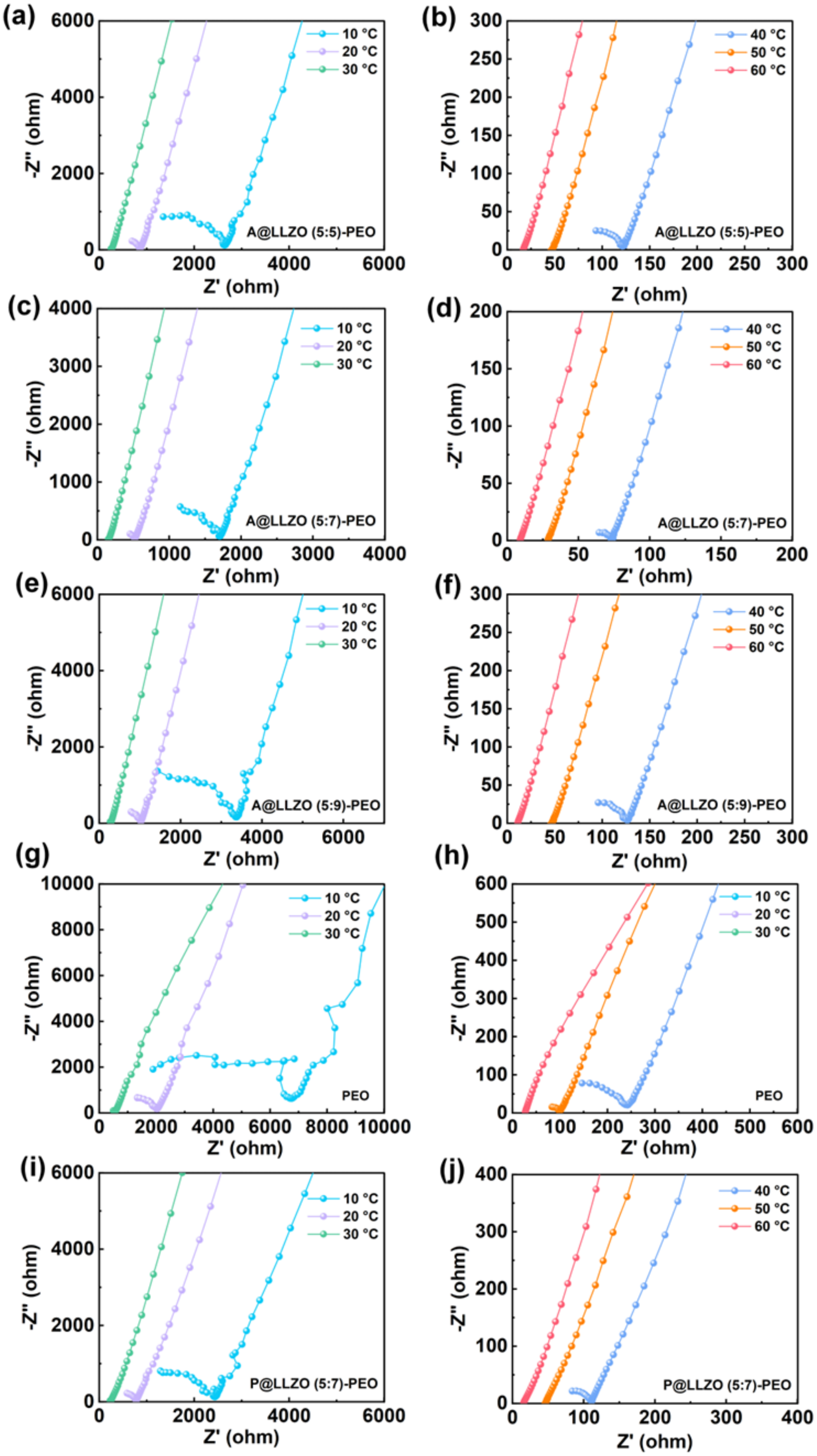

Fig. S11 EIS spectra of different CSEs at 10 ℃ ~ 60 ℃.

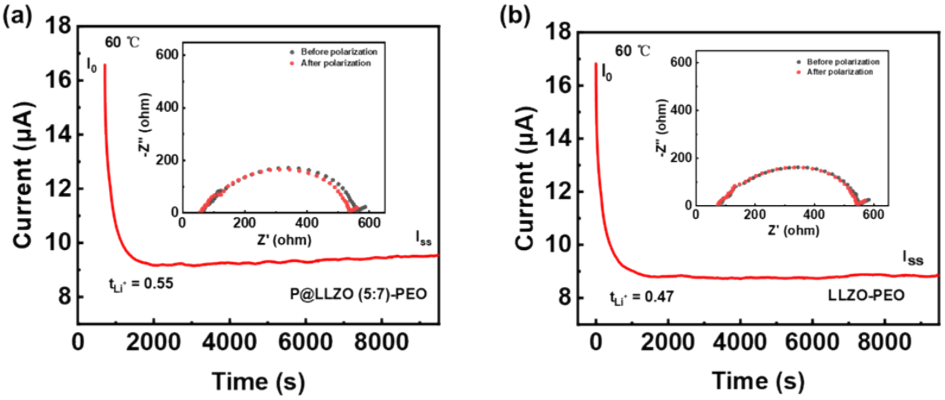

Fig. S12 Lithium-ion transference numbers of (a) P@LLZO (5:7)-PEO and (b)LLZO-PEO electrolytes.

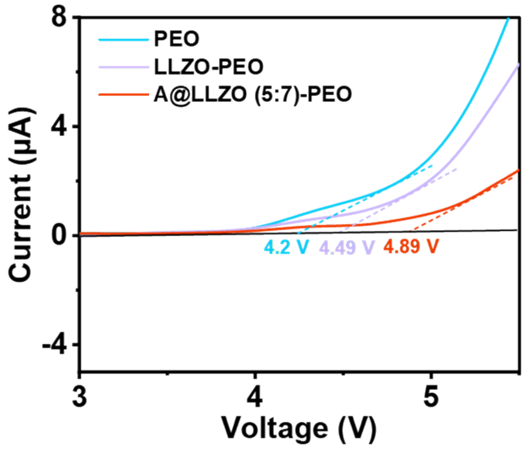

Fig. S13 LSV curves of different CSEs in the voltage range of 3~5.5 V.

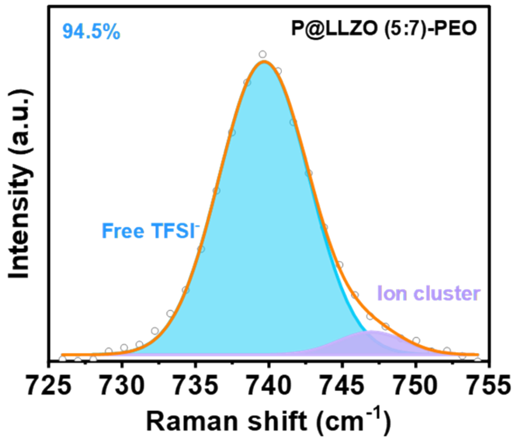

Fig. S14 Raman spectra and corresponding Gaussian-Lorentzian fitting curves of P@LLZO (5:7)-PEO.

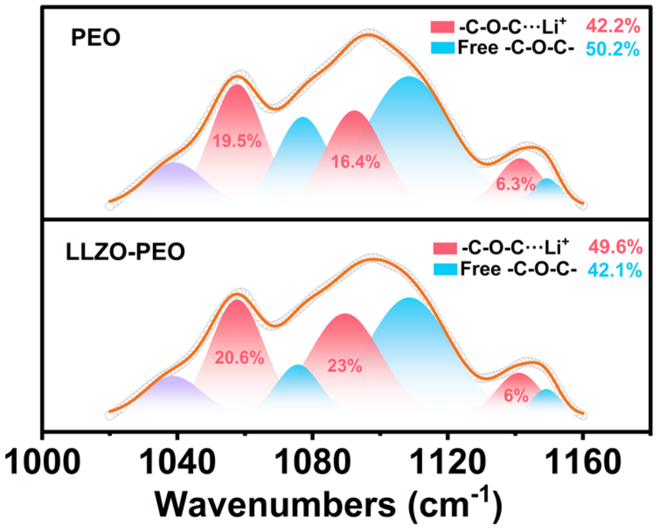

Fig. S15 FTIR spectra of different CSEs in the range of 1020-1160 cm^{-1}.

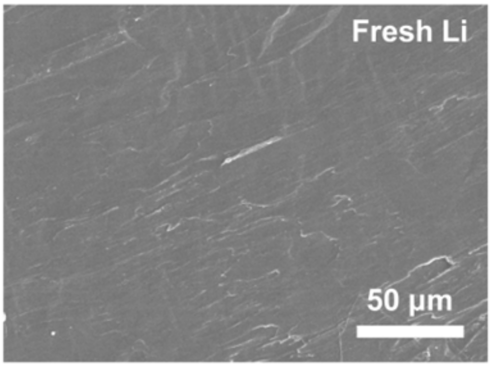

Fig. S16 The SEM image of fresh Li.

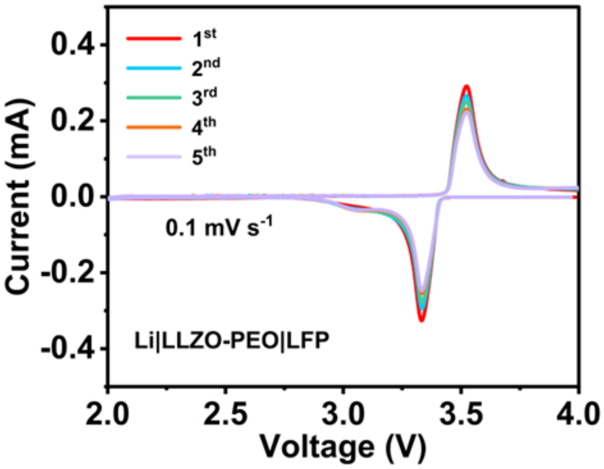

Fig. S17 CV curves of the Li || LLZO-PEO || LFP full cell.

References

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