# Constructing highly efficient "solid-polymer-solid" elastic ion transport network in cathode activates room temperature performance of all-solidstate lithium batteries

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## **Experimental Section**

**Preparation of LZONs.** Zirconium oxynitrate hydrate (99.99% metals basis,  $ZrO(NO_3)_2 \cdot xH_2O$ , Macklin), Lanthanum nitrate (99.99% metals basis,  $La(NO_3)_3 \cdot 6H_2O$ , Macklin), Acetate (AR,99.5%,  $C_2H_4O_2$ , Macklin), N,N-Dimethylformamide (DMF, Gc>99.99%  $C_3H_7NO$ , Macklin), Polyvinylpyrrolidone (PVP, Mw~1300000, Sigma-Aldrich) were applied as raw materials to prepare the LZONs. In a typical experiment, 0.866 g La(NO\_3)\_3 \cdot 6H\_2O, 0.462 g ZrO(NO\_3)\_2  $\cdot xH_2O$ , and 1.88 g PVP were dissolved in a mixed solution of 15 mL Dimethylformamide (DMF) and 3 mL acetate, and then stirred for 24 h. The obtained viscolloid was electrospun into LZO fiber precursors at a high voltage (-1/20 kV), which was calcined at 800 °C, 1000 °C, and 1200 °C for 6 h in air to obtain LZO nanofibers.

**Preparation of PEO-based electrolyte**. Poly(ethylene oxide) (PEO, Mw=600,000, Sigma-Aldrich) and Lithium trifluoromethane-sulphonylimide (LiTFSI, Canrd) were used to prepare the PEO-based electrolyte. In a typical experiment, 0.7 g of PEO and 0.2875 g of LiTFSI (O/Li = 16:1) were added to 15 mL acetonitrile solution in a glove box and stirred for 12 h. The slurry was then poured into a Teflon mold. The PEO polymer electrolyte film was obtained after vacuum extraction and drying for 48 h at 60 °C. PEO@LZON electrolyte was prepared in a similar way. In a typical experiment, 0.7 g of PEO and 0.2875 g of LiTFSI were added to 15 mL acetonitrile solution in a glove box specified in a similar way. In a typical experiment, 0.7 g of PEO and 0.2875 g of LiTFSI were added to 15 mL acetonitrile solution in a glove box and stirred for 6 h, then the 15 mg LZONs were added into the solution and stirred for 24h. After that, the homogenized mixture was poured into Teflon mold and dried for 48 h in the air-blower oven. All the electrolytes were stored in glovebox for 24 h before application.

**Preparation of PVDF-based electrolyte**. Poly(vinylidenefluoride) (PVDF, 300000, kynar, 761), Lithium bis(fluorosulfonyl)imide (LiFSI, Tinci Materials Technology Co., Ltd.) and DMF were used to prepare the PVDF-based electrolyte. In a typical experiment, PVDF powders were dried at 80 °C for 24 h before use to remove trapped water. 0.4 g PVDF, 0.267 g LiFSI were dissolved into 15 mL DMF solvent and stirred at 40 °C for 4 h to obtain a homogeneous solution. The solution was then poured into culture dish mold and the PVDF-based electrolytes were obtained by drying for 24 h at 55 °C under air-blower oven.

**Preparation of the PLL composite cathode and full cell.** The PLL-LFP composite cathode was prepared through a traditional slurry mixing process and coated on an aluminum foil. The PLL-LFP cathode slurry was prepared by mixing LFP particles, PEO, LiTFSI and LZONs with the weight radio of the Table S3. LZONs with different weight ratios of 0% (PL-LFP), 1%, 2%, 4%, 6%, 8%, and 10% were added to the composite cathode slurry (PLL-LFP). Accordingly, the super P was

reduced to ensure that the same weight ratios of LFP. Then, the cathode slurry was cast on an Al foil and dried at 60 °C for 12 h. CR2032 coin cells were assembled using Li foil as the anode, PL-LFP or PLL-LFP as the cathode, and PEO as the electrolyte in a glove box. In a typical experiment, both PLL-LFP and PL-LFP cathodes were pressed to half of their initial thickness before battery assembly. The assembled cells were put into the vacuum oven at 60 °C over 24 h to construct better interface of PEO electrolyte with both cathode and Li metal anode inside the cells and activated at 0.05C at RT. At the same time, since the PEO was used as binder in cathode, the PLL-LFP or PL-LFP cathodes and the PEO electrolyte would be fused to form an integrated structure at high temperature.

**Material characterization.** XRD measurements of the samples were performed on a Bruker D8 Advance diffractometer with Cu-K $\alpha$  radiation. Their morphologies and structures were analyzed using a SEM (HITACH S4800) with EDS for elemental analysis and field emission transmission electron microscopy (FE-TEM, FEI Tecnai F30). XPS measurements were performed on a PHI 5000 VersaProbe II instrument, and depth profiling was performed using Ar gas cluster ion beam sputtering at 15 kV and 35 nA over a 2 × 2 mm area. In order to obtain an air-stable powder sample, all the cathode samples used for testing were removed PEO binder and LiTFSI with anhydrous ethanol. Solid-state <sup>7</sup>Li NMR was performed in a 9.4 T magnetic field with a Bruker 400 MHz AVANCE III spectrometer. The specific surface areas were characterized on Micromeritics ASAP 2020 apparatus with the Brunauer–Emmett–Teller (BET) method. Raman spectra were recorded using a LabRAM HR800 spectrometer with 532 incident radiation. DSC measurements were performed on the above thermal analyzer at a rate of 10 °C min<sup>-1</sup> in the 30–300 °C temperature range under a N<sub>2</sub> atmosphere.

**Electrochemical measurements.** The ionic conductivities of PEO, PEO@LZONs, and PVDF SSE were calculated using Electrochemical impedance spectroscopy (EIS) obtained from  $10^{-2}$  to  $7 \times 10^{6}$  Hz with a 5 mV AC oscillation on a VMP3 multichannel electrochemical station (Bio Logic Science Instruments, France). The test cells were assembled by sandwiching a small piece of PEO, PEO@LZONs, or PVDF slices between two stainless-steel blocking electrodes. The Linear sweep voltammetry (LSV) curves were examined from the open-circuit voltage to 6 V versus Li/Li<sup>+</sup> at a scanning rate of 1 mV s<sup>-1</sup> using a VMP3 multichannel electrochemical station.

Galvanostatic charge/discharge tests of the cells were performed on a battery test system (LAND CT2001A) with a voltage range from 2.4 to 4.2 V for LFP cells and 2.8 to 4.3 V for NCM811 cells at RT, 45 °C and 60 °C. The EIS of the cells cycled for different times was examined

using the VMP3 multichannel electrochemical station in the frequency range of  $10^{-2}$  to  $7 \times 10^{6}$  Hz by applying a 5 mV AC oscillation. The cells were transferred into a glovebox and disassembled for further examination.

**Ionic conductivities.** The film thickness of the solid-state electrolyte (SSE) is around 110  $\mu$ m. The Li ion conductivity ( $\sigma$ ) of SSE can be calculated by measuring the electrochemical impedance spectra (EIS) in the temperature range from 25 °C to 80 °C via the following equation:

$$\sigma = L / RS \tag{1}$$

where S is the area of the stainless steel, L is the thickness of the electrolyte, and R is the resistance which is obtained by EIS measurement of the electrolyte sandwiched between two stainless steels.

Li ion diffusion coefficient. The Li ion diffusion coefficient can be calculated as the following equation by EIS method:

$$Z' = R_{ct} + R_s + \sigma \omega^{-1/2} \tag{2}$$

$$D_{Li} = \frac{\left(RT\right)^2}{2\left(An^2F^2C\sigma\right)^2}$$
(3)

where F is the Faraday constant (96486 C mol<sup>-1</sup>),  $\sigma$  is the Warburg coefficient. A is the surface area of the electrode (cm<sup>2</sup>), R is the gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>), T is the absolute temperature (298 K) and *C* is the shuttle concentration (mol cm<sup>-3</sup>). The  $\sigma$  is obtained from the slope of Z' vs.  $\omega^{-1/2}$  ( $\omega$  is the angular frequency) in the Warburg region.

Li ion transference number. The Li ion transference number  $\binom{l_{Li}}{Li}$  is evaluated via the following equation:

$$t_{LI^{+}} = \frac{I^{s} R_{b}^{s} \left(\Delta V - I^{0} R_{i}^{0}\right)}{I^{0} R_{b}^{0} \left(\Delta V - I^{s} R_{i}^{s}\right)}$$
(4)

The initial and the steady-state values of current ( $I^o$  and  $I^s$ ) for the cells were recorded. At the same time, the initial and steady-state values of the bulk resistances ( $R_b^o$  and  $R_b^s$ ) and interfacial resistances ( $R_i^o$  and  $R_i^s$ ) were examined by impedance measurements before and after the polarization.

**Computational details.** Finite element method (FEM) was used to investigate the Li ion distribution and electrolyte potential within two PL-LFP and PLL-LFP cathodes across the interface based on different Li ion diffusion coefficients. The final concentration field at the discharge state was

coupled by a thin substance transfer interface and electrostatic field interface, which reveals the Li ion concentration distribution at this solid-solid interface. Specifically, the thin substance transfer interface and electrostatic field interface were operated based on the following Nernst–Planck equation (Eq. 5) and Poisson's equation (Eq. 6), respectively.

$$\mathbf{J} = -D\nabla c - \mu z \mathbf{F} c \nabla \varphi \tag{5}$$

$$\nabla \cdot (-\varepsilon \nabla \varphi) = \rho \tag{6}$$

where J is the ion flux vector, D is the ion diffusion coefficient, c is the ion concentration,  $\mu$  is the ion mobility, z is the charge number, F is Faraday's constant (96485 C mol<sup>-1</sup>),  $\varphi$  is the electric potential,  $\varepsilon$  is the dielectric constant, and  $\rho$  is the charge density. Ion mobility is the result of the diffusion coefficient divided by the potential. The initial Li ion concentration was 1000 mol m<sup>-3</sup>. A partial unit composed of electrodes was represented by ellipse particles, and a heterogeneous model was constructed including the porous structure in the model geometry. During discharge, Li ions migrate from the solid polymer (PEO binder) to the LFP cathode, which is driven by the enormous discrepancy in the chemical potential.

First principles density-functional theory (DFT) calculations for adsorption energy. The Cambridge Serial Total Energy Package was used to conduct the DFT calculations for the adsorption energy of TFSI- on PEO, LZO and La<sub>2</sub>Zr<sub>2</sub>O<sub>8</sub>. The exchange-correlation energy was described using the revised Perdew-Burke-Ernzerhof exchange-correlation density functional (PBESOL) within the generalized-gradient approximation (GGA). A 400 eV plane-wave kinetic energy cutoff was chosen. The Brillouin zone was sampled with  $3 \times 3 \times 3$  and  $2 \times 2 \times 1$  by Monkhorst–Pack grids, respectively, for PEO, LZO and La<sub>2</sub>Zr<sub>2</sub>O<sub>8</sub> and primitive cell and surface calculations. The atomic positions were fully relaxed until a maximum energy difference and residual force on atoms, respectively, converged to  $10^{-5}$  eV and 0.03 eV Å<sup>-1</sup>. A 15 Å thick vacuum layer was used to avoid the interaction between top and bottom surfaces.

The Vienna ab initio Simulation Package was used to conduct the DFT calculations for the adsorption energy of adsorption energy of PEO with LZO and LFP. The Generalized Gradient Approximation of Perdew-Burke-Ernzerh (GGA-PBE) function was used to describe the exchange and correlation effects. The kinetic energy cutoff is set at 520 eV for the plane-wave expansion. A k-points were sampled with  $3 \times 3 \times 3$  and  $2 \times 2 \times 1$  by Monkhorst–Pack grids, respectively, for LZO and LFP and primitive cell and surface calculations. The convergence criterions were  $10^{-4}$  eV for the total energy and  $10^{-2}$  eV/Å for the force and a 20 Å thick vacuum layer was used to avoid the

interaction between top and bottom surfaces. The atoms of matrix slab are fixed for reducing calculation only when evaluated adsorption energy. The similar treatment method is also used in other researches.

## **Figures and Tables**



Fig. S1 (a) Schematic of electrostatic spinning. (b) SEM images of LZONs under the annealing temperature at 800 °C and (c) 1000 °C.



Fig. S2 Optical image of LZONs annealed at 1200 °C.



Fig. S3 (a) Nitrogen isothermal adsorption desorption curve of LZONs. (b) BET-plot of LZONs. (c) Pore distribution of LZONs.

Physical quantities	Numerical	Unit
V <sub>m</sub>	1.0581	$[cm^3(STP) g^{-1}]$
a <sub>s,BET</sub>	4.6054	$[m^2 g^{-1}]$
С	880.86	
Total pore volume (p/p <sub>0</sub> =0.990)	0.030908	$[cm^3 g^{-1}]$
Mean pore diameter	26.846	[nm]



Fig. S4 (a) SEM images of PLL-LFP cathode with 2 wt.% LZONs at different magnification. (b) EDS mapping of the PLL-LFP cathode of Fe, La and O elements.



Fig. S5 (a) SEM images of PLL-LFP with 2 wt.% LZONs at different magnification. (b) EDS mapping of the PLL-LFP cathode.



Fig. S6 (a) Cross section SEM image of the PLL-LFP with 2 wt.% LZONs and (b) its EDS mapping of the Al and (c) Zr elements. (d-e) SEM images of the PLL-LFP and (f) EDS mapping of the La element that shows uniform distribution of LZONs in the PLL-LFP cathode.



Fig. S7 (a, b) SEM images of the PL-LFP cathode and (c) its EDS mapping of La element.



Fig. S8 SEM image of the rolled PLL-LFP cathode.



Fig. S9 (a) Cross section SEM image of the rolled PLL-NCM811 with 2 wt.% LZONs and (b) EDS mapping of the Ni and (c) La elements. (d) Surface SEM image of the rolled PLL-NCM811 cathode and (e) EDS mapping of the Ni and (f) La showing the uniform distribution of LZONs in PLL-NCM811.



Fig. S10 (a) SEM image of the PL-NCM811 and EDS mapping of (b) Ni and (c) La elements.



Fig. S11 (a) Teflon mold used to prepare PEO solid electrolyte. (b) Optical image of PEO SE. (c) The thickness of PEO-based electrolyte.

Temperature/°C	Charge transfer resistance/ $\Omega$	Ionic conductivity/S cm <sup>-1</sup>
25	1200	4.56×10 <sup>-6</sup>
45	26	2.11×10-4
60	13	4.21×10 <sup>-4</sup>
80	4.4	1.24×10 <sup>-3</sup>

Table S2 Ionic conductivity of PEO-based electrolyte at different temperatures



Fig. S12 (a) EIS plots of PLL-LFP/PEO/Li fresh cell with different weight ratios of LZONs and Super P. (b) EI EIS plots of PLL-LFP/PEO/Li cell and with different weight ratios of LZONs and Super P after activation. (c) Discharge capacity and coulombic efficiency of PLL-LFP/PEO/Li full cell with different weight ratios of LZONs annealed at 1200 °C under RT. (d) Discharge capacity and coulombic efficiency of PLL-LFP/PEO/Li full cell with 2 wt.% LZONs annealed at 1200 °C and 1000 °C under RT.

LZO	LFP	<b>PEO/LiTFSI</b>	Super P
1 wt.%	80 wt.%	10 wt.%	9 wt.%
2 wt.%	80 wt.%	10 wt.%	8 wt.%
10 wt.%	72 wt.%	10 wt.%	8 wt.%
4 wt.%	80 wt.%	10 wt.%	6 wt.%
6 wt.%	80 wt.%	9 wt.%	5 wt.%
8 wt.%	80 wt.%	8 wt.%	4 wt.%
10 wt.%	80 wt.%	7 wt.%	3 wt.%
2 wt.%	85 wt.%	10 wt.%	3 wt.%

Table S3 Content of each component in the PLL-LFP cathode

#### The optimum weight ratio of LZONs in PLL

Table S3 presents the content of each component in the PLL-LFP cathode. Fig. S12a shows the EIS of fresh batteries, which exhibits a large interfacial resistance. All the fresh batteries were

subjected to high temperature fusion at 60 °C for 24 hours before activation. Fig. S12b shows the EIS of the activated PLL-LFP/PEO/Li cells using PLL-LFP cathode with same amount of super P (3 wt.% Super P or 8 wt.% Super P) and different amounts of LZONs (2 wt.% LZONs and 10 wt.% LZONs). It is seen that the resistance of all PLL-LFP/PEO/Li batteries decreases greatly compared to those before activation. In addition, the PLL-LFP/PEO/Li cell with 2 wt.% LZONs and 3 wt.% Super P or 10 wt.% LZONs and 3 wt.% Super P presents an obviously lower total resistance (1032  $\Omega$  or 1094 Ω) than PLL-LFP/PEO/Li cell with 2 wt.% LZONs and 8 wt.% Super P or 10 wt.% LZONs and 8 wt.% Super P (1526  $\Omega$  or 1615  $\Omega$ ). Furthermore, it is seen that the PLL-LFP cathode with the same amount of super P (3 wt.% Super P or 8 wt. % Super P) presents a minor increase of total resistance with increase of the content of LZONs from 2 wt.% LZONs to 10 wt.% LZONs, which may account for a minor smaller discharge capacity of the PLL-LFP/PEO/Li cell with the higher amount of LZONs than that with 2 wt. % LZONs (Fig. S12c). The higher amount of LZONs may prolong the Li ion transport path among LFP active materials in PLL-LFP/PEO/Li cell to increase the resistance. These results suggest that 2% LZON is an optimized cathode component formulation. Whereas, large amount of Super P may also prolong the Li ion transport pathway and decreases the Li ion transfer efficiency. This work inspires us to further construct both highly efficient ion and electron conductive networks in PLL-LFP cathode by optimizing the content of Super P in the future work. Fig. S12d indicates that the LZONs annealed at 1200 °C demonstrates superior cycle performance compared to the LZONs annealed at 1000 °C with the same weight ratio in the cathode. This is because the LZONs annealed at 1200 °C have a higher crystallinity and pyrochlore structure.



Fig. S13 Cycling performance of all-solid-state LFP/Li cells based on different kinds of PEO-based solid electrolytes and binder at RT and 0.1 C.

#### Performance of all-solid-state cathodes at RT

To prove that the cathode restricts ASSLB performance at RT, we first examined the RT performance of the all-solid-state cathodes using PEO and PVDF as binders, matched with different SSEs (Fig. S13). It can be observed that regardless of the binder or SSEs used, including the PEO@LLZO-based electrolyte, which was reported to have a high ionic conductance, the all-solid-state cathodes exhibited extremely low capacity at RT, i.e., < 50 mAh g<sup>-1</sup>. This suggests that improving the ionic conductivity of the SSEs alone is not sufficient to support high ASSLB performance at RT. Thus, facilitating ion transport inside the all-solid-state cathode is critical to developing high performance.



Fig. S14 (a) Cycling performance of LFP cathode (PEO binder and 2 wt.% Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> nanofibers)/PEO/Li cell. (b) EIS plots of LFP cathode (PEO binder and 2 wt.% LLZO nanofibers)/PEO/Li cell and the equivalent circuit used for fitting the impedance spectra at 1<sup>st</sup> and 500<sup>th</sup> cycle. (c) Cycling performance of LFP (PEO binder and 2 wt.% Al<sub>2</sub>O<sub>3</sub> nanofibers)/PEO/Li cell and (d) LFP (20wt.% PEO binder)/PEO/Li cell at RT and 0.1 C.

#### Other strategies to improve efficiency of ion transport in cathode

Apart from the LZONs discussed in this work, other materials to improve ion transport have also been used in ASSLBs. First, a fast-ion conductor such as  $Li_7La_3Zr_2O_{12}$  (LLZO) was also applied to improve the Li ion transport efficiency. A composite LFP cathode consisting of a PEO binder and 2 wt.% LLZO nanofibers was prepared. Fig. S14a displays the cycle performance of the LFP/PEO/Li cell with 2 wt.% LLZO nanofibers. The cell presented an initial capacity of more than 150 mAh g<sup>-1</sup> owning to the increased ion transport paths inside the cathode. However, its discharge capacity was only 75 mAh g<sup>-1</sup> after 500 cycles. This is mainly because the formation of a Li<sub>2</sub>CO<sub>3</sub> layer on the surface of the LLZO. As reported, the Li<sub>2</sub>CO<sub>3</sub> on garnet particles effectively affect the electrochemical properties of the LLZO and its cells. [*ACS Energy Lett.*, **2020**, 5, 252–262, *Nano* 

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*Energy*, **2020**, 73, 104836.] The Li<sub>2</sub>CO<sub>3</sub> was decomposed at high charging potentials to form CO<sub>2</sub>, which degraded the LLZO/PEO/LFP particle interface to cause their bad contact in LFP cathode (PEO binder and 2 wt.% LLZO nanofibers)/PEO/Li cell [*Adv. Funct. Mater.* **2021**, 31, 2103716.]. Fig. S14b show the EIS of LFP cathode (PEO binder and 2 wt.% LLZO nanofibers)/PEO/Li cell before and after 500 cycles. It is seen that the charge transfer resistance of batteries after 500 cycles increases greatly due to the reduced Li ion transport ability derived by the poor LLZO/PEO/LFP particle interface, which is responsible for the capacity fade of full battery.

Secondly, ceramics such as  $Al_2O_3$  (ALO) can reduce the crystallinity of the polymer and promote the dissociation of lithium salts, which were also added to the LFP cathode. The addition of ALO can increase the Li transport speed inside the cathode by reducing the crystallinity of the PEO binder. A composite LFP cathode with 2 wt.%  $Al_2O_3$  nanofibers could deliver a discharge capacity of 130.2 mAh g<sup>-1</sup>, while which presents an extremely short cycle life (Fig. S14b). Although the ion transport speed was improved, the number and type of transport paths were limited, which could not support the long cycle.

The third approach is increasing the content of the binder and immersing the active substance in an "ocean" of binder. Unfortunately, this method reduces the content of the active substance and energy density of the cathode, and is not suitable for industrial applications. Fig. S14c displays the cycle performance of a cell with an LFP cathode (20 wt.% PEO binder). The LFP (20 wt.% PEO binder)/PEO/Li full cell had an initial capacity of 136.4 mAh g<sup>-1</sup> and failed after 30 cycles.

In summary, the strategies to promote the ion transport behavior of the cathode can improve ASSLB RT performance more effectively compared to the enhancement of the ionic conductivity of the SSE. LZONs can combine the above advantages, and are an ideal material for regulating the ion transport efficiency in the cathode.



Fig. S15 Cycling performance of PLL-LFP/PEO@LZONS/Li full cell at RT and 0.1 C.

The improvement of SE can further improve the RT performance of ASSLBs. Fig. S14 shows the cycle performance of the PLL-LFP/PEO@LZONs/Li full cell, which can deliver the initial capacity of 145.5 mA  $h^{-1}$  and 125.2 mA  $h^{-1}$  after 250 cycles at the rate of 0.1 C.



Fig. S16 Charge and discharge profiles for PLL-LFP/PEO/Li (a) and PL-LFP/PEO/Li (b) full cell during cycling at RT and 0.1 C.

The Fig. S16 shows that the 1<sup>st</sup> cycle overpotential of PLL-LFP/PEO/Li cell at 0.1C (the current density is 0.02 mA cm<sup>-2</sup>) under RT is around 0.1 V. The smaller overpotential of PLL-LFP/PEO/Li full cell in Fig. S16 is ascribed to the much lower cycling current density of 0.02 mA cm<sup>-2</sup> than that applied in Li symmetric cell with PEO electrolyte during cycling (0.1 mA cm<sup>-2</sup>).



Fig. S17 EIS of PL-LFP/PEO/Li and PLL-LFP/PEO/Li full cells at RT after 2 cycle at 0.05C and the equivalent circuit used for fitting the EIS.



Fig. S18 DFT calculation results of adsorption configuration of LZO (a, b) and LFP (c, d) with PEO. (a, c) Top view of the adsorption configuration. (b, d) Side view of the adsorption configuration



Fig. S19 Stress-strain curve of PEO@LZONs and PEO at RT.

Table S4 Breaking	elongation	and tensile strength of PEO	and PEO@LZONs
U	0	$\mathcal{O}$	$\bigcirc$

Sample	Breaking elongation $\epsilon_{\rm B}$ (%)	Tensile strength $\sigma_M$ (MPa)
PEO	622.86	9.11
PEO@LZONs	877.91	10.08



Fig. S20 SEM image of initial (a, b) PL-LFP and (c, d) PLL-LFP cathode after rolling. SEM image of (e, f) PL-LFP and (g, h) PLL-LFP after four folds.



Fig. S21 EIS of PL-LFP/PEO/Li and PLL-LFP/PEO/Li full cells before and after cycle at RT.



Fig. S22 Voltage–time curves of the Li/PEO@LZONs/Li and Li/PEO/Li symmetric cells (a) at current density of 0.05 mA cm<sup>-2</sup> and Li plating/stripping of 0.05 mAh cm<sup>-2</sup>, and (b) at current density of 0.1 mA cm<sup>-2</sup> and Li plating/stripping of 0.05 mAh cm<sup>-2</sup> under RT.



Fig. S23 Voltage profiles of Li plating/stripping of Li/PEO/Li symmetric cell at current density of 0.1 mA cm<sup>-2</sup> and Li plating/stripping of 0.1 mAh cm<sup>-2</sup> under RT.



Fig. S24 Initial state of the full cell. a, Lithium concentration surface and b, electrolyte potential.



Fig. S25 Lithium concentration and potential distribution simulation results of two kinds of all-solidstate cathodes after discharge for 10 s. (a) PLL-LFP composite cathode, (b) PL-LFP cathode.

Models	E-TFSI-	E_PEO/LZO/ Li <sub>2</sub> Zr <sub>2</sub> O <sub>8</sub>	E-slab	Adsorption energy
LZO-TFSI	-6831.455460	-58764.245600	-65600.347200	-4.646140
PEO(C <sub>12</sub> H <sub>28</sub> O <sub>8</sub> )-TFSI	-6831.455460	-5777.613010	-12610.317600	-1.249130
Li <sub>2</sub> Zr <sub>2</sub> O <sub>8</sub> -TSFI	-6831.455460	-62248.569500	-69082.375100	-2.350140

Table S5 Adsor	ption energy	of PEO.	LZO and	La <sub>2</sub> Zr <sub>2</sub> O <sub>8</sub>	for '	TFSI-
		,				



Fig. S26 EISs of Li/Li symmetrical cells using PEO solid electrode (a) and PEO@LZONs composite electrolyte (b) before and after the polarization. The inset figures are the chronoamperometry profiles under a polarization voltage of 10 mV.



Fig. S27 DSC profiles of PEO and PEO@LZONs solid electrolytes.



Fig. S28 EIS of PEO solid electrolyte (blue) and PEO@LZONs solid electrolyte (purple) with ionblocking stainless-steel electrodes. The ionic conductivity of PEO and PEO@LZONs is calculated as  $4.56 \times 10^{-6}$  S cm<sup>-1</sup> and  $2.1 \times 10^{-5}$  S cm<sup>-1</sup>.



Fig. S29 <sup>7</sup>Li NMR spectra and side bands of discharged LFP and PLL-LFP without PEO binder. (a) Full <sup>7</sup>Li NMR spectrum of discharged LFP and PLL-LFP without PEO binder. (b) <sup>7</sup>Li NMR spectral decomposition of discharged PLL-LFP without PEO binder. (c) <sup>7</sup>Li NMR spectral decomposition of initial PLL-LFP (-1.7 ppm is assigned to the Li in the PEO binder), discharged PLL-LFP without PEO binder (-0.7 ppm is assigned to the lithiated LZO compounds.), initial LZO (No <sup>7</sup>Li signal) and LFP.

LFP and Discharged PLL-LFP without PEO binder samples were obtained as follows: the discharged LFP and PLL-LFP cathode were put into the anhydrous ethanol solution and stirred for 24 hours to reduce the PEO binder with LiTFSI. The discharged LFP and PLL-LFP without PEO binder samples were obtained after being put into the vacuum oven at 60 °C over 24 h for NMR spectrum test.

Initial PLL-LFP and initial LZO samples were obtained as follows: the initial PLL-LFP sample was obtained from the initial cathode preparation before cycle. The initial LZO sample was prepared by an electrospinning method followed by an annealing process.

We have tested the NMR spectrum of initial LZO and initial PLL-LFP with PEO binder as shown in **Fig. S29c**. Since the LZO ( $La_2Zr_2O_7$ ) is a kind of lithium-free ceramics, which has not Li signal in <sup>7</sup>Li NMR spectra. The sharp Li peak of initial PLL-LFP with PEO binder at approximately -1.7 ppm is assigned to the lithium ions bound to PEO binder containing LiTFSI [*Energy Stor. Mater.*, **2021**,

11.052]. Therefore, the sharp Li peak of discharge PLL-LFP without PEO binder at -0.7 ppm is assigned to the lithiated LZO compounds.



Fig. S30 (a) EELS spectra and (b) ADF-STEM image of discharged LZO. (c) Corresponding EELS spectrum imaging of Li edge.



Fig. S31 Li ion content of cycled LZONs in both LZONs/PEO/Li full cell and Li/PEO@LZONs/Li symmetric cell examined using ICP.

The LZONs were separated from the LZONs/PEO/Li full cell and Li/PEO@LZONs/Li symmetric cell respectively and dissolved into the solution of 15 mL concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), stirred for 12 hours at 60 °C. After that, the solutions were diluted in 1,500mL deionized water and Li ion content of cycled LZONs in both LZONs/PEO/Li full cell and Li/PEO@LZONs/Li symmetric cell were tested by the inductively coupled plasma (ICP, MDTC-EQ-M29-01).



Fig. S32 XPS spectra of discharged LZONs, discharged LFP and LiTFSI. (a) Li 1s, Fe 3p, (b) O 1s.

The XPS of the discharged LFP cathode with PEO binder but without LZO and LiTFSI after 10th cycles and the LiTFSI powder to eliminate them exclude the possible disturbance (Fig. S28). The Fe 3p XPS spectrum of the discharged LFP presents two peaks corresponding to Fe 3p (Fe<sup>2+</sup>) at 55.81 eV of LiFePO<sub>4</sub> and 3p (Fe<sup>3+</sup>) at 58.34 eV of FePO<sub>4</sub> [*Anal. Methods.* 2014, 6, 5708–5711; *Appl. Catal. A Gen.* 1992, 90, 51–60.]. In addition, the Li 1s XPS spectrum of the discharged LFP presents a peak corresponding to Li 1s (Li<sup>+</sup>) at 54.70 eV of LFP. These typical peaks did not appear in discharged LZO. In addition, the O1s XPS spectrum of the discharged LFP shows two peaks at 531.60 eV and 533.21 eV, which are ascribed to the lattice oxygen of LZO and C-O functional group absorbed on LZO [*Energies,* 2019, 12(24), 4652]. These typical peaks also did not appear in discharged LZO. Above results further confirm that the LFP does not influence of the XPS results of discharged LZO. Furthermore, the Li 1s and O 1s spectrum of LiTFSI presents a peak at 56.17 eV and 533.08 eV, respectively, which is corresponding to Li ions and S=O bond of LiTFSI. All the binding energies of these peaks are higher than that of discharge LZO. Above results indicates that the XPS results of discharged LZO is not influenced by LiTFSI.



Fig. S33 XRD (a) and synchrotron-based XRD (b) patterns of PLL-LFP cathode before (blue) and after (purple) cycle.



Fig. S34 High-resolution Zr  $3d_{3/2}$  XPS spectra of the initial LZO and the discharged LZO.



Fig. S35 Corresponding charge and discharge profiles for PLL-LFP/PEO/Li full cell at RT and different rates (0.2 C/0.3 C/0.4 C/0.5 C).



Fig. S36 Rate performance of PLL-LFP/PEO/Li (purple) and PL-LFP/PEO/Li (blue) full cell at 60 °C.

Battery	Tempera-ture (°C)	Rate performance (rate and capacity/mAh g <sup>-1</sup> )	Cycle rate	Cycle number	1 <sup>st</sup> capa (mAh g	city <sup>(1)</sup> Reference
PLL-LFP/PEO/Li	60	0.1C/165, 0.2C/165, 0.3C165, 0.5C/159, 1C/140, 2C/120, 3C/86	0.5 C	150	154	This work
LFP/PEO-Mg(ClO <sub>4</sub> ) <sub>2</sub> /Li	55	0.05 mA cm <sup>-2</sup> /163, 0.1 mA cm <sup>-2</sup> /157, 0.2 mA cm <sup>-2</sup> /146, 0.4 mA cm <sup>-</sup> <sup>2</sup> /140, 0.6 mA cm <sup>-2</sup> /126	0.2 mA cm <sup>-2</sup>	100	110	J. Am. Chem. Soc. 2021, <b>143</b> , 6542- 6550.
LFP/PEO-10%TiO <sub>2</sub> -1%Li <sub>2</sub> S <sub>6</sub> /Li	50	0.1 mA cm <sup>-2</sup> /140, 0.2 mA cm <sup>-2</sup> /118, 0.3 mA cm <sup>-2</sup> /102	0.1 mA cm <sup>-2</sup>	700	~120	Angew. Chem. Int. Ed. Engl. 2021, <b>60</b> , 19306-19313.
LFP/PEO-LiTFSI-10%Ca- CeO <sub>2</sub> /Li	60	0.1C/164, 0.2C/159, 0.5C/147, 1C/121, 2C/100	1 C	100	121	<i>Adv. Energy Mater.</i> 2010, 202000049 2020.
LFP/LiTFSI-Al2O3-PEO/Li	50	0.05C/169, 0.1C/167, 0.24C/163, 0.5C/137, 1C/36				Energy Environ. Sci. 2019, <b>12</b> , 938-944.
LFP/PEO-LSTZ/Li	45	20μA cm <sup>-2</sup> /154, 100μA cm <sup>-2</sup> /149, 200μA cm <sup>-</sup> <sup>2</sup> /128	150 μA cm <sup>-2</sup>	350	136	Natl. Acad. Sci. U.S.A. 2019, <b>116</b> , 18815-18821.
LFP/Li2SO4-PEO-SiO2/Li	60	/	0.5 C	50	90	Small. 2019, <b>15</b> , e1902729.
LFP/PEO-PPC-LiTFSI/Li	60	0.1C/125, 0.2C/123, 0.5C/117, 1C/101	0.5 C	100	110	Mater Chem 4 2010
LFP/LLZTO-PEO/Li	50	/	0.2 C	50	135	<b>7</b> , 16425-16436.
LFP/LLZTO@PDA-PEO/Li	50	/	0.2 C	50	147	
LFP/PEO-LiTFSI-5%g-C <sub>3</sub> N <sub>4</sub> /Li	60	/	0.2 C	100	161	J. Mater. Chem. A 2019, <b>7</b> , 11069- 11076.
LFP/PI-PEO-LiTFSI/LFP	60	0.1C/176, 0.2C/156, 0.5C/138, 1C/125	0.5 C	300	110	<i>Nat. Nanotechnol.</i> 2018, <b>3</b> , 985-993.
LFP/PEO-LiTFSI- 10%LLZTO/Li	55	/	0.2 C	100	149	Nano Energy 2018, <b>46</b> , 176-184.
LFP/ (LiTFSI-A <sub>2</sub> O:-CPEO)- LLZT/Li	65	/	80 μA cm <sup>-2</sup>	<sup>2</sup> 100	142	Angew. Chem. Int. Ed. Engl. 2017, <b>56</b> , 753-756.
LFP/PEO- Li <sub>2</sub> (OH) <sub>0.9</sub> F <sub>0.1</sub> Cl/Li	65	/	0.2 C	20	125	Angew. Chem. Int. Ed. Engl. 2016, <b>55</b> , 9965-9968.
LFP/PEO-LiTFSI-1%LGPS/Li	60	0.1C/158, 0.2C/148, 0.5C/138, 1C/99	0.5 C	50	148	<i>J. Power Sources.</i> 2016, <b>301</b> , 47-53.
LFP/ P(STFSILi)-b-PEO/Li	85	/	1/15 C		165	<i>Nat. Mater.</i> 2013, <b>12</b> , 452-457.

## Table S6 Electrochemical performance of reported Li metal batteries



Fig. S37 LSV of PEO solid electrolyte (blue) and PEO@LZONs solid electrolyte (purple). The onset is defined as the potential at which 10% of the current value at the peak potential was reached.



Fig. S38 (a) Cycling performance of PLL-NCM811/PEO/Li full cell at RT and 0.05 C and (b) 0.1 C.



Fig. S39 Corresponding charge and discharge profiles for PLL-NCM811/PEO/Li full cell at 45 °C and different rates.



Fig. S40 EIS of PVDF electrolyte with ion-blocking stainless-steel electrodes. The ionic conductivity of PVDF is  $2 \times 10^{-4}$  S cm<sup>-1</sup>.



Fig. S41 Rate performance of PLL-NCM/PVDF/Li full cell with a mass loading of 7 mg cm<sup>2</sup> at RT and different rates.



Fig. S42 Charge and discharge profiles for PL-NCM811/PVDF/Li full cell with a mass loading of 5 mg cm<sup>2</sup> at RT and 0.1 C.



Fig. S43 Charge and discharge profiles for PL-NCM811/PEO/Li pouch cell at RT.



Fig. S44 (a) Flexible test, (b) nail penetrating test, and (c) shear test of solid-state PLL-LFP/PVDF/Li pouch cell.



Fig. S45 Schematic of PLL-NCM811/PVDF/Li pouch cell.



Fig. S46 (a) EIS plots and charge and (b) discharge profiles for PL-NCM811/PVDF/Li and (c) PLL-NCM811/PVDF/Li pouch cell at RT.

Figure	Sample	Mass loading	Figure	Sample	Mass loading
Fig. 3a	PLL-LFP/PEO/Li - RT	1.4 mg cm <sup>-2</sup>	Fig. S12c	PLL-LFP/PEO/Li-8 wt.%	1.4 mg cm <sup>-2</sup>
Fig. 3a	PL-LFP/PEO/Li - RT	1.1 mg cm <sup>-2</sup>	Fig. S12c	PLL-LFP/PEO/Li -10 wt.%	1.4 mg cm <sup>-2</sup>
Fig. 5a	PLL-LFP/PEO/Li – rate - RT	1.1 mg cm <sup>-2</sup>	Fig. S12d	PLL-LFP/PEO/Li -2 wt.% (1000 °C)	1.1 mg cm <sup>-2</sup>
Fig. 5b	PLL-LFP/PEO/Li – 60 °C	3.8 mg cm <sup>-2</sup>	Fig. S13	LFP(PEO+LITFSI+Super P)/PEO/Li	1.8 mg cm <sup>-2</sup>
Fig. 5b	PL-LFP/PEO/Li - 60 °C	3.8 mg cm <sup>-2</sup>	Fig. S13	LFP(PEO+LITFSI+Super P)/PEO@LLZONs/Li	1.6 mg cm <sup>-2</sup>
Fig. 5c	PLL-NCM811/PEO/Li - RT	1.2 mg cm <sup>-2</sup>	Fig. S13	LFP(PVDF+Super P/PEO(LITFSI)/Li	1.6 mg cm <sup>-2</sup>
Fig. 5c	PL-NCM811/PEO/Li - RT	1.3 mg cm <sup>-2</sup>	Fig. S13	LFP(PVDF+Super P/PEO@LLZONs/Li	1.1 mg cm <sup>-2</sup>
Fig. 5d	PLL-NCM811/PEO/Li - 60 °C	3.8 mg cm <sup>-2</sup>	Fig. S14a	LFP cathode (PEO binder and Li <sub>7</sub> La <sub>3</sub> Zr <sub>2</sub> O <sub>12</sub> nanofibers)/PEO/Li	1.2 mg cm <sup>-2</sup>
Fig. 5d	PL-NCM811/PEO/Li - 60 °C	3.8 mg cm <sup>-2</sup>	Fig. S14c	LFP (PEO binder and 2 wt.% Al <sub>2</sub> O <sub>3</sub> nanofibers)/PEO/Li	1.2 mg cm <sup>-2</sup>
Fig. 5e	PLL-NCM811/PVDF/Li - RT	2.0 mg cm <sup>-2</sup>	Fig. S14d	LFP (20wt.% PEO binder)/PEO/Li cell	1.1 mg cm <sup>-2</sup>
Fig. 5e	PL-NCM811/PVDF/Li - RT	2.2 mg cm <sup>-2</sup>	Fig. S15	PLL-LFP/PEO@LZONS/Li	1.1 mg cm <sup>-2</sup>
Fig. 5h	PLL-LFP/PVDF/Li pouch cell	1.2 mg cm <sup>-2</sup>	Fig. S36	PLL-LFP/PEO/Li - 60 °C	2.8 mg cm <sup>-2</sup>
Fig. S12c	PLL-LFP/PEO/Li – 1 wt.%	1.1 mg cm <sup>-2</sup>	Fig. S36	PL-LFP/PEO/Li - 60 °C	2.7 mg cm <sup>-2</sup>
Fig. S12c	PLL-LFP/PEO/Li – 2 wt.%	1.1 mg cm <sup>-2</sup>	Fig. S38a	PLL-NCM811/PEO/Li	1.1 mg cm <sup>-2</sup>
Fig. S12c	PLL-LFP/PEO/Li – 4 wt.%	1.2 mg cm <sup>-2</sup>	Fig. S38b	PLL-NCM811/PEO/Li	1.1 mg cm <sup>-2</sup>
Fig. S12c	PLL-LFP/PEO/Li – 6wt.%	1.4 mg cm <sup>-2</sup>	Fig. S43	PL-LFP/PVDF/Li pouch cell	1.2 mg cm <sup>-2</sup>

Table S7 Mass loading of active materials in this work