Supporting Information

Experimental section

1. Synthesis of Zn-MOF.

The $Zn(NO_3)_2·6H_2O$ (99.9%, Aladdin), 1,3,5-benzene tricarboxylic acid (H_3BTC, 98%, Aladdin), and 4,4′-Dimethyl-2,2′-bipyridine (99.9%, Aladdin) were used as received, without further treatment. To synthesize Zn-MOF, 6 mmol of H_3BTC and 2.25 mmol of 4,4′-Dimethyl-2,2′-bipyridine were dissolved in 70 mL of DMF and stirred magnetically for 20 minutes at room temperature (RT). Then, 9 mmol of $Zn(NO_3)_2·6H_2O$ was added, and the mixture was stirred for an additional 30 minutes at RT to obtain a homogeneous solution. Subsequently, the resulting mixture was subjected to a hydrothermal synthesis at 150 °C for 20 hours, yielding the Zn-MOF product.

2. Preparation of SPEs.

The PZM-10 was synthesized using the solution casting method. First, 0.6 g of PVDF-HFP (Mw≈400,000, Aldrich) and 0.4 g of LiTFSI (99.95%, Aldrich) were dissolved in 4 g of NMP, and the mixture was magnetically stirred for 10 hours. Then, 0.1 g of Zn-MOF was incorporated into the solution, and the mixture was stirred for an additional 8 hours. The resulting solution was then cast into a Teflon pan and dried under vacuum at 70 °C for 24 h to obtain the PZM-10 solid electrolyte. Similarly, PSE was prepared using the same method, but without the addition of Zn-MOF.

3. Materials characterization

The morphology of the SPEs was analyzed using scanning electron microscopy (SEM, FEI-Quanta 250 FEG), while the crystal structure of the SPEs was investigated by X-ray diffraction (XRD, Bruker D8 Advance). The functional groups were analyzed using Fourier-transform infrared spectroscopy (FT-IR, Nicolet IS5) in the wavenumber range of 400 to 4000 cm^{-1}. Thermal characterization was performed using differential scanning calorimetry (DSC, DSC200F3) over a temperature range of -60 to 180 °C. Thermogravimetric analysis (TGA, STA2500) was conducted in a nitrogen atmosphere over the temperature range of 0 to 800°C, with a heating rate of 10 °C min^{-1}. Raman spectroscopy (Horiba Scientific-LabRAM HR Evolution) with a 785 nm laser was employed to investigate the chemical environment of the SPEs. The mechanical properties of the SPEs were evaluated using dynamic mechanical analysis (DMA, AGX, MTS Criterion Model 42).

4. Electrochemical measurements

The ionic conductivity of the solid polymer electrolytes (SPEs) across a temperature range of 20 to 80 °C was determined using an electrochemical workstation (CHI660E). Measurements were conducted with stainless steel (SS)|SPEs|SS coin cells over a frequency range of 10^{-1} to 10^{-6} Hz. The ionic conductivity was then calculated using the following equation:

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

where R represents the resistance of the SPEs, L is the thickness of the SPEs, and S is the effective contact area between the solid electrolyte and stainless steel. The activation energy (E_a) for Li^+ migration was determined using the following equation:

$$\sigma = \sigma_0 \exp(Ea/kT) \tag{2}$$

where σ_0, Ea, k, and T were the prefactor, activation energy, Boltzmann's constant, and temperature, respectively. The t_{Li^+} of SPEs were measured using a CHI660E electrochemical workstation, employing AC impedance spectroscopy and 10 mV DC polarization in a symmetric Li//Li cell. The t_{Li^+} can be calculated using the following equation:

$$t_{Li^+} = I_{ss}(\Delta V - R_0 I_0)/[I_0(\Delta V - R_{ss} I_{ss})] \tag{3}$$

Where ΔV represents the applied voltage, I_0 and I_{ss} are the initial and steady-state DC currents, respectively, and R_0 and R_{ss} denote the initial and steady-state interfacial resistances, respectively.

The composite cathode was fabricated by uniformly mixing LFP (Kelude, China), Super-P (Kelude, China), and solid polymer electrolytes (SPEs) in a mass ratio of 6:1:3. The as-fabricated electrodes were densified using a roll-pressing process to prepare LFP and NCM622 cathodes with active material loadings of 3 mg cm^{-2}, corresponding to areal capacities of approximately 0.45 mAh cm^{-2} and 0.49 mAh cm^{-2}, respectively. The compressed electrodes were then punched into 16 mm diameter disks for coin cell assembly or cut into 5 × 6 cm^2 sheets for pouch cell fabrication. The CR2025-type coin cells were assembled by placing the SPEs between the composite LFP cathode and the lithium metal anode, without the addition of any liquid electrolyte. The assembly procedure for the pouch cells was consistent with that of the coin cells, except that aluminum-plastic laminate films were used as the packaging material. Notably, the coin cells employed lithium metal disks (0.5 mm thick, 16 mm in diameter) as the anodes, whereas the pouch cells utilized lithium metal anodes fabricated by depositing a 20 μm-thick lithium layer onto copper foil. The galvanostatic measurements of LFP/SPEs/Li coin cells were conducted using a LANBTS battery testing system (LANBTS BT-2018AS).

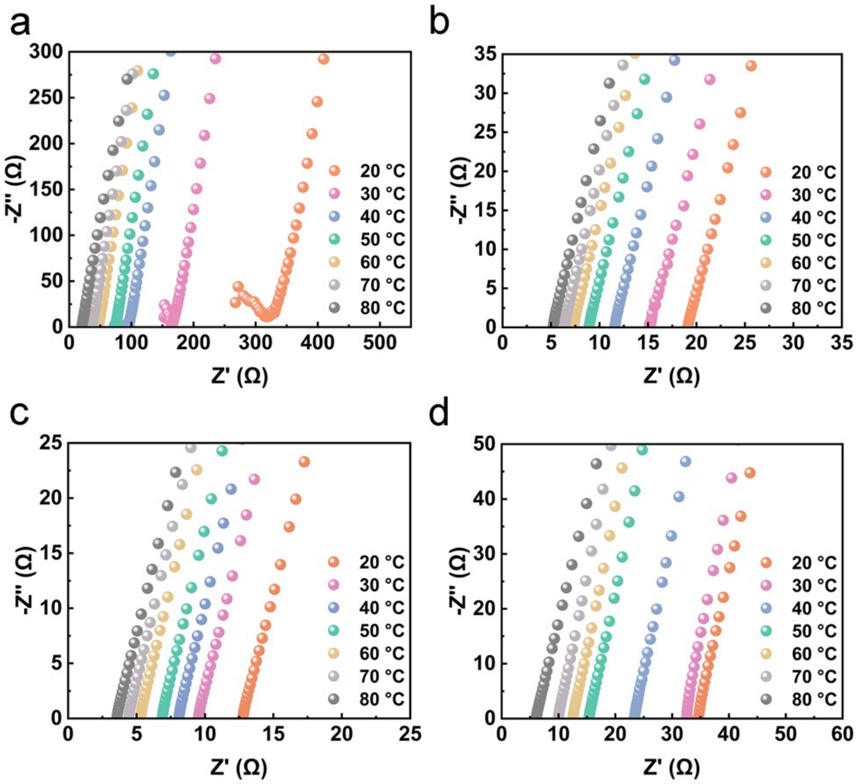

Figure S1. Nyquist plots of (a) SS|PSE|SS, (b) SS|PZM-5|SS, (c)SS|PZM-10|SS, and (d)SS|PZM-15|SS at various temperatures.

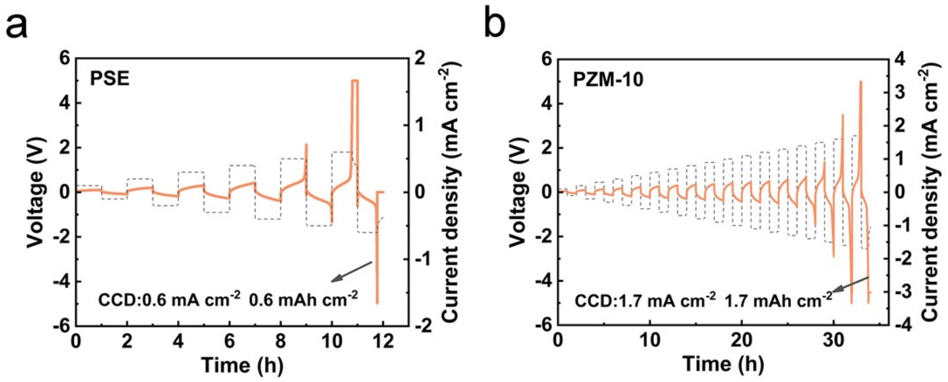

Figure S2 Voltage profiles of the symmetric cells under step-increased current densities (0.1 mA cm^{-2} per step) at room temperature with (a) PSE and (b) PZM-10.

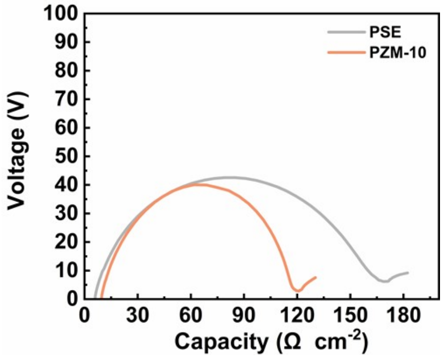

Figure S3 The area-specific resistance of the PSE and PZM-10.

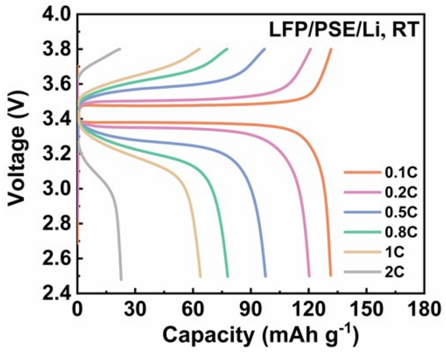

Figure S4. Charge-discharge profiles of LFP/PSE/Li at various rates at room temperature.

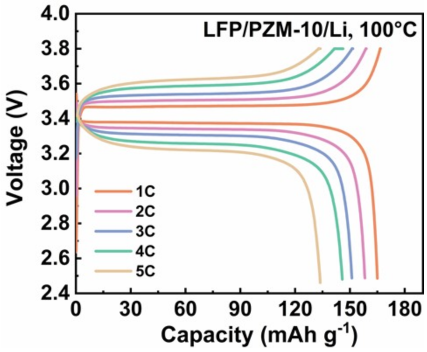

Figure S5. Charge-discharge profiles of LFP/PZM-10/Li at various rates at 100 °C.

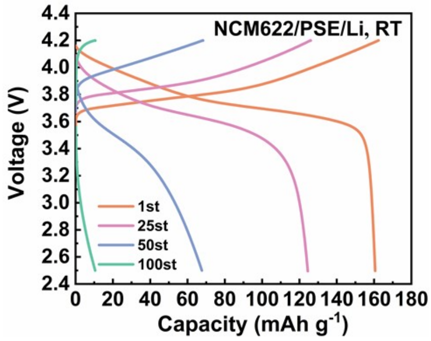

Figure S6. Charge-discharge profiles of NCM622/PSE/Li at 0.2C at room temperature.

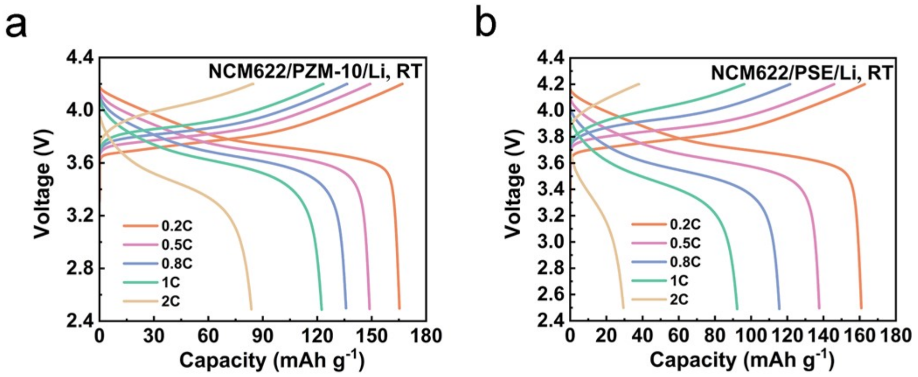

Figure S7. Charge-discharge profiles of the NCM622/PZM-10/Li and NCM622/PSE/Li cells at various rates at room temperature.

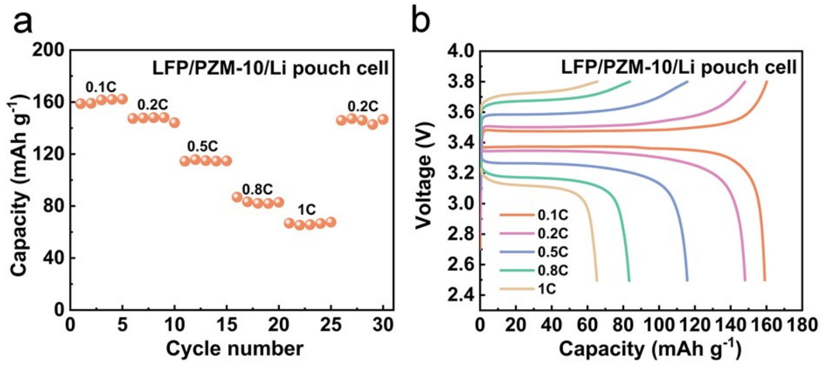

Figure S8. (a) Rate performances of the LFP/PZM-10/Li pouch cell (b) Charge-discharge profiles of LFP/PZM-10/Li pouch cell at various rates at room temperature.