Regulating the dielectricity of solid polymer electrolytes to promote cation mobility for high-performance solid zinc hybrid batteries

Yue Hou[1], Zhiquan Wei[1], Zhuoxi Wu[1], Yiqiao Wang[1], Zhaodong Huang[1], Qing Li[1], Ze Chen[1], Xinliang Li[2], Pei Li[1], Huilin Cui[1], Guojin Liang[1]*, Chunyi Zhi[1,3,4,5]*

[1]Department of Materials Science and Engineering, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong 999077, China

[2]Key Laboratory of Material Physics, Ministry of Education, School of Physics and Microelectronics, Zhengzhou University, Zhengzhou 450001, China

[3]Hong Kong Institute for Advanced Study, City University of Hong Kong, Kowloon, Hong Kong, 999077, China

[4]Hong Kong Institute for Clean Energy, City University of Hong Kong, Kowloon 999077, Hong Kong

[5]Centre for Functional Photonics, City University of Hong Kong, Kowloon, Hong Kong

*E-mail: gj.liang@siat.ac.cn; cy.zhi@cityu.edu.hk

Experimental Section

Materials: N-Methyl-2-pyrrolidone (NMP), N, N-Dimethylformamide (DMF), poly(vinylidene fluoride-co-trifluoroethylene-co-chlorotrifluoroethylene) (PVDF-TrFE-CTFE) (denoted as PVTF), polyvinylidene difluoride (PVDF), Poly(ethylene oxide) average Mv 400,000 PEO, Lithium triflate (LiOTf), Zinc trifluoromethanesulfonate ($Zn(OTf)_2$), Zinc sulfate ($ZnSO_4$), Zinc acetate ($(CH_3COO)_2Zn$), Zinc bis(trifluoromethanesulfonyl)imide ($Zn(TFSI)_2$), Lithium Manganate (LMO), Lithium iron phosphate (LFP) are all purchased from Aladdin.

Preparation of PVTF SPE: PVTF, $Zn(OTf)_2$ and LiOTf with various weight ratios (1:0.15:0.15, 1:0.3:0.3, 1:0.45:0.45, 1:0.6:0.6) were dissolved in moderate DMF, followed by mechanically stirred at 70 ºC to obtain a homogeneous solution. Based on the total metal salt content, these samples were marked as PVTF0.3, PVTF0.6, PVTF0.9 and PVTF1.2, respectively. Finally, the transparent solution was dropped

onto a glass plate and dried at 50 °C in an oven for 8 h to remove the residual DMF.

Preparation of PVDF SPE: PVDF polymer (0.5 g) was added into a beaker containing 10 mL DMF, followed by dissolving LiOTf (0.225 g) and $Zn(OTf)_2$ (0.225 g) in the DMF solution. Then, the solution was stirred for 2 h and heated at 70 °C. Finally, the transparent solution was dropped onto a glass plate and dried at 50 °C in an oven for 8 h to remove the residual DMF.

Preparation of LMO cathode: LMO powder was coated on carbon clothes with 2.5 mg cm^{-2} loading mass as the cathode (LMO: PVDF: carbon black = 8:1:1).

Preparation of LFP cathode: LFP powder was coated on carbon clothes with 2.0 mg cm^{-2} loading mass as the cathode (LFP: PVDF: carbon black = 8:1:1)

Characterization methods: Fourier-transform infrared spectroscopy (FT-IR) was collected based on the PerkinElmer Spectrum II. Raman spectra were detected on the WITec alpha300 R Raman System. The high-resolution solid-state nuclear magnetic resonance (NMR) spectroscopy was recorded with Agilent 600M. Differential scanning calorimetry (DSC) experiments were conducted using a DSC Q2000 (TA Instruments) with Tzero pans. Thermogravimetric Analysis (TGA) was applied on TG/DTA 6300 to obtain the polymer content in the composite. A field-emission scanning electron microscope (SEM, FEI Quanta 450 FEG) was used to investigate the morphologies of the products. Powder X-ray diffraction (PXRD) was performed at ambient temperature on Bruker D2 Phaser equipment, using Cu-Kα radiation with a monochromator. Dielectric constant and dielectric losses were conducted on Agilent 4294A precision impedance analyzer with frequencies ranging from 40Hz-10MHz at ambient temperature. The strain tests for the fabricated PVTF-based SPE with different contents of OTf$^-$-based salts were detected by an electronic universal testing machine (HS-3001D).

Electrochemical measurement:

The Ti‖Ti coin cell with the prepared SPE was assembled to measure the EIS. We can calculate the ionic conductivity by using the following equation:

σ=L/(A*R)

where L is the thickness of the polymer electrolytes, R is obtained by the above EIS

measurements, and S is the area of stainless steel.

We calculated the activation energy E_a by using the Arrhenius equation:

$\sigma = \sigma_0 \exp(-E_a/RT)$

The Zn|SPE|Zn symmetric batteries with our fabricated SPE were used to conduct EIS measurements from 10 MHz to 0.01 Hz with a 20 mV AC oscillation. The transference number of cations, including Li^+ and Zn^{2+} can be calculated according to the following equation:

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

Where I_s and I_0 are the steady-state and initial currents, respectively, R_0 and R_s are the interfacial resistance before and after polarization.

The electrochemical stability window of the SPE was determined by conducting linear sweep voltammetry (LSV) measurements on the assembled Zn|SPE|Ti cells. All these electrochemical properties were carried out on the electrochemical workstation CHI 760D.

CR2032 coin cells were assembled using a Zn foil as the anode, LFP or LMO as the cathode, and PVTF and PVDF as SPEs for electrochemical measurements. All these cycling tests were conducted on the Land CT2001A battery testing system.

Computational calculation:

Density functional theory calculation (DFT): The first principles calculation in this work was conducted using the Dmol3 code on the Materials Studio software on the basis of DFT, in which the projector augmented wave (PAW) pseudopotentials are selected to analyze the ion-electron interactions. The generalized gradient approximation in the Perdew-Burke-Ernzerhof (GGA-PBE) form was selected to treat the exchange-correlation function. The cutoff energy for the plane-wave basis set was set as 489.80 eV. Truncatedchain models of PVTF were used to calculate the binding energies. Visualization of the structures is made by using the VESTA software. To achieve a reasonable structure, the convergence criterion of the total energy was set to be within 1×10^{-5} eV within the k points integration, and all the geometries were optimized until the maximum force was less than 0.02 eV Å^{-1}.

The following formula guided the adsorption energy (E_{ads}):

$$E_{ads}=E_{all}-E_{PVTF}-E_{ions}$$

in which E_{total}, E_{PVTF}, and E_{ions} represent the energy of PVTF molecules adsorbed with ions, pure PVTF, and pure ions, respectively.

Molecular dynamics (MD) simulations: Solid polymer electrolytes model was built by 106 PVDF, 58 $Zn(OTf)_2$ and 135 LiOTf. PVTF SPE was built by 76 PVTF, 60 $Zn(OTf)_2$, and 140 LiOTf. MD simulations were performed using the Forcite module of Materials Studio to study the coordination number between cations and the polymer networks. The COMPASSIII force fields have been chosen as distributing charges of Zn^{2+}, Li^+, OTf^-, PVDF, and PVTF. The geometry optimization was first conducted using the Forcite module with the convergence of the total energy (0.001 kcal mol-1) with the force of 0.5 kcal mol-1 Å -1. Then, NPT and NVT ensembles were successively carried out in MD simulations at 298 K. The repulsive cutoff distance for the electrostatic interactions is 12 Å with an Ewald accuracy of 0.001 kcal/mol. The cutoff distance for van der Waals was 12.5 Å. To achieve the equilibrium states of the SPE systems, NPT was run for 1000 ps at 298 K under the pressure of 0.1 MPa. The time step was 1 fs. The thermostat condition is according to the Nose approach. After that, NVT was run for 1000 ps at 298 K, using the Nose method as the thermostat condition. The coordination conditions were analyzed after all of the simulations. The corresponding number of molecules or ions was constructed according to their content or weight fraction.
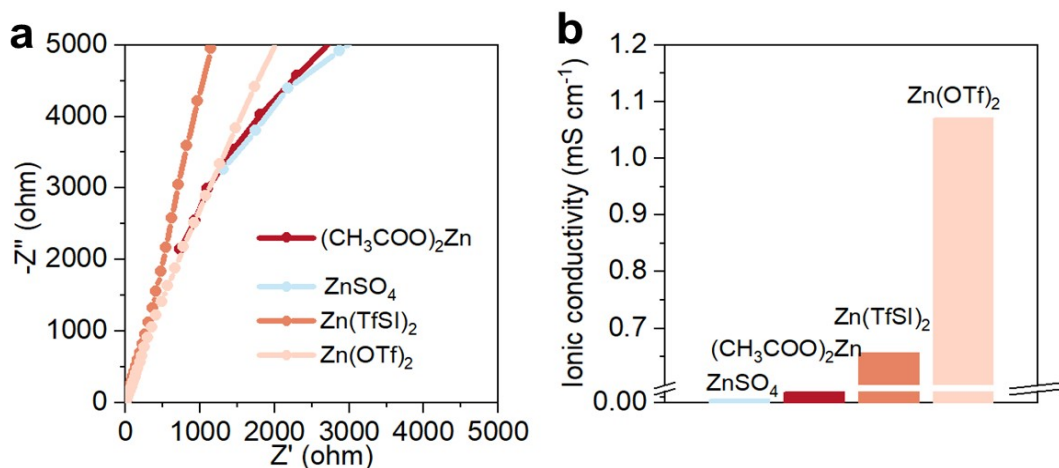
Figure S1. EIS patterns (a) and the corresponding ionic conductivities (b) of the fabricated PVTF-based SPE with different metal salts.
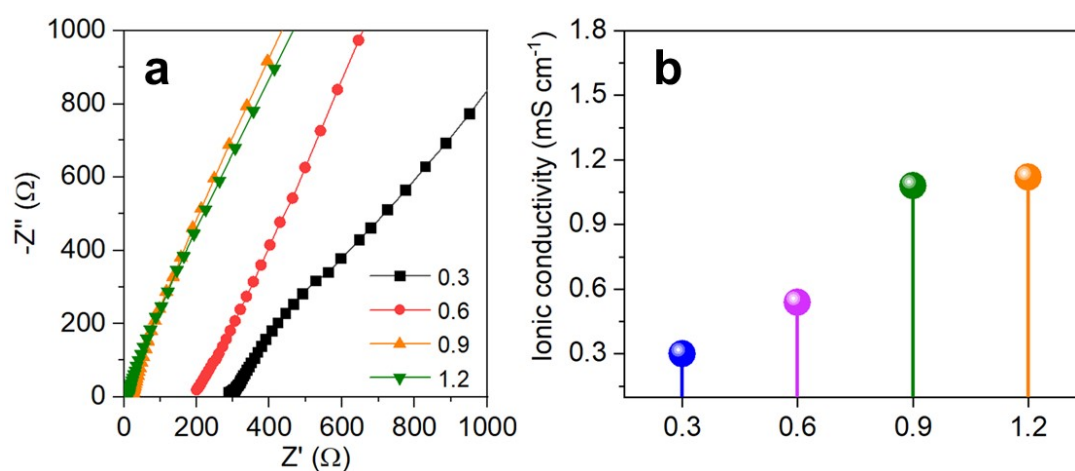

Figure S2. EIS patterns (a) and the corresponding ionic conductivities (b) of the fabricated PVTF-based SPE with different contents of OTf-based salts.
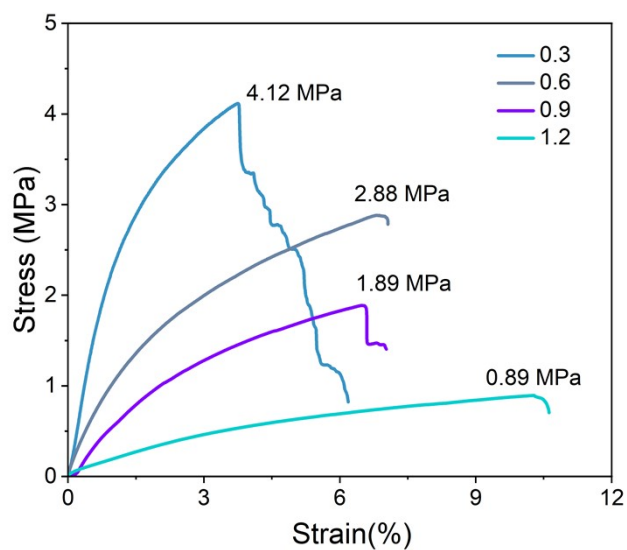
Figure S3. The stress-strain curves of the fabricated PVTF-based SPE with different OTf--based salts contents.
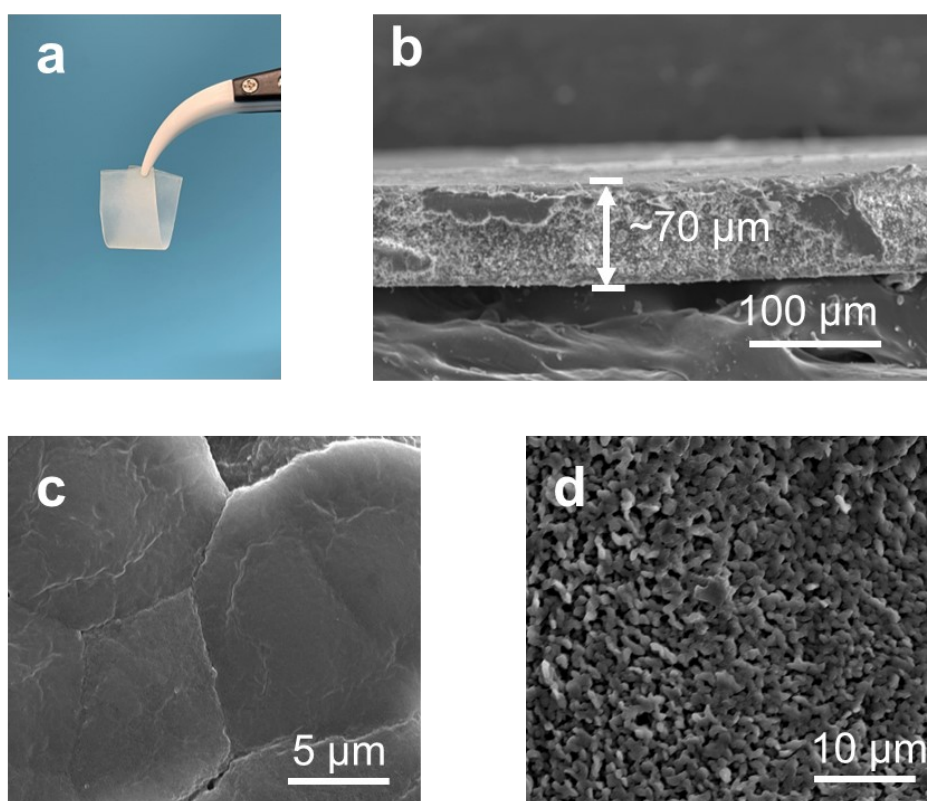

Figure S4. The optical images of the PVTF SPEs (a). The cross-sectional SEM image of the fabricated PVTF SPE (b).The side-view SEM image (c) of the fabricated PVTF SPE and PVDF SPE.
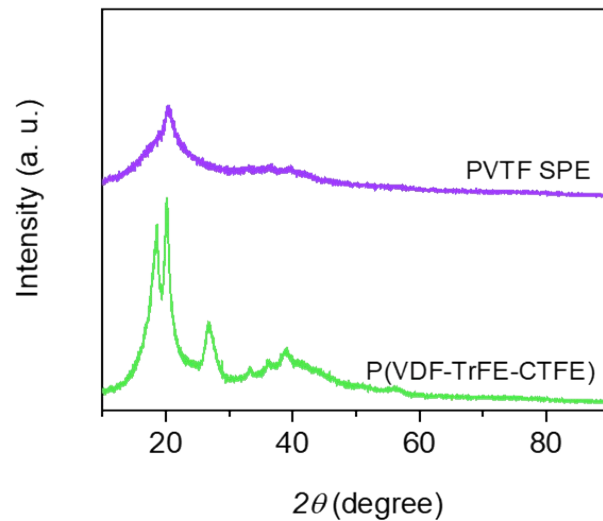
Figure S5. XRD results of the fabricated PVTF SPE and PVTF.
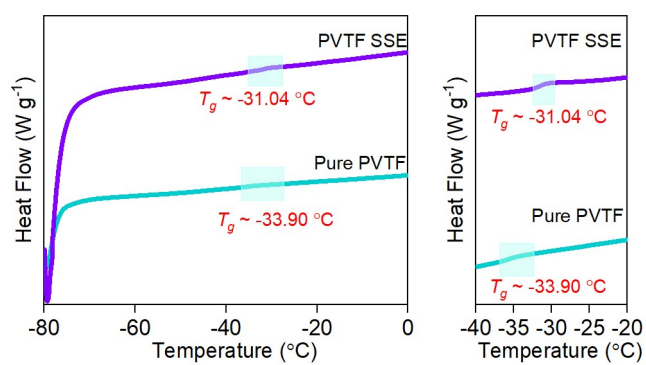
Figure S6. DSC curves of the fabricated PVTF SPE and PVTF.
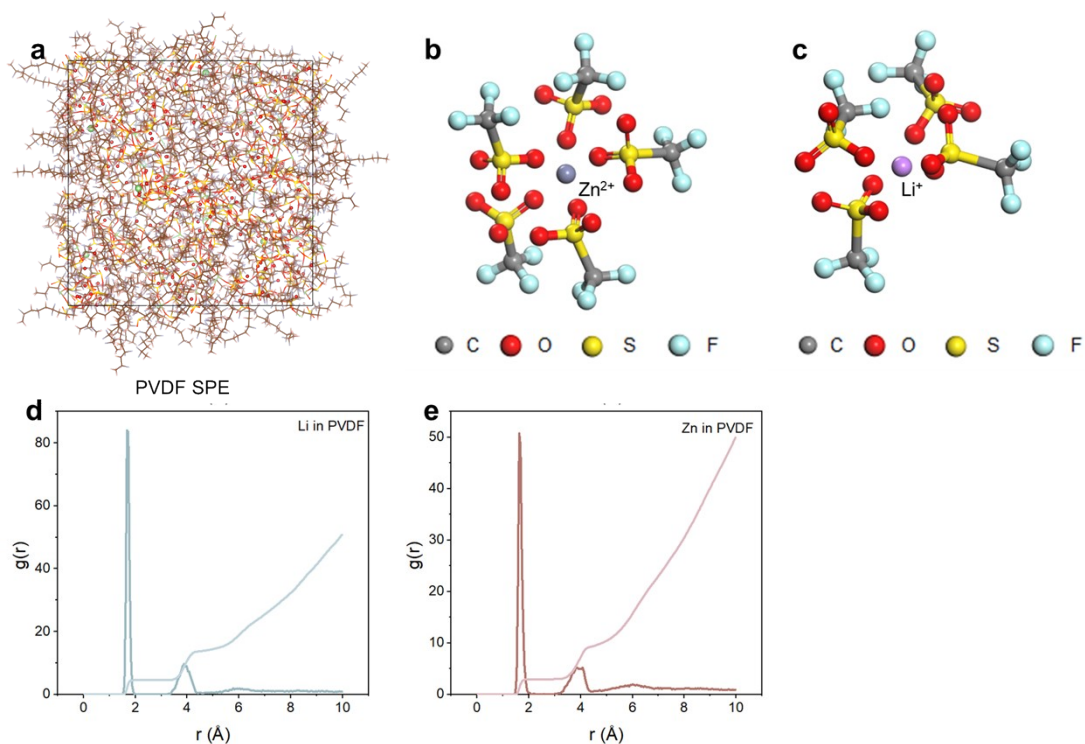
Figure S7. (a) Snapshots of the MD simulation boxes of PVDF SPE. (b) Schematic illustration of the coordination structure between Zn ions and OTf⁻ anions. (c) Schematic illustration of the coordination structure between Li ions and OTf⁻ anions. Colours of elements: Zn, grey; Li, purple; C, grey; O, red; F, cyan; S, yellow. The radial distribution function (RDF) plots of Li-OTf⁻ (d) and Zn-OTf⁻ (e) pairs in PVTF SPE.
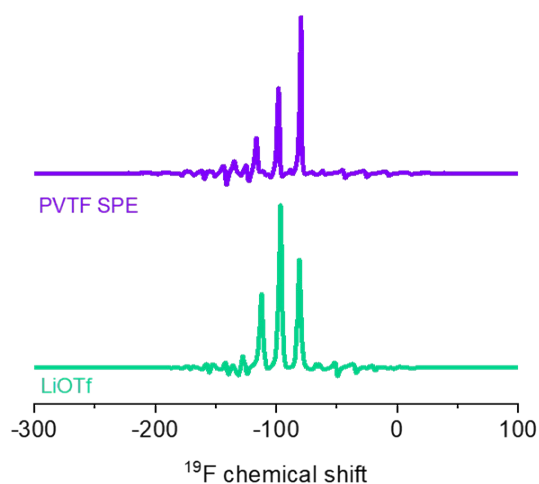
Figure S8. The ¹⁹F NMR spectra of the fabricated PVTF SPE and LiOTf.
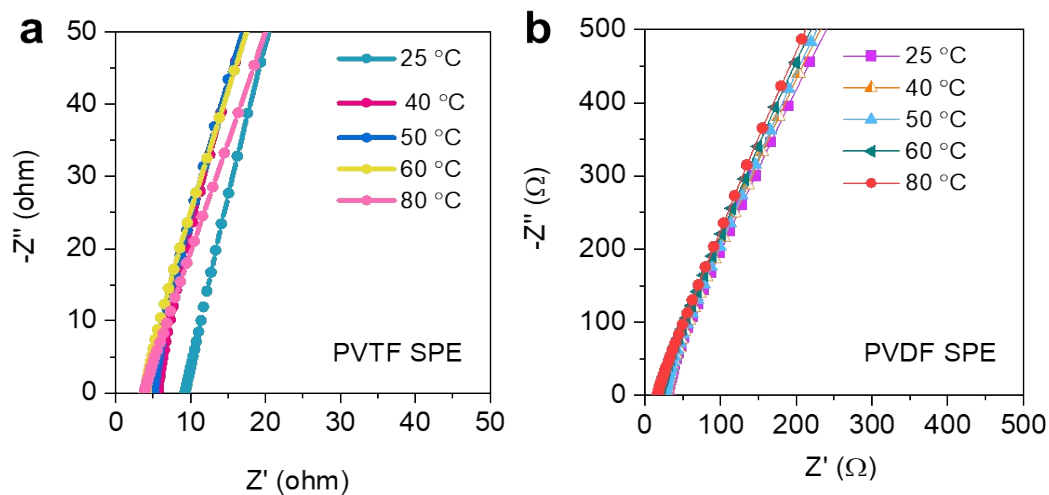
Figure S9. The EIS patterns of the PVTF SPE (a) and PVDF SPE (b) in a broad temperature range of 25 to 80 °C.
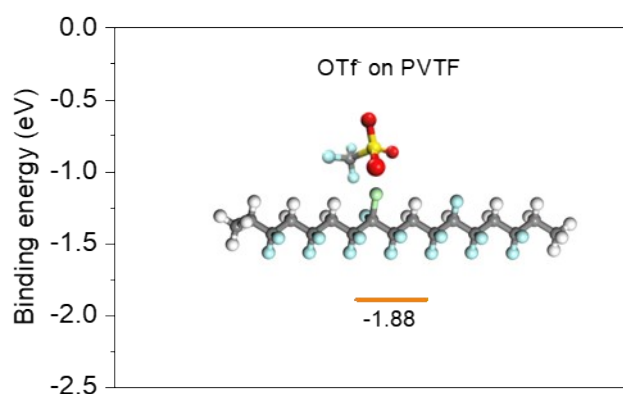
Figure S10. The adsorption energy of OTf⁻ on PVTF SPE by DFT calculations.
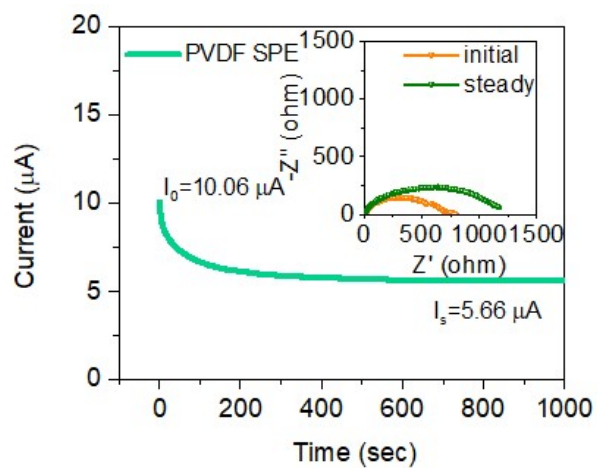
Figure S11. Chronoamperometry profiles of the Zn|PVDF SPE|Zn cells under a polarization voltage of 20 mV.
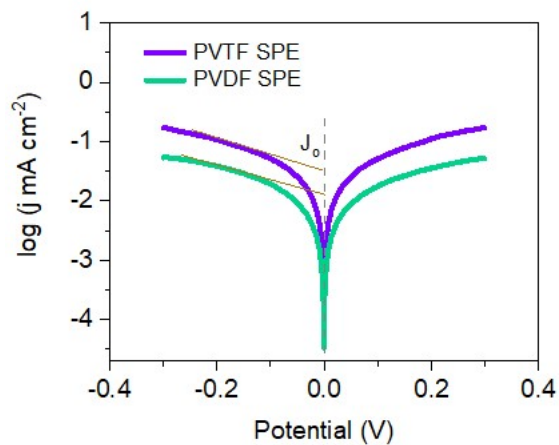

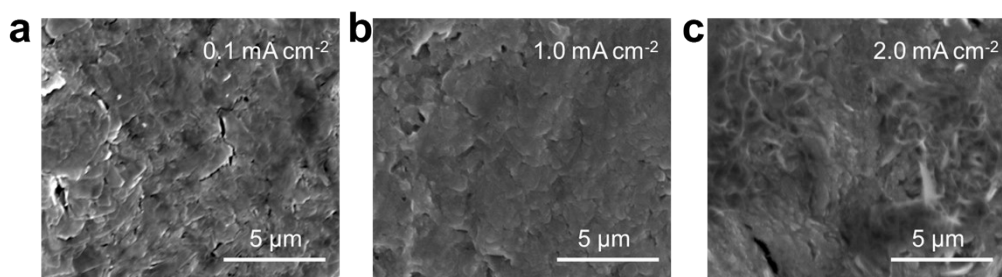**Figure S12.** Tafel plots of the Zn|PVTF SPE|Zn and Zn|PVDF SPE|Zn cells.

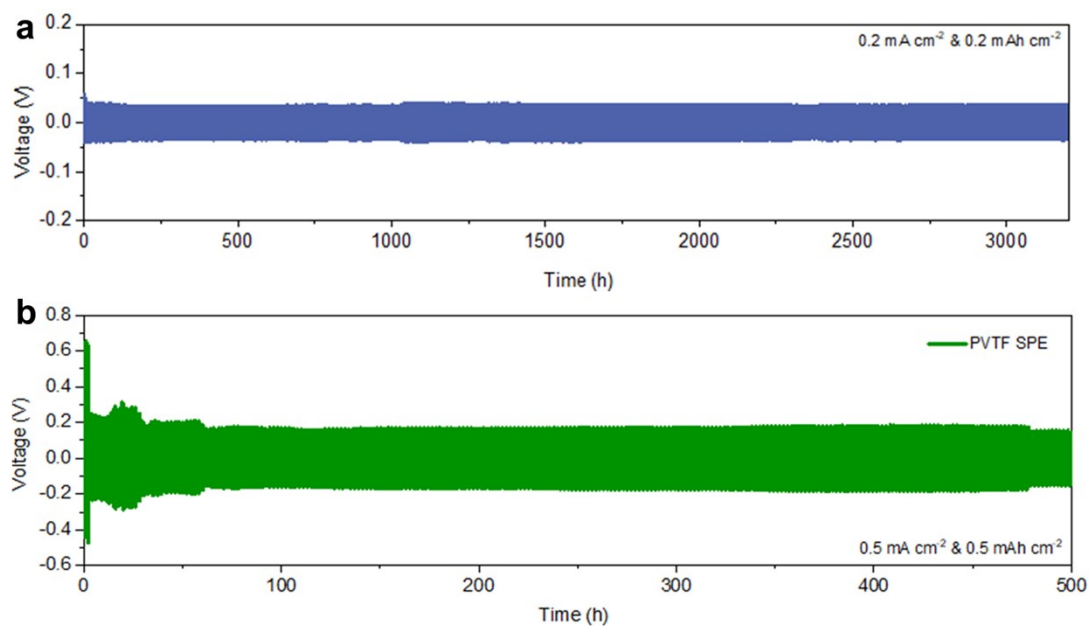**Figure S13.** SEM image of the Zn electrode after 50 cycles at 0.1 (a), 1.0 (b), and 2.0 mA cm^{-2} (c).

Figure S14. (a) Long-term cycling test of the Zn||Zn cells based on the PVTF SPE at 0.2 mA cm^{-2} with 0.2 mAh cm^{-2}. (b) Long-term cycling test of the Zn||Zn cells based on the PVTF SPE at 0.5 mA cm^{-2} with 0.5 mAh cm^{-2}.
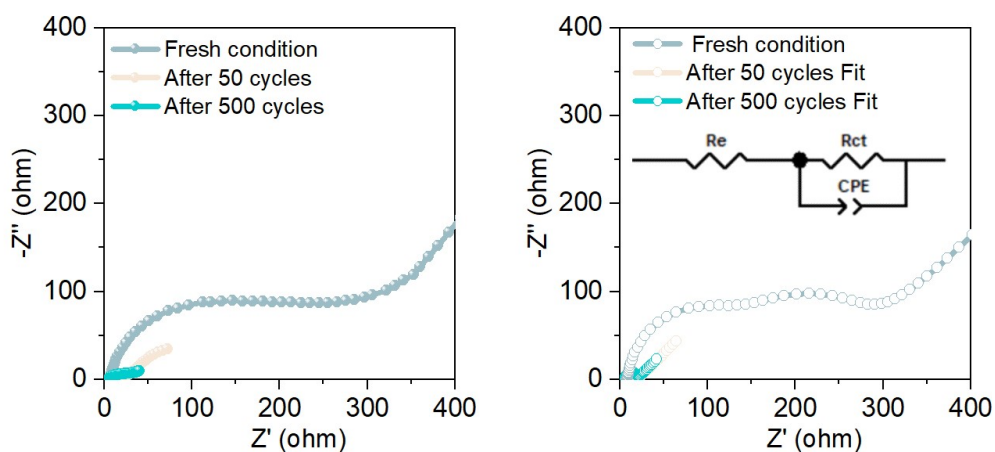

Figure S15. (a) The fitted equivalent circuit used to fit the experimental data. The corresponding EIS patterns at different charge conditions during the long-term cycling test of the Zn||Zn cells based on the PVTF SPE at 0.1 mA cm^{-2} (b).
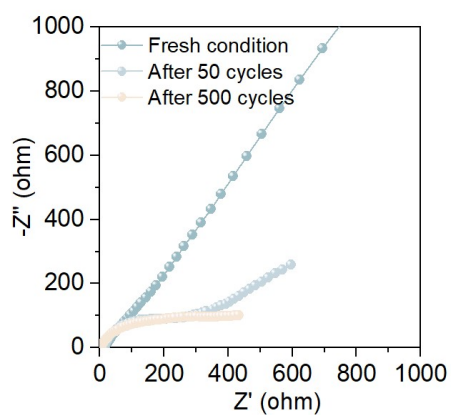
Figure S16. EIS patterns at different charge conditions during the long-term cycling test of the Zn‖Zn cells based on the PVTF SPE at 0.2 mA cm^{-2}.
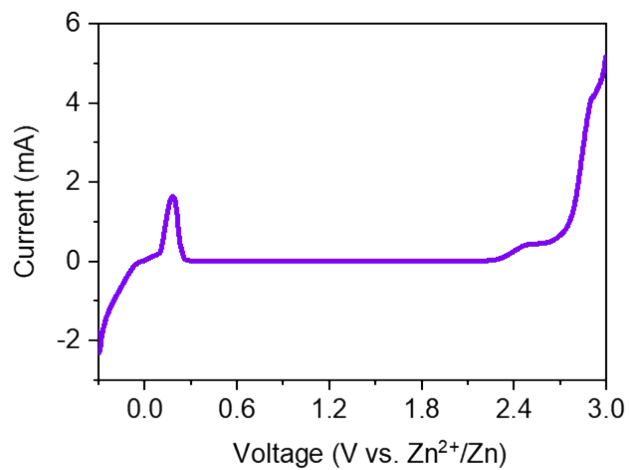

Figure S17. Linear sweep voltammetry (LSV) measurement of the Zn‖Ti solid-state battery assembled by PVTF SPE.
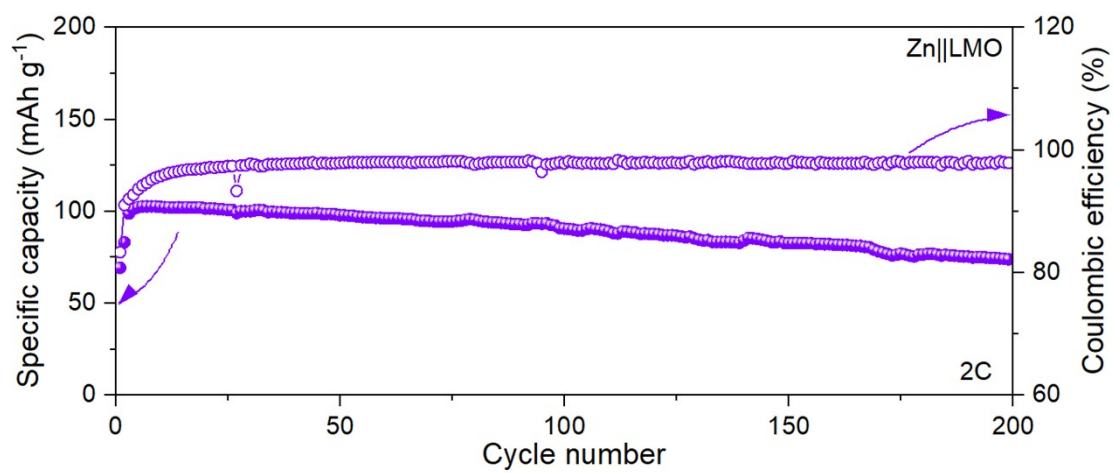
Figure S18. The cycling tests of the Zn‖LMO solid-state cells with PVTF SPE.