Supporting information

Engineering Well-connected Ion-conduction Network and Interface Chemistry

for High-performance PVDF-based Polymer-in-Salt Electrolytes

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Experimental Section

Preparation of solid-state electrolytes. The solid-state polymer electrolytes were prepared via a solution-casting procedure. PVDF was dried under a vacuum at 80 °C for 12 h to remove trapped water before use. Firstly, PVDF and LiTFSI with a weight ratio of 1:1.25 were dissolved in moderate DMF, followed by magnetic stirring at 60 °C to obtain a homogeneous solution. Then, 1, 5 and 10% HFA of PVDF matrix were added to the above solution. After that, the mixed solution continues to be stirred at 60 °C for 12 h. Afterward, the slurry was cast on a glass plate with a doctor blade and dried at 40 °C for 12 h and then 60 °C for 3 h . Finally, the solid-state membranes were punched into circles (~125 μm in thickness) for subsequent use. All the fabricating processes were carried out in the Ar-filled glove box (H$_2$O＜0.1 ppm, O$_2$＜0.1 ppm). Based on the HFA content, the solid-state electrolytes were named as PVH-0, PVH-1, PVH-5 and PVH-10, respectively. Additionally, the solid-state electrolyte without HFA but with a salt content of 10% was named as PV10.

Preparation of LiFePO$_4$ and NCM622 cathode. The cathode powder (LiFePO$_4$ and NCM622), super P and PVDF were mixed with the weight ratio of 8:1:1 in N-methyl pyrrolidone (NMP) to obtain a homogeneous slurry. Then, the slurry was cast on aluminum foil and dried at 80 °C overnight under vacuum. The mass loading of LiFePO$_4$ and NCM622 cathode is about 2 mg cm^{-2}.

Electrochemical Measurements. The ionic conductivities were measured by electrochemical impedance spectra (EIS) of the stainless steel (SS)‖SS blocking cells with various temperature ranges of 25-80 °C in the frequency range from 1 to 10^6 Hz with an alternating current (AC) amplitude of 10 mV. The EIS results obtained in this work were carried out by the electrochemical workstation (Solartron, 1260/1287). And the ion conductivity (σ) was calculated by the below equation S1:

$$\sigma = \frac{L}{RS} \quad (S1)$$

where L is the thickness of the solid-state electrolyte, R is the bulk resistance and S is the area of the solid-state electrolyte (10 mm in diameter).

The energy activation (Ea) was calculated from the Arrhenius formula (equation S2):

$$\sigma = \sigma_0 \exp(\frac{Ea}{RT}) \quad (S2)$$

where σ_0 is the pre-exponential factor, Ea is the energy activation of ionic conduction and T represents the absolute temperature.

The electrochemical windows of the solid-state membranes were examined by linear sweep voltammetry (LSV) of Li/SS cells at the voltage of 0 to 6 V with a scan rate of 1 mV s^{-1} using an electrochemical workstation (Solartron, 1260/1287).

The electrochemical performance of $LiFePO_4$‖Li and NCM622‖Li full cells were measured by a battery test system (Land CT2001A) in the voltage range of 2.5-4.2 V and 2.8-4.3 V at room temperature.

Materials characterization. The crystallinity phases of the samples were characterized by X-ray diffraction (XRD, Rigaku, MiniFlex 600). The Raman spectra were obtained by (Horiba，LabRAM HR). The chemical structure of the samples was evaluated by the FTIR(Thermo Scientific iN10). Thermogravametric analysis (TGA) was executed the thermal stability of the samples using (METTLER TOLEDO 3+). The structures and morphologies were performed by scanning electron microscope (SEM, TESCAN MIRA LMS). The components of the cycled Li electrode were examined by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, K-Alpha).

Density Functional Theory (DFT) Calculations. The energy of Li^+ absorbed on substrates was calculated using $DMol^3$ module of Materials Studio.[1] The exchange-correlation energy employed Becke three parameter hybrid functional incorporated

with the Lee−Yang−Parr correlation (B3LYP) functional.[2] Convergence tolerance was set to 5.0×10^{-3} Å for maximum displacement, 1.0×10^{-5} Ha for energy and 2.0×10^{-3} Ha Å^{-1} for maximum force. The self-consistent field (SCF) tolerance was performed with convergence criteria of 1.0×10^{-6}. Adsorption energy were calculated as follows:

$$E_a = E_{n\,(A+B)} - nE_A - nE_B \quad (S3)$$

E_A, E_B and $E_{n\,(A+B)}$ correspond to the energy of A, B and A+B with molecular number of n, respectively.

Molecular Dynamics Simulations. A structural optimization was firstly employed to relax the simulation box. Then, an isothermal-isobaric (NPT) ensemble with a 1.0 fs time step was employed to optimize the simulation box. The pressure of both systems was set to 1.0 atm, which was kept via the Berendsen barostat.[3] The temperature was set to 298.15 K, which was kept via the Nose-Hoover thermostat barostat.[3] The NPT optimization time was set to 0.5 ns, which is long enough to obtain a stable box size. Following the NPT simulation, a canonical 0.5 ns NVT simulation was performed to collect the trajectory coordinates of molecules with a storage frequency of 100 steps. The time step of NVT simulation was set to 1.0 fs. For all the MD simulations, the motion of atoms was described by classical Newton's equation, which was solved using the Velocity-Verlet algorithm. All simulations were performed with compass II forcefield using the forcite module.[4]
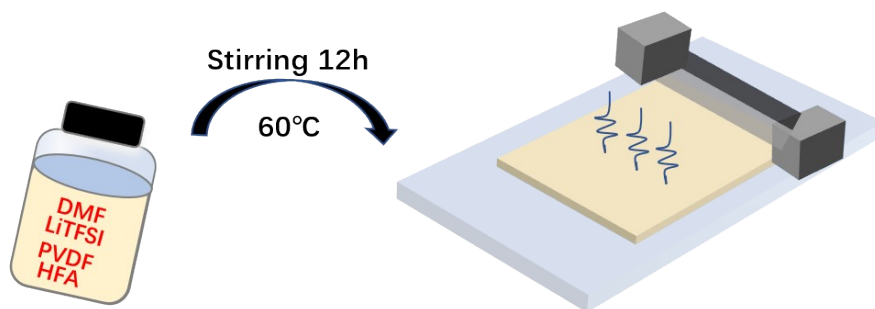
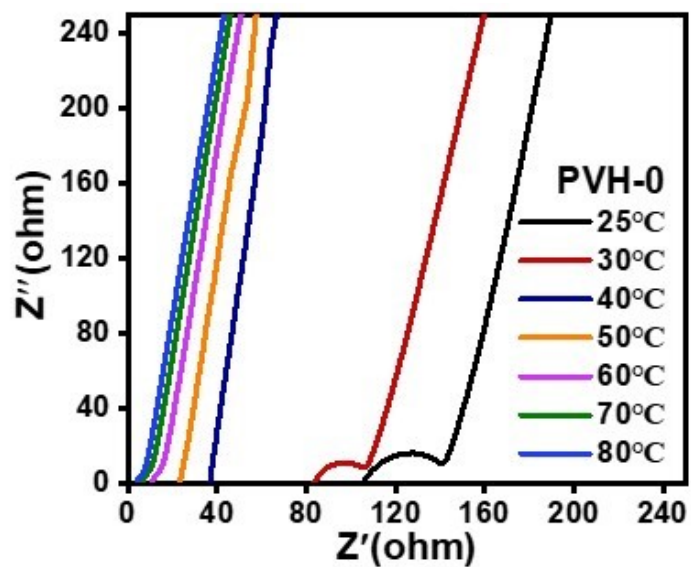**Figure S1.** The schematic diagram of the solution-casting method.

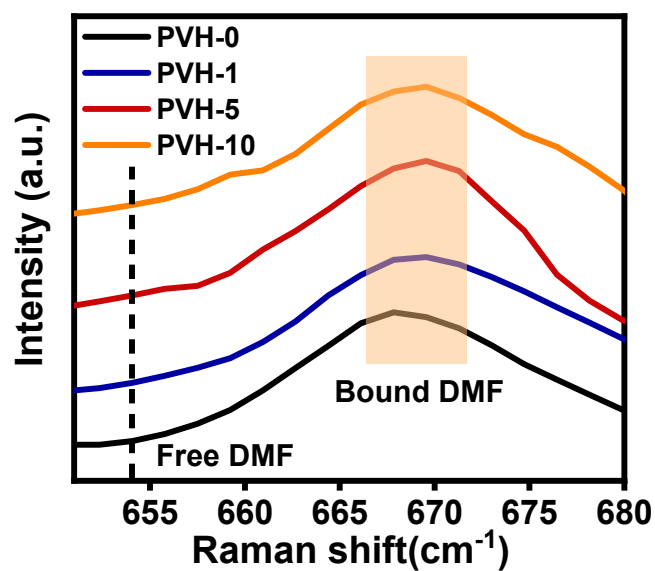**Figure S2.** Nyquist plots of PVH-0 at different temperatures.

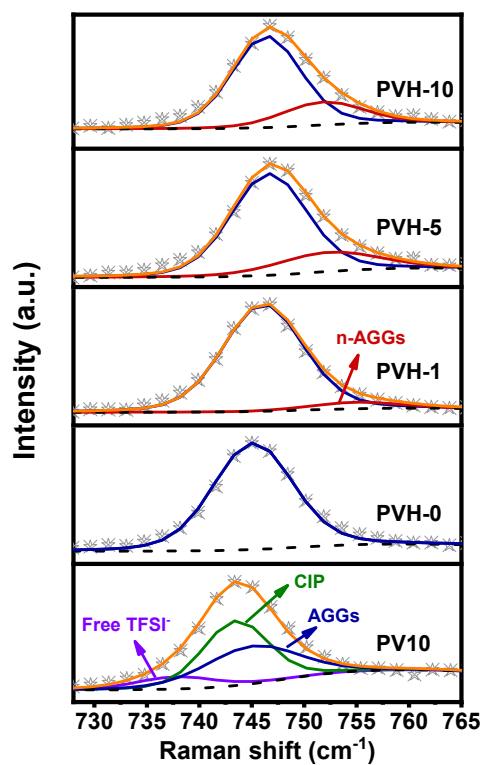**Figure S3.** Raman spectra of PVH-0, PVH-1, PVH-5 and PVH-10 solid electrolytes in 650-680 cm^{-1}.

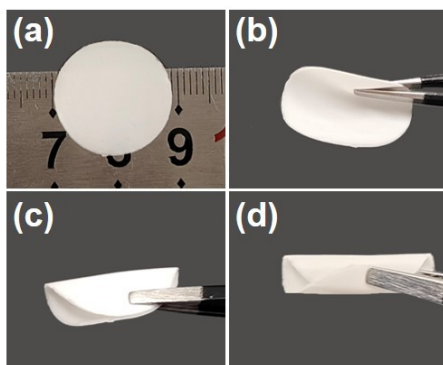**Figure S4.** Fitted Raman spectra of PV-10, PVH-0, PVH-1, PVH-5 and PVH-10 solid electrolytes.

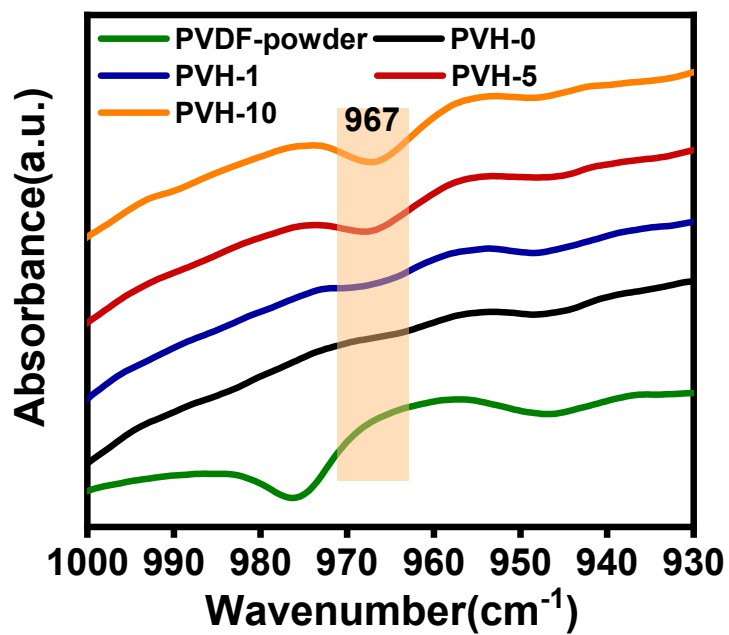**Figure S5.** Optical image of PVH-0 solid electrolytes.

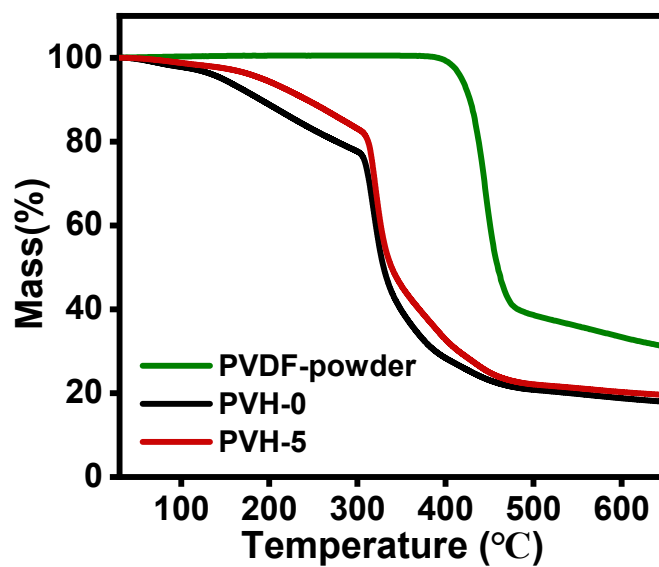**Figure S6.** FTIR spectra of PVDF-powder, PVH-0, PVH-1, PVH-5 and PVH-10 solid electrolytes in 1000-930 cm^{-1}.

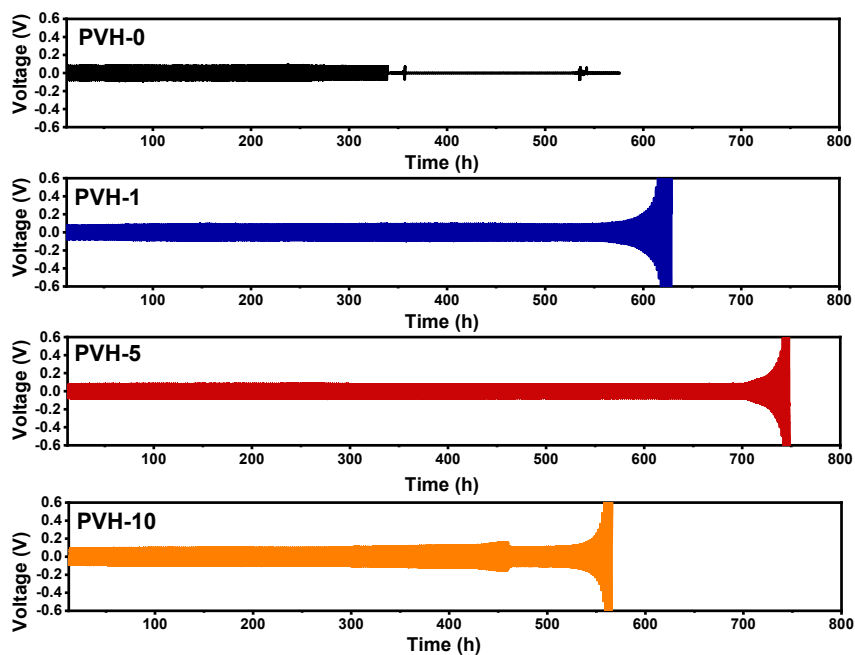**Figure S7.** TG curves of PVDF-powder, PVH-0 and PVH-5 solid electrolytes.

Figure S8. Voltage profiles of PVH-0, PVH-1, PVH-5 and PVH-10 in Li symmetric batteries at 0.1 mA cm^{-2} with a capacity of 0.1 mAh cm^{-2}.
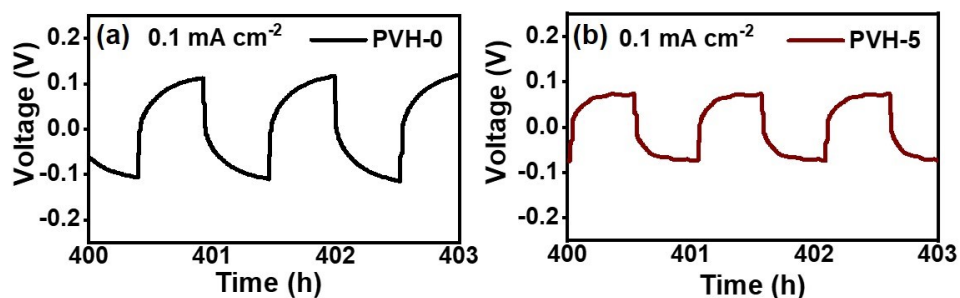

Figure S9. Selected discharge-charge curves of the Li||PVH-0||Li and Li||PVH-5||Li symmetrical cells at 0.1 mA cm^{-2} with a capacity of 0.05 mAh cm^{-2}, respectively.
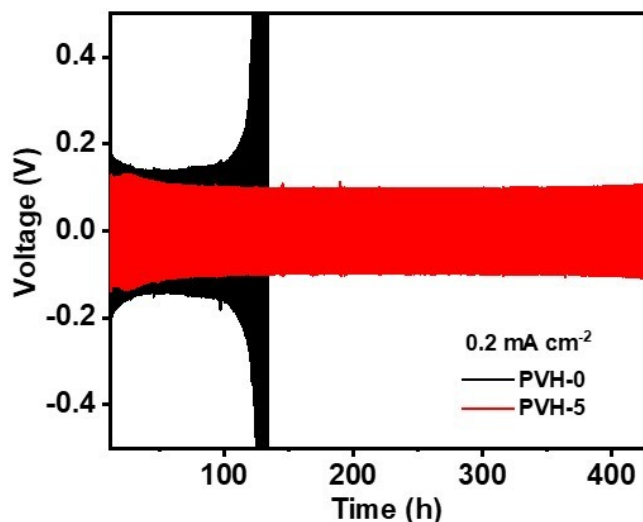

Figure S10. Voltage profiles of PVH-0 and PVH-5 in Li symmetric batteries at 0.2 mA cm^{-2} with a capacity of 0.1 mAh cm^{-2}.
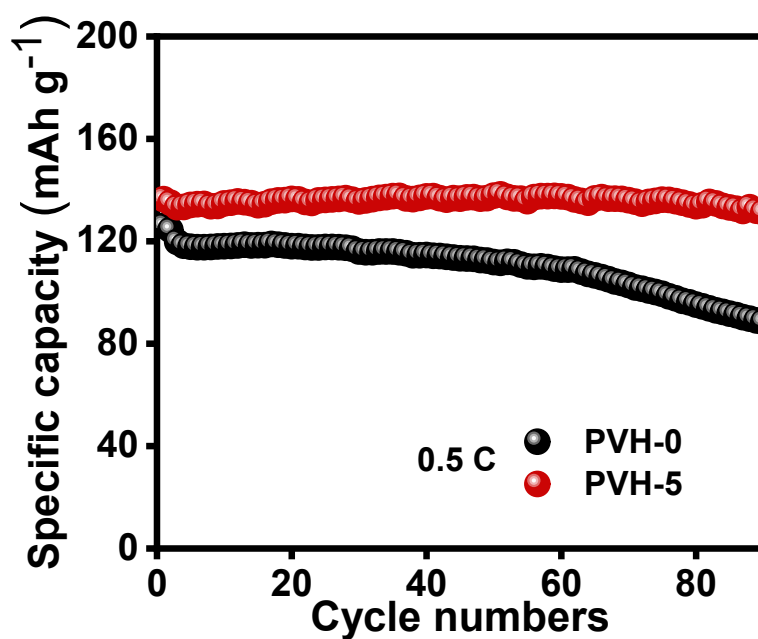
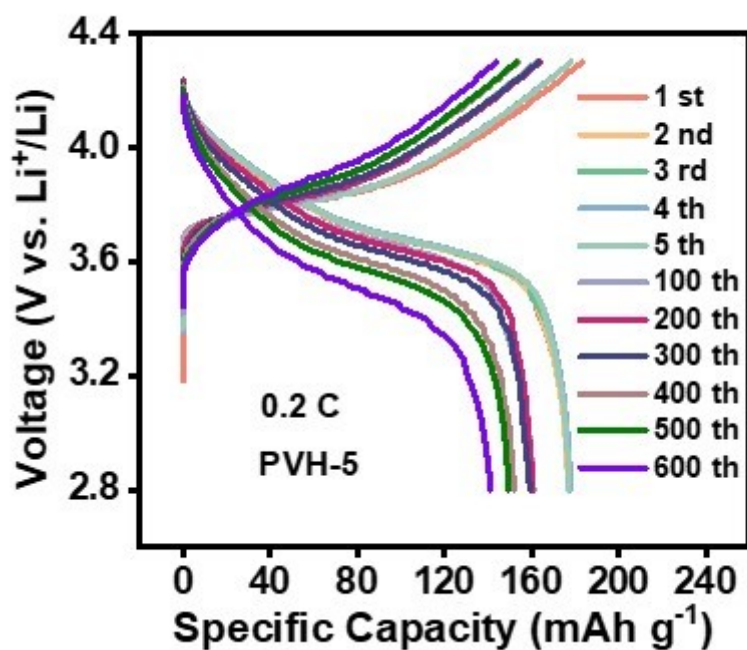**Figure S11.** Cycling performance of Li||PVH-5||LiFePO$_4$ at 0.5 C.

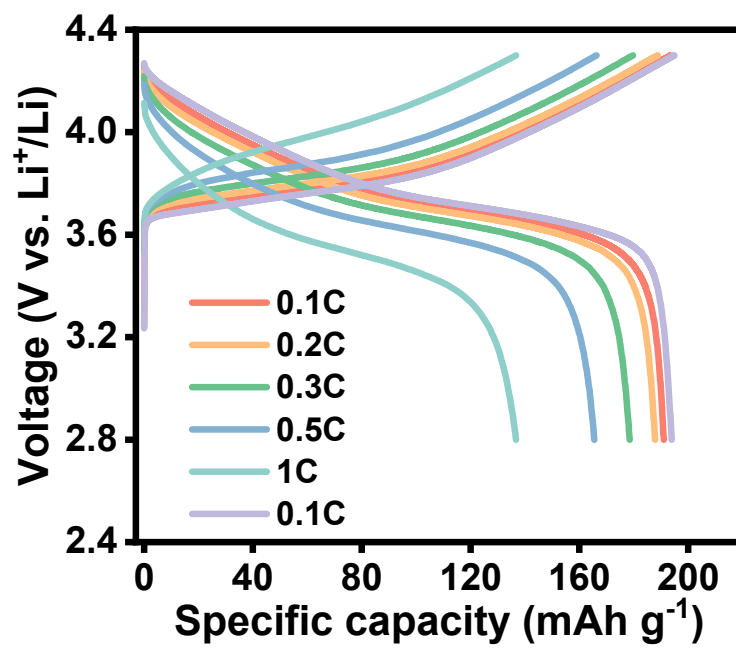**Figure S12.** Charge-discharge curves of Li||PVH-5||NCM622 at 0.2 C.

Figure S13. Charge-discharge curves of Li‖PVH-5‖NCM622 at different rate.

References

[1]   B. Delley, *J. Chem. Phys.* **1990**, 92, 508.

[2]   A. D. Becke, *J. Chem. Phys.* **1992**, 96, 2155.

[3]   H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. DiNola, J. R. Haak, *J. Chem. Phys.* **1984**, 81, 3684.

[4]   R. L. C. Akkermans, N. A. Spenley, S. H. Robertson, *Mol. Simulat.* **2020**, 47, 540.