

## ***Supplementary Information***

### **Cationic Chain-Anchored Monolayer Enables Wide-Temperature Composite Polymer Electrolytes for Lithium-Metal Batteries**

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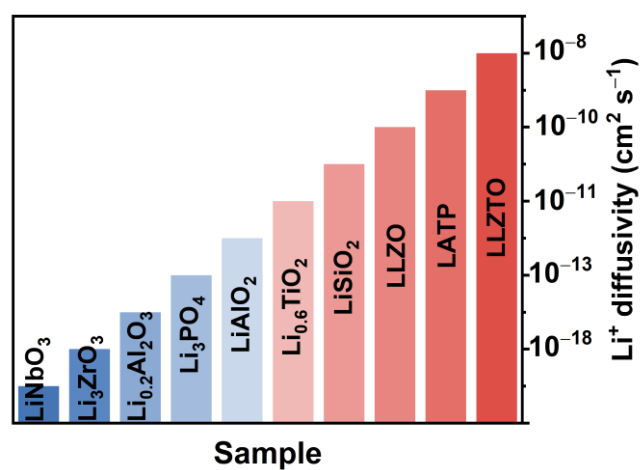
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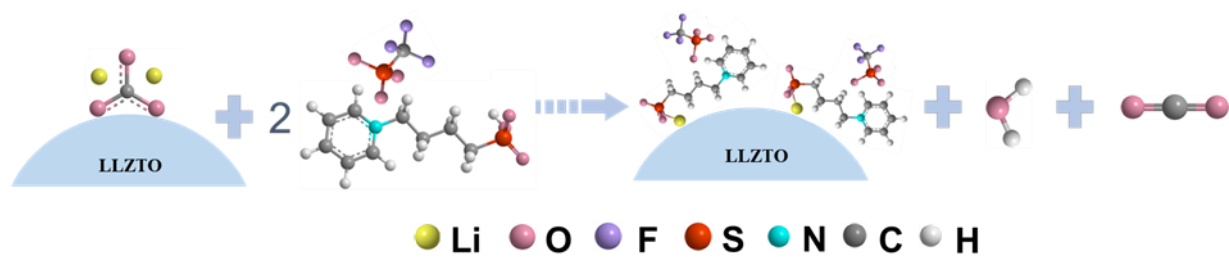
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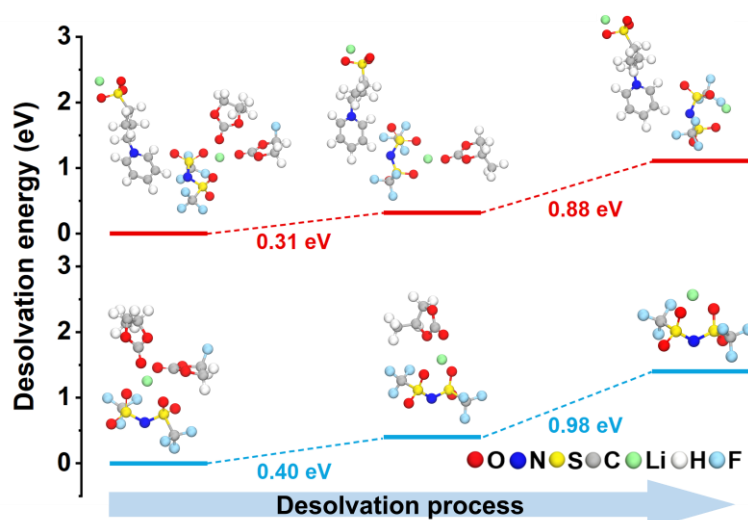
References



**Supplementary Fig. 1** | Li<sup>+</sup> ion diffusivity of inorganic ceramic oxide solid electrolytes and different coating materials. Source data are provided as a Source Data file.

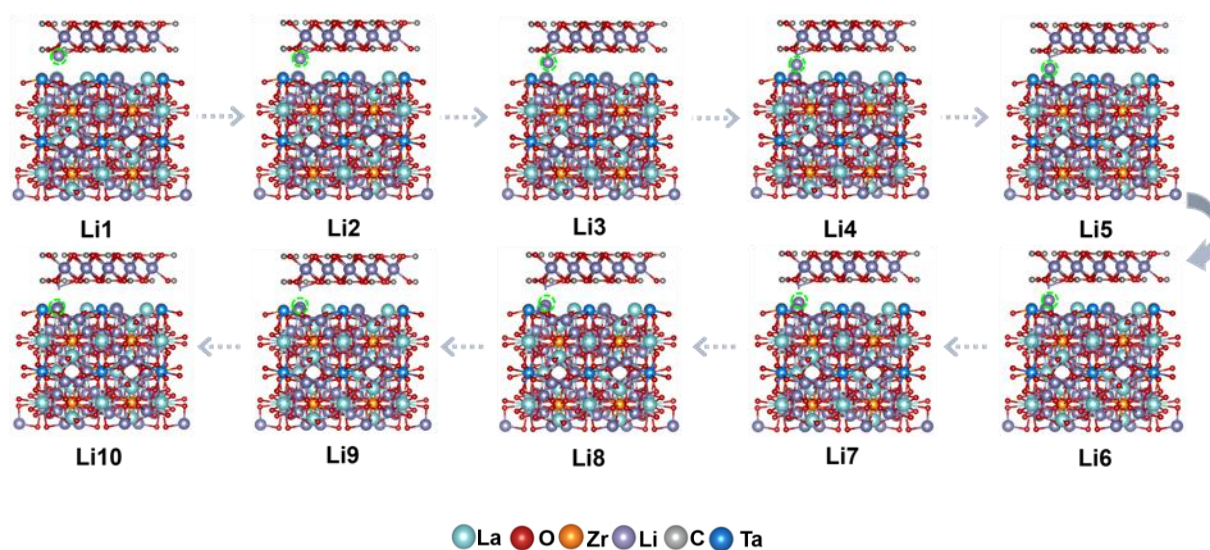


**Supplementary Fig. 2** | Synthesis diagram of PTS@LLZTO.

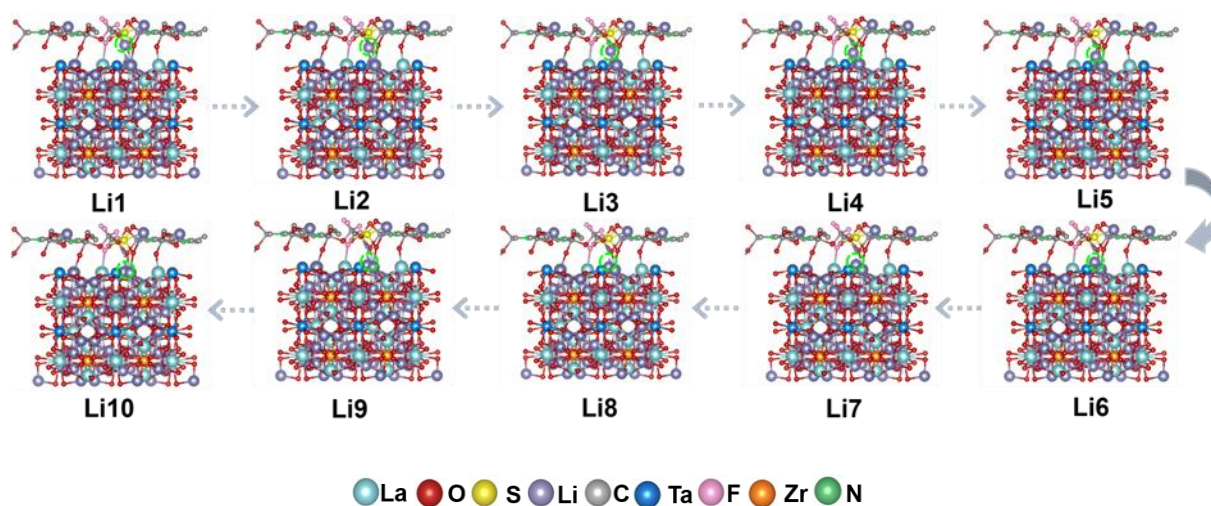


**Supplementary Fig. 3** | Calculated desolvation energies in the PTS-PVHL and PVHL ( $\text{Li}[(\text{TFSI})^-(\text{PC})(\text{FEC})(\text{PTS}_4(\text{N}^+))]^-$  and  $\text{Li}[(\text{TFSI})^-(\text{PC})(\text{FEC})]^-$  configurations are used for calculation). Source data are provided as a Source Data file.

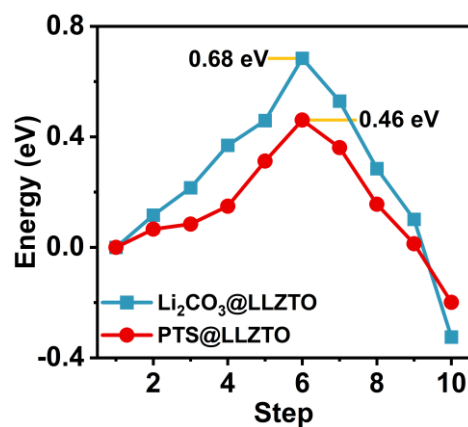
Note: In the pristine PVHL electrolyte system, the two-step desolvation energy barriers are 0.40 eV and 0.98 eV, while the corresponding barriers decreased to 0.31 eV and 0.88 eV in the PTS-modified PTS-PVHL electrolyte. The lower overall desolvation energy of the PTS-PVHL system clearly verifies that PTS can weaken the interaction between  $\text{Li}^+$  and solvent molecules, and effectively accelerate the desolvation kinetics.



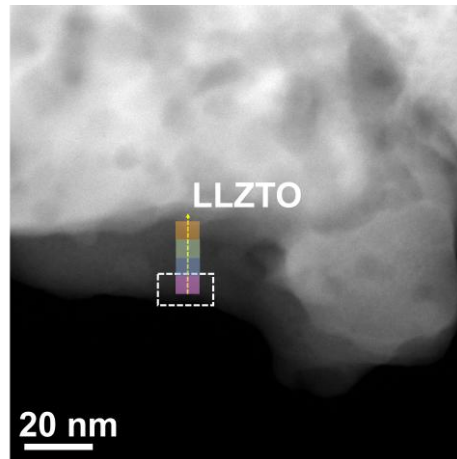
**Supplementary Fig. 4** | The coordination environment of Li1, Li2, Li3, Li4, Li5, Li6, Li7, Li8, Li9, and Li10 ions in  $\text{Li}_2\text{CO}_3@\text{LLZTO}$ .



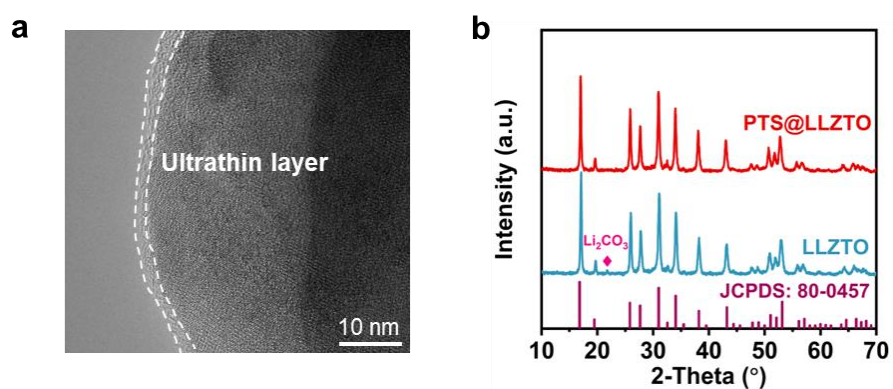
**Supplementary Fig. 5** | The coordination environment of Li1, Li2, Li3, Li4, Li5, Li6, Li7, Li8, Li9, and Li10 ions in PTS@LLZTO.



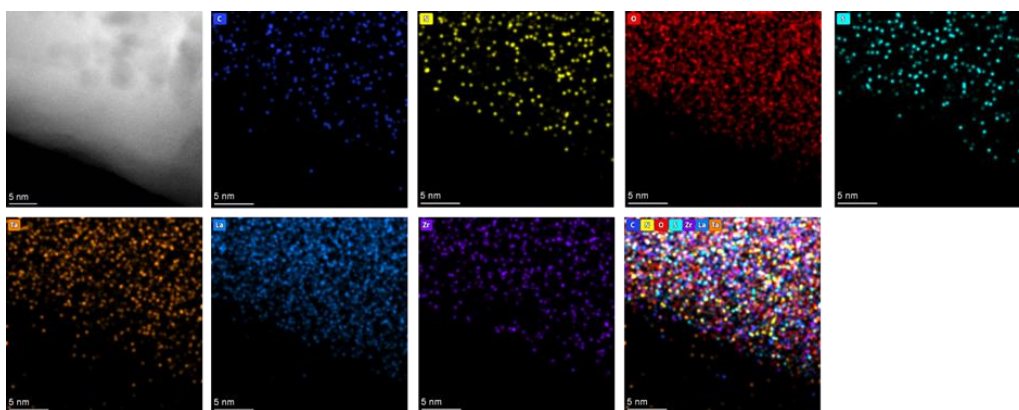
**Supplementary Fig. 6** | Energy profiles show the corresponding  $\text{Li}^+$  migration energy barriers. These calculations specifically describe  $\text{Li}^+$  transport under a solvent-free condition, where coordinating solvent molecules do not participate. Source data are provided as a Source Data file.



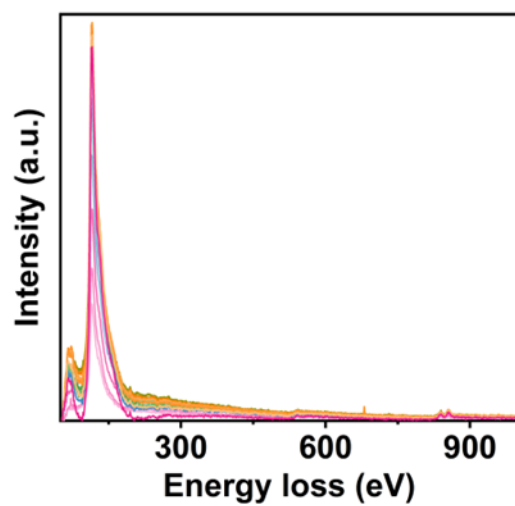
**Supplementary Fig. 7** | HAADF-STEM image of PTS@LLZTO.



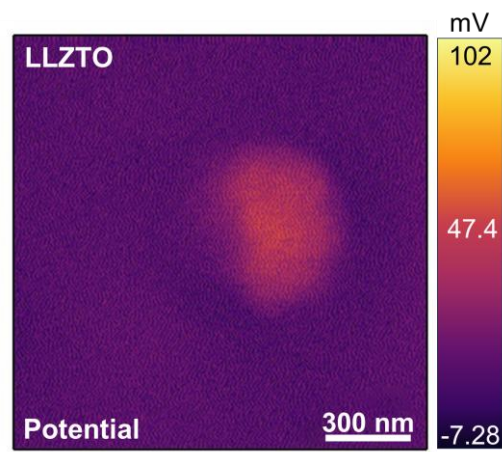
**Supplementary Fig. 8** | **a**, TEM image of PTS@LLZTO. **b**, XRD profiles of LLZTO and PTS@LLZTO. Source data are provided as a Source Data file.



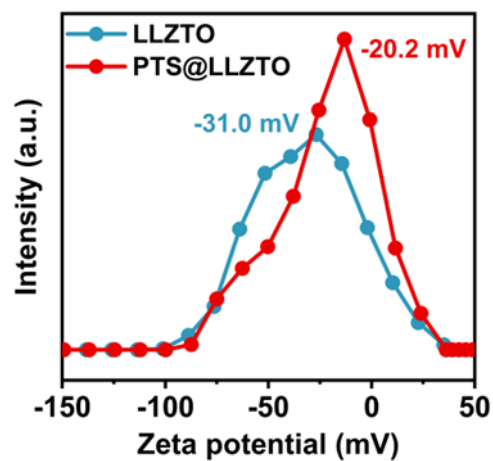
**Supplementary Fig. 9** | EDS elemental images of C, N, O, S, Ta, La, and Zr elements in PTS@LLZTO.



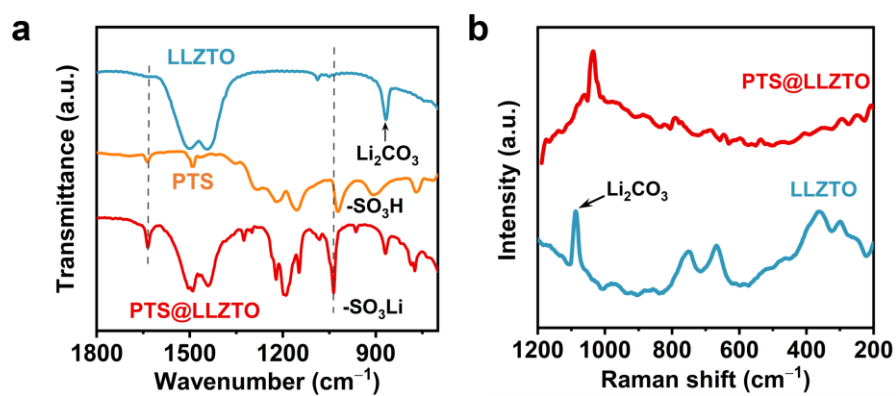
**Supplementary Fig. 10** | EELS profiles of PTS@LLZTO in different depth. Source data are provided as a Source Data file.



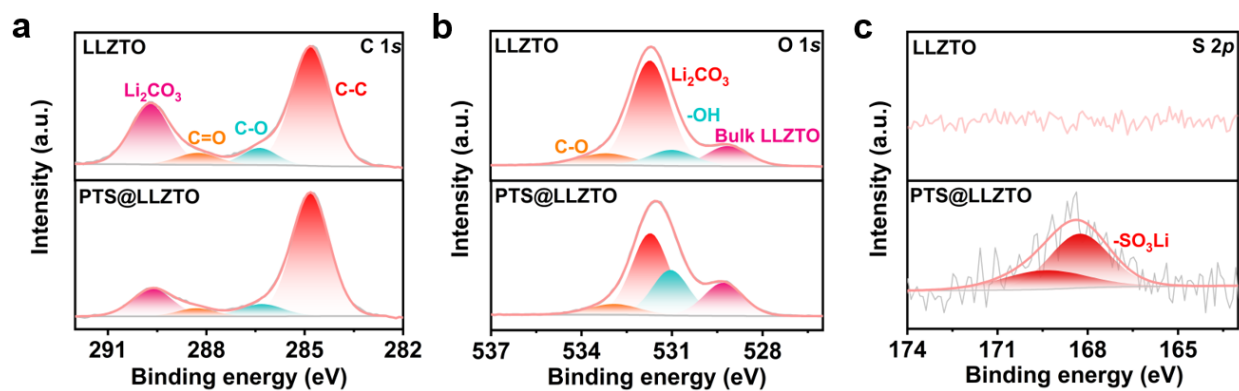
**Supplementary Fig. 11** | KPFM images of LLZTO.



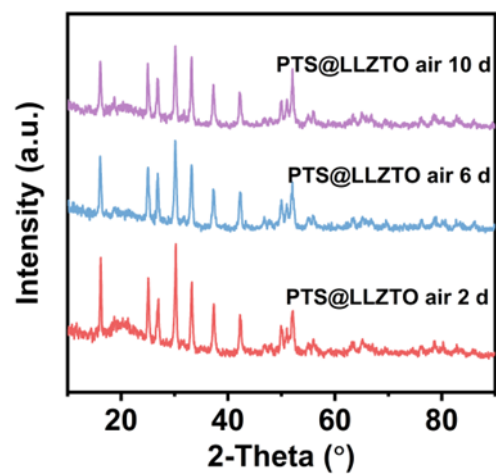
**Supplementary Fig. 12** | Zeta potential diagrams of LLZTO and PTS@LLZTO. Source data are provided as a Source Data file.



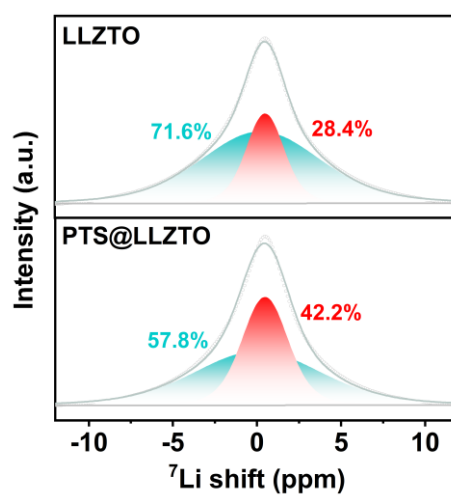
**Supplementary Fig. 13** | **a**, FTIR spectra of LLZTO, PTS, and PTS@LLZTO. **b**, Raman spectra of LLZTO and PTS@LLZTO. Source data are provided as a Source Data file.



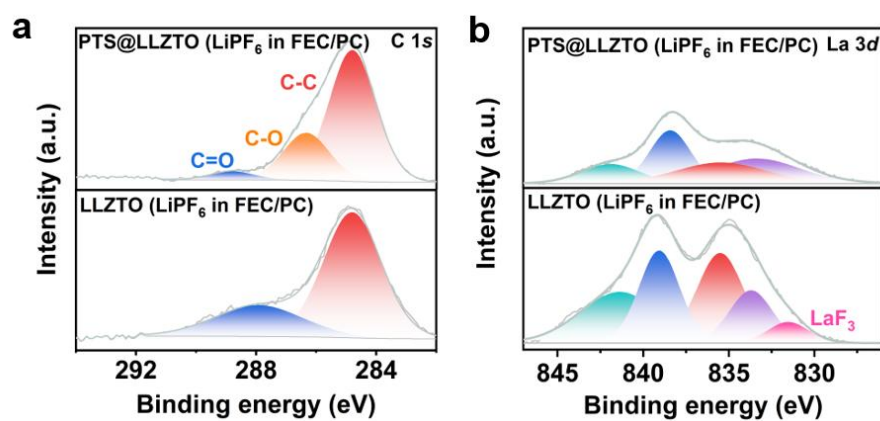
**Supplementary Fig. 14** | X-rays photoelectron spectra (XPS) of (a) C 1s, (b) O 1s, and (c) S 2p for LLZTO and PTS@LLZTO. Source data are provided as a Source Data file.



**Supplementary Fig. 15** | XRD patterns of PTS@LLZTO exposed to air for different times. Source data are provided as a Source Data file.

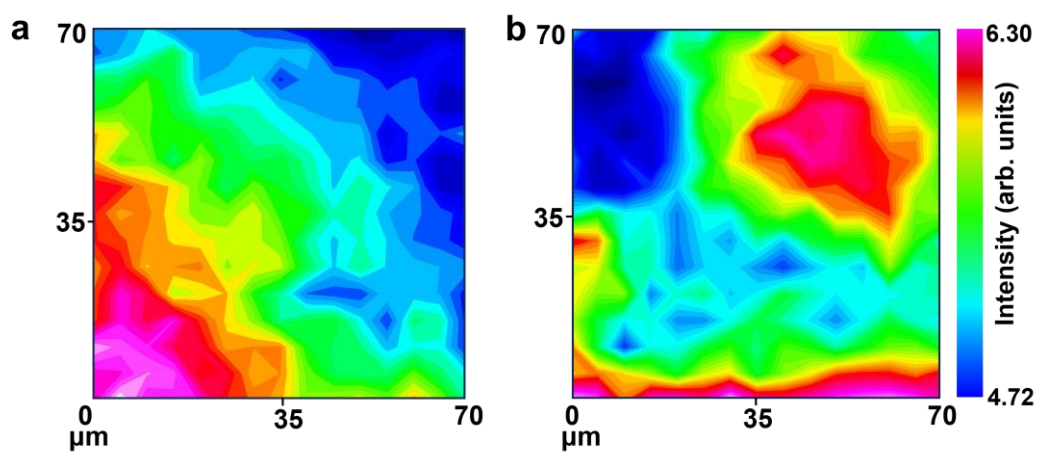


**Supplementary Fig. 16** |  $^7\text{Li}$  ss-NMR spectra of LLZTO and PTS@LLZTO powders. Source data are provided as a Source Data file.

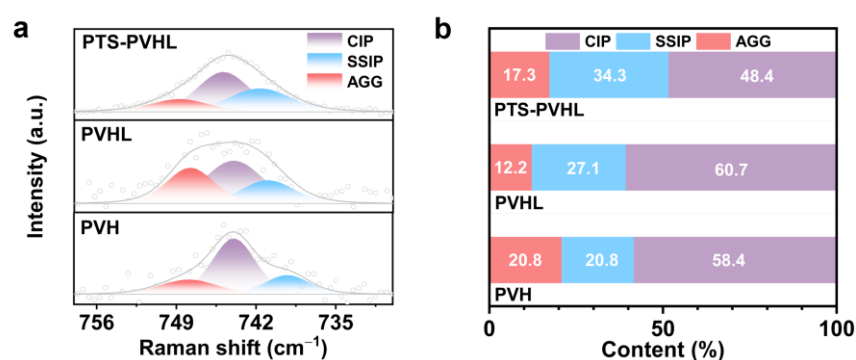


**Supplementary Fig. 17** | X-rays photoelectron spectra (XPS) of (a) C 1s and (b) La 3d of LLZTO and PTS@LLZTO immersed in liquid electrolytes for 24 h. Source data are provided as a Source Data file.

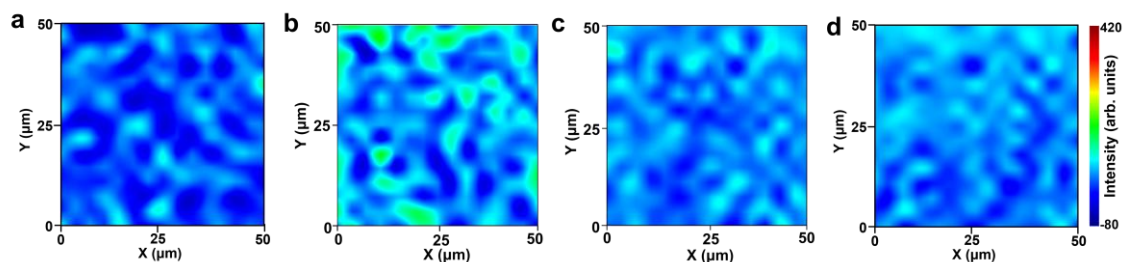
Note: To accelerate electrolyte decomposition, LiPF<sub>6</sub> was employed as the lithium salt (1 M LiPF<sub>6</sub> in FEC: PC, 1:1, wt.%).



**Supplementary Fig. 18** | Synchrotron-based infrared mapping results of (a) PTS-PVHL and (b) PVHL in the  $1350\text{ cm}^{-1}$  of TFSI<sup>-</sup>.

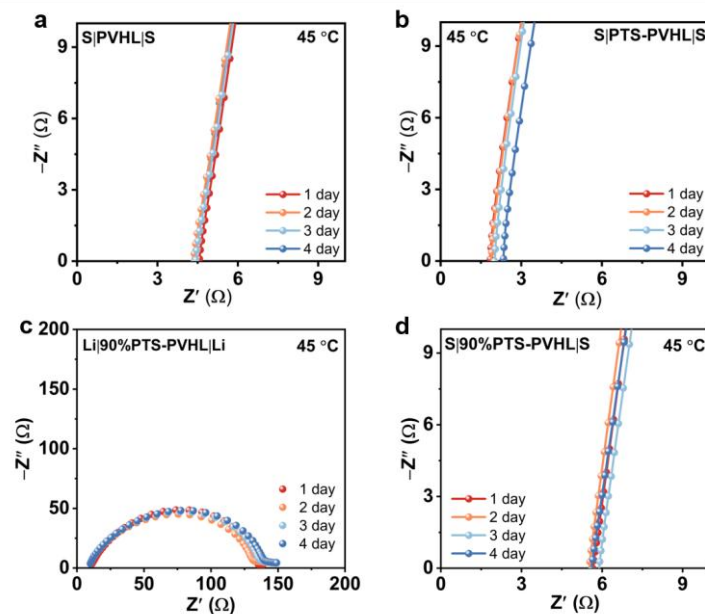


**Supplementary Fig. 19** | **a**, Raman spectra of PTS-PVHL, PVHL, and PVH electrolytes. **b**, Summary of the proportion of SSIP, CIP, and AGG. Source data are provided as a Source Data file.

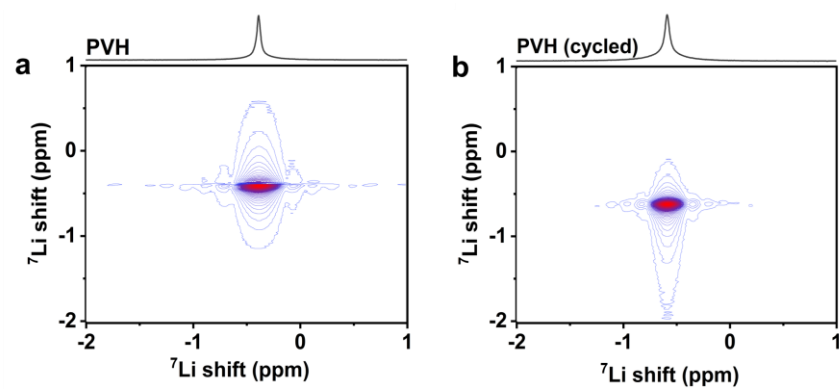


**Supplementary Fig. 20** | Raman mappings in the range of  $730\text{--}770\text{ cm}^{-1}$  of the (a) PVH membrane, (b) PVHL membrane, (c) PTS-PVHL membrane, and (d) PTS-PVHL after cycling. (Li||NCM811 cell,  $1\text{ C}/200\text{ mA g}^{-1}$ ,  $2.8\text{ V--}4.3\text{ V}$ , 20 cycles) at  $25\text{ }^{\circ}\text{C}$ .

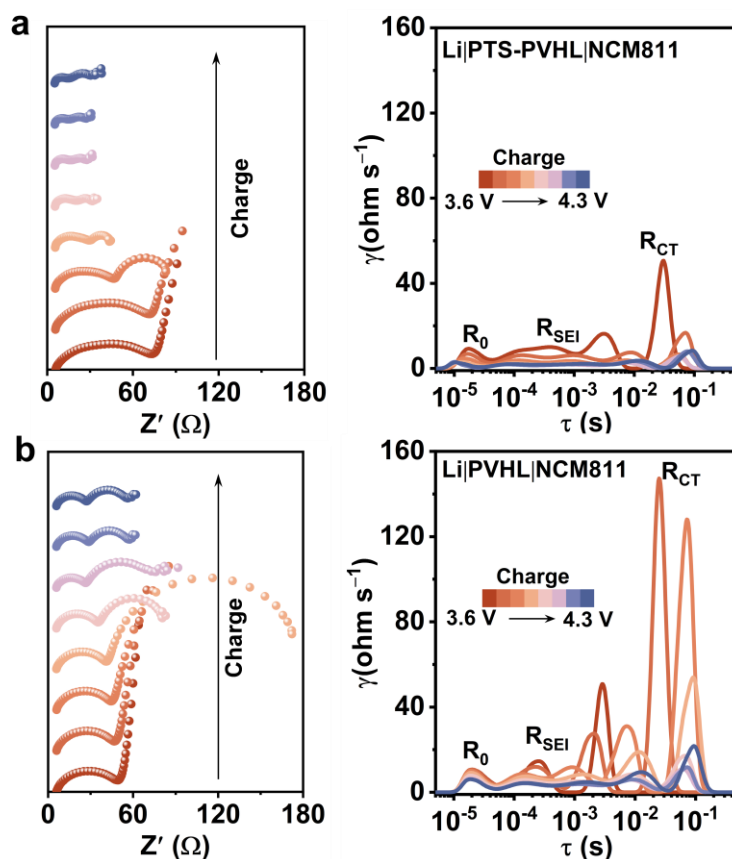
Note: The PTS alkyl chain acts as a nonpolar hydrocarbon segment, enabling repulsion toward most polar organic species. Combined with the cell impedance and interfacial chemistry analyses, these results indicate that PTS@LLZTO constructs homogeneous and interconnected  $\text{Li}^{+}$ -transport pathways within the composite phase. The solvent-phobic nature of PTS further stabilizes these pathways, thereby reducing electrolyte consumption. The presence and uniform distribution of lithium salts in the solvent repellent layer of the electrolyte before and after cycling indicate the stability of the electrolyte structure and composition.



**Supplementary Fig. 21** | Impedance spectra (presented as Nyquist plots) of S||S symmetrical cells measured at the same time over 4 days at 45 °C, containing (a) PVHL and (b) PTS-PVHL. Impedance spectra (presented as Nyquist plots) of (c) Li|90%PTS-PVHL|Li and (d) S|90%PTS-PVHL|S symmetrical cells measured at the same time over 4 days at 45 °C. Source data are provided as a Source Data file.

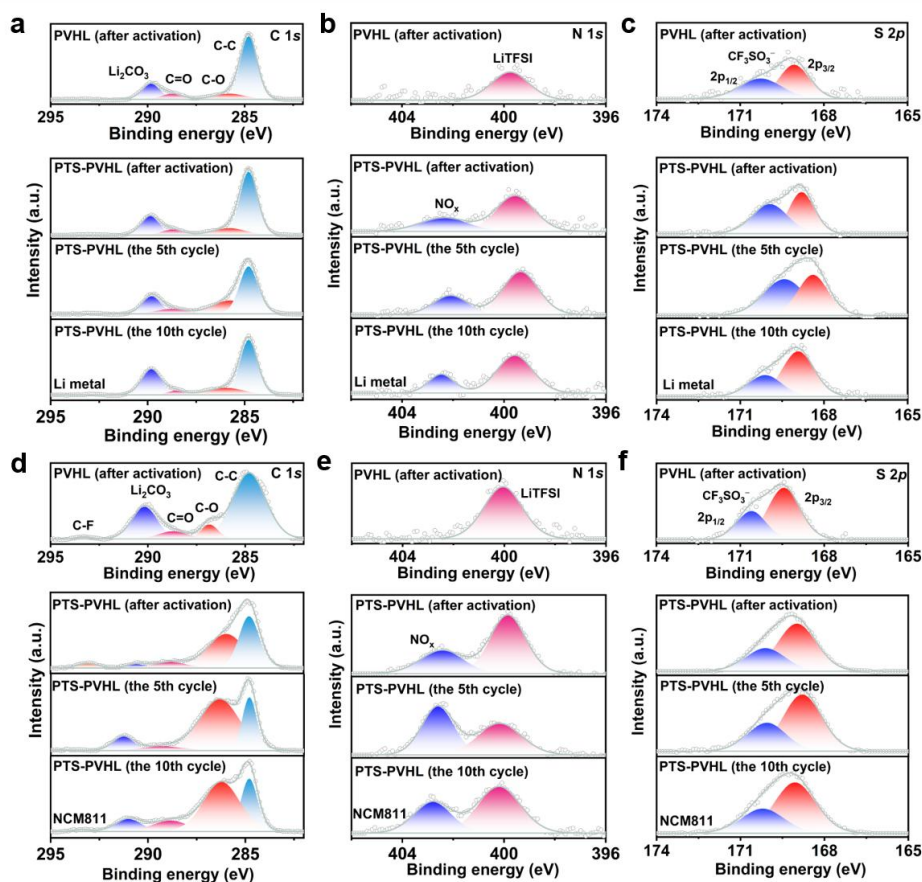


**Supplementary Fig. 22** | 2D  $^7\text{Li}$ - $^7\text{Li}$  EXSY spectra of PVH (a) before and (b) after cycling (Li||NCM811 cell, 2.8 V-4.3 V, 0.2 C/40 mA g<sup>-1</sup>, 3 cycles) at 25 °C. Source data are provided as a Source Data file.



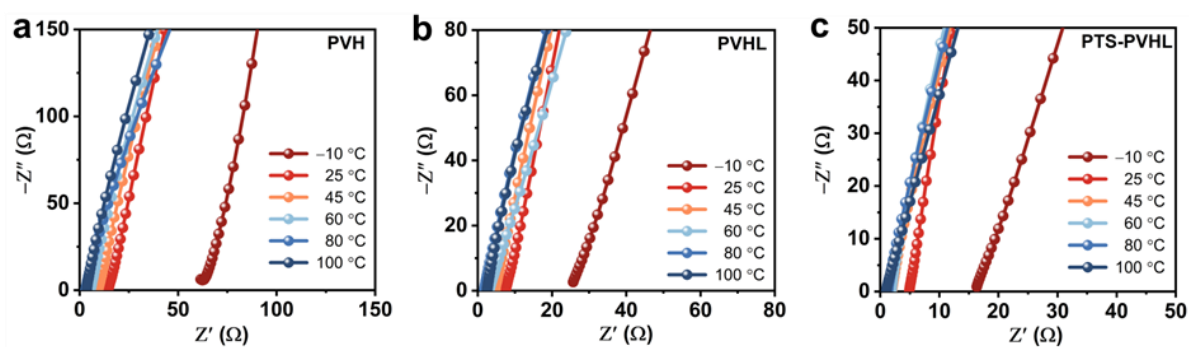
**Supplementary Fig. 23** | In situ EIS and DRT of **a** Li|PTS-PVHL|NCM811 and **b** Li|PVHL|NCM811 cells (0.2 C/40 mA g<sup>-1</sup>, 2.8 V-4.3 V) at 25 °C. Source data are provided as a Source Data file.

Note: During high-voltage charging, the full cell with PTS-PVHL electrolyte maintains stable interfacial and charge-transfer resistance. In contrast, the cell based on pure PVHL exhibits a evident impedance rise with increasing voltage, indicating severe degradation of the interfacial structure and charge-transfer kinetics. Further DRT analysis reveals that the interfacial film resistance ( $R_{SEI}$ ) of the PTS-PVHL cell remains stable under high voltage. This confirms that the PTS-PVHL electrolyte effectively suppresses high-voltage interfacial side reactions and preserves the integrity of the electrode-electrolyte interface as well as favorable charge-transfer kinetics. By comparison, the PVHL cell shows a sharp increase in charge-transfer resistance ( $R_{CT}$ ) and severely deteriorated reaction kinetics, reflecting poor high-voltage tolerance, insufficient interfacial stability, and pronounced parasitic side reactions.

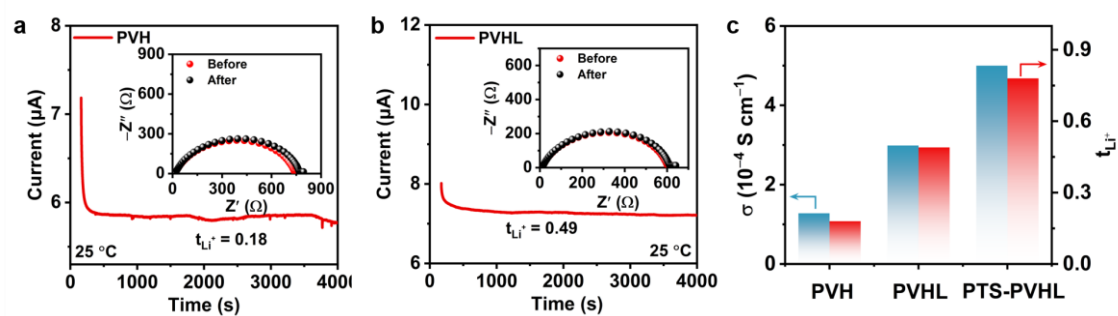


**Supplementary Fig. 24** | XPS profiles of **a** C 1s, **b** N 1s, and **c** S 2p for Li metal negative electrodes with PVHL and PTS-PVHL after 3 activation cycles, and PTS-PVHL after 5 and 10 cycles within 2.8 V-4.3 V at 25 °C (Li||NCM811 cell, 1 C/200 mA g<sup>-1</sup>). XPS profiles of **d** C 1s, **e** N 1s, and **f** S 2p for NCM811 positive electrodes with PVHL and PTS-PVHL after 3 activation cycles, and PTS-PVHL after 5 and 10 cycles within 2.8 V-4.3 V at 25 °C (Li||NCM811 cell, 1 C/200 mA g<sup>-1</sup>). Source data are provided as a Source Data file.

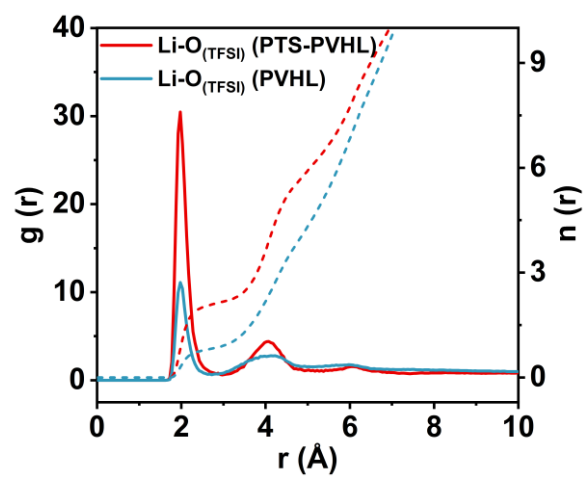
Note: For SEI, the decrease in the N/S ratio with increasing cycles indicates that the NO<sub>x</sub> species mainly originate from the decomposition of anions. Meanwhile, the contents of organic components and sulfur-containing species in the positive electrode-electrolyte interface remain stable throughout cycling, demonstrating that the electrode interface maintains favorable structural stability after activation.



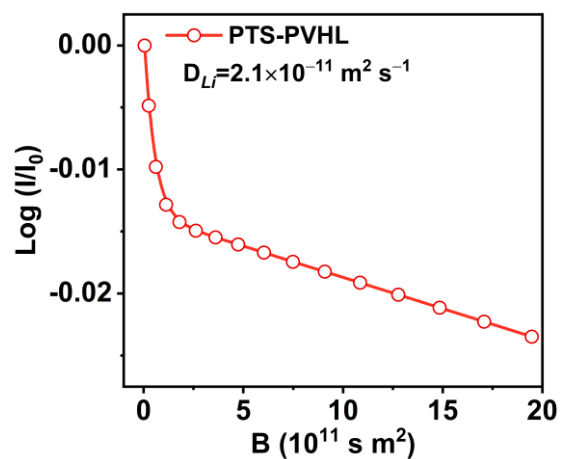
**Supplementary Fig. 25** | Impedance spectra presented as Nyquist plots of S||S symmetric cells at different temperatures using (a) PVH, (b) PVHL, and (c) PTS-PVHL electrolytes. Source data are provided as a Source Data file.



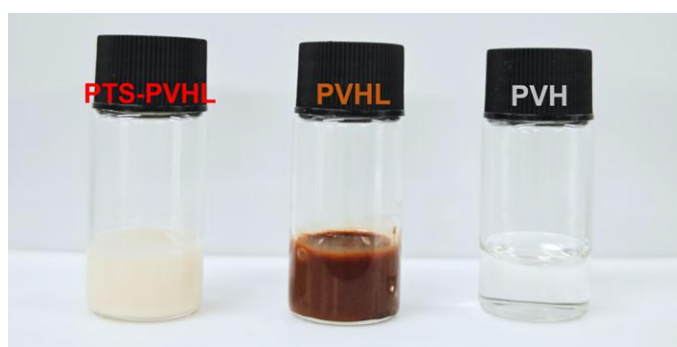
**Supplementary Fig. 26** | Polarization curves of (a) Li|PVH|Li, (b) Li|PVHL|Li symmetrical cells at 25 °C. Impedance spectra of Li||Li cells before and after polarization. **c**, Summary of ionic conductivity and  $\text{Li}^+$  transference number at 25 °C. Source data are provided as a Source Data file.



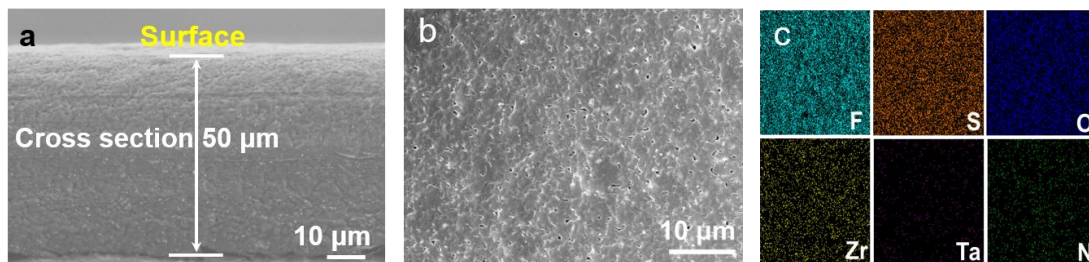
**Supplementary Fig. 27** | Radial distribution function (RDF) and coordination number (CN) for PVHL and PTS-PVHL electrolytes. Source data are provided as a Source Data file.



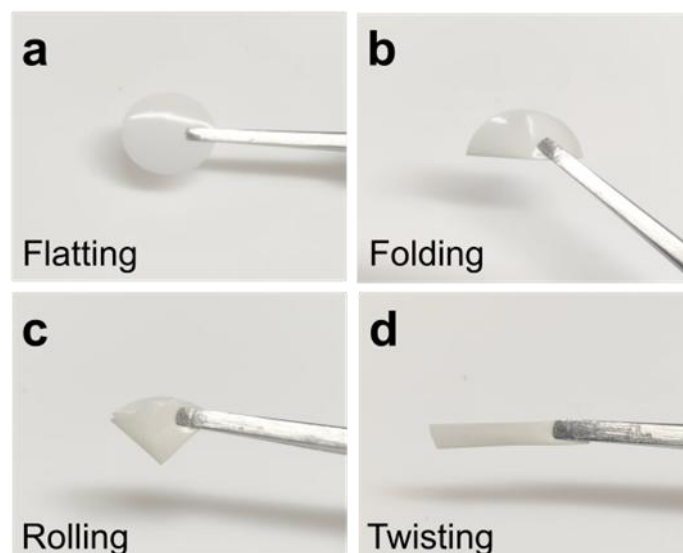
**Supplementary Fig. 28** | Diffusion plots of  $^7\text{Li}$  in the PTS-PVHL electrolyte measured by PFG-NMR. Source data are provided as a Source Data file.



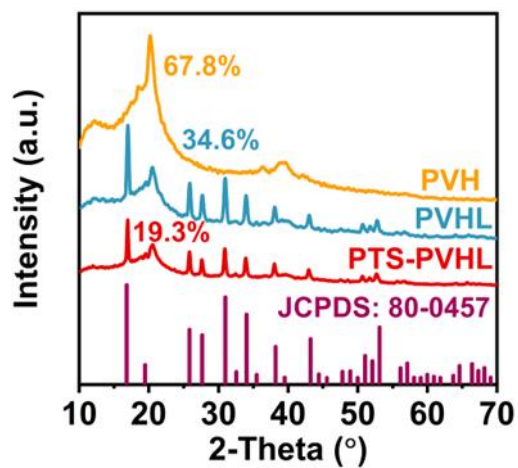
**Supplementary Fig. 29** | Optical images of PTS-PVHL, PVHL and PVH electrolytes. No evident defluorination was observed in the PTS-modified LLZTO-containing solution, demonstrating the substantially enhanced composite compatibility.



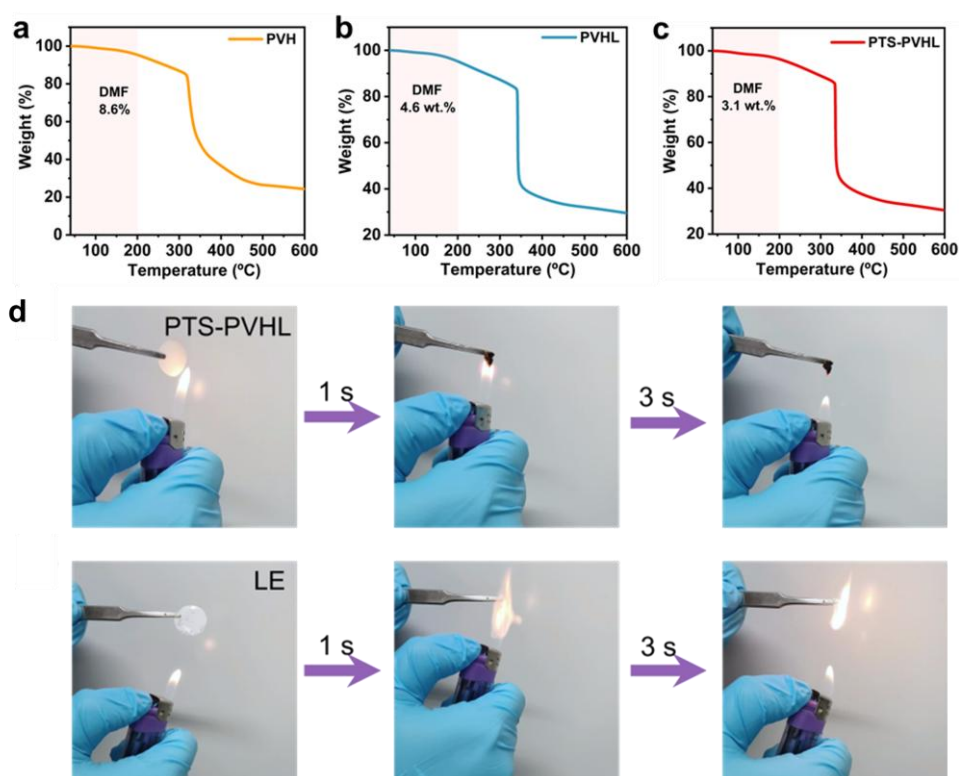
**Supplementary Fig. 30** | **a**, SEM images of the cross-section and **b**, the surface of the PTS-PVHL. **c**, The corresponding EDS elemental mappings of PTS-PVHL electrolyte. No obvious nanoparticle aggregation or precipitation was observed, confirming the favorable organic-inorganic compatibility of the composite system.



**Supplementary Fig. 31** | Optical images with different states of the PTS-PVHL membrane **(a)** flatting, **(b)** folding, **(c)** rolling, and **(d)** twisting. The membrane can withstand folding and bending, demonstrating its favorable flexibility.



**Supplementary Fig. 32** | XRD patterns of PVH, PVHL, and PTS-PVHL. The reduced crystalline phase indicates an increased amorphous fraction, which is favorable for ion transport. Source data are provided as a Source Data file.

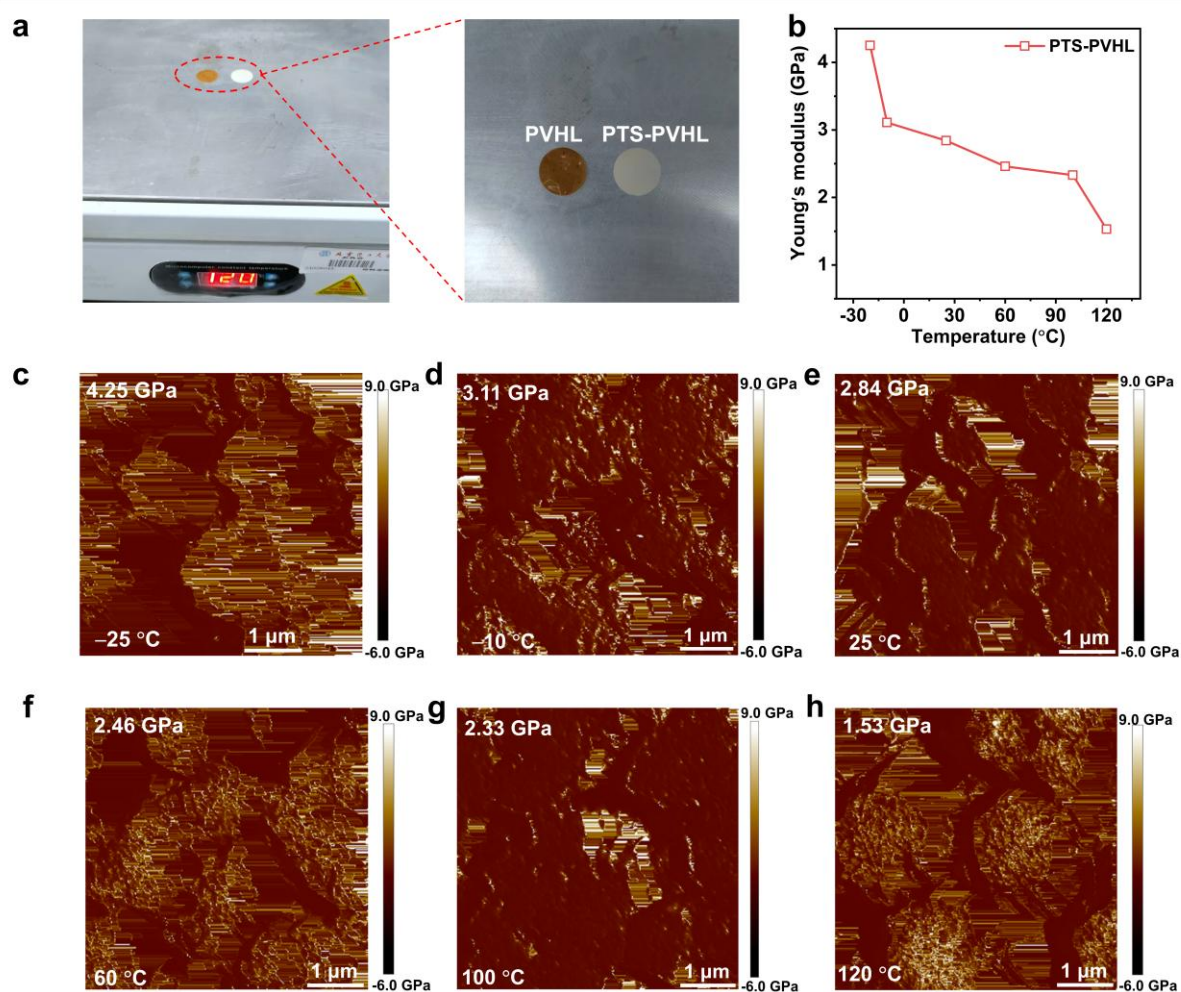


**Supplementary Fig. 33** | TGA curves of (a) PVH, (b) PVHL, and (c) PTS-PVHL electrolytes. Source data are provided as a Source Data file. **d**, Flammability tests of the PTS-PVHL and liquid electrolyte (LE) electrolytes.

Note: The alkyl chain in PTS is a nonpolar hydrocarbon skeleton, while carbonate-based electrolyte solvents are highly polar molecules. The polarity difference between them prevents the formation of stable dipole-dipole or hydrogen-bonding interactions; polar solvent molecules preferentially self-associate rather than wet or adsorb onto the nonpolar alkyl chain regions, fundamentally inhibiting solvent adhesion and retention. Meanwhile, the alkyl chains can spontaneously assemble into a low-surface-energy hydrophobic layer at the electrolyte/electrode interface and on the surface of inorganic fillers, making it difficult for polar solvents to spread and wet these low-energy interfaces, thus preventing solvent molecules from penetrating into the electrolyte interior and remaining. In addition, the coiled conformation of long alkyl chains forms a dense steric hindrance network, exerting a physical barrier effect on polar solvent molecules and effectively blocking their diffusion and penetration into the electrolyte interior, further avoiding solvent enrichment and entrapment in the system. The synergistic effect of these multiple mechanisms ultimately results in extremely low solvent residue in the as-prepared electrolyte membrane.

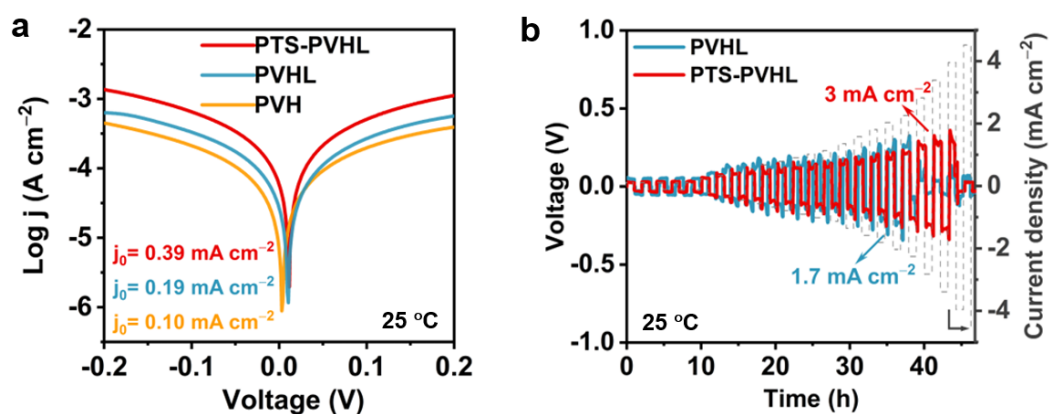
The weight percentage of residual DMF was derived from the mass loss between 40 °C and 200 °C, where only DMF volatilization occurs and polymer backbone decomposition is absent.

$$w_{\text{residual DMF}} = \frac{m_{40^{\circ}\text{C}} - m_{200^{\circ}\text{C}}}{m_{30^{\circ}\text{C}}} \times 100\%$$

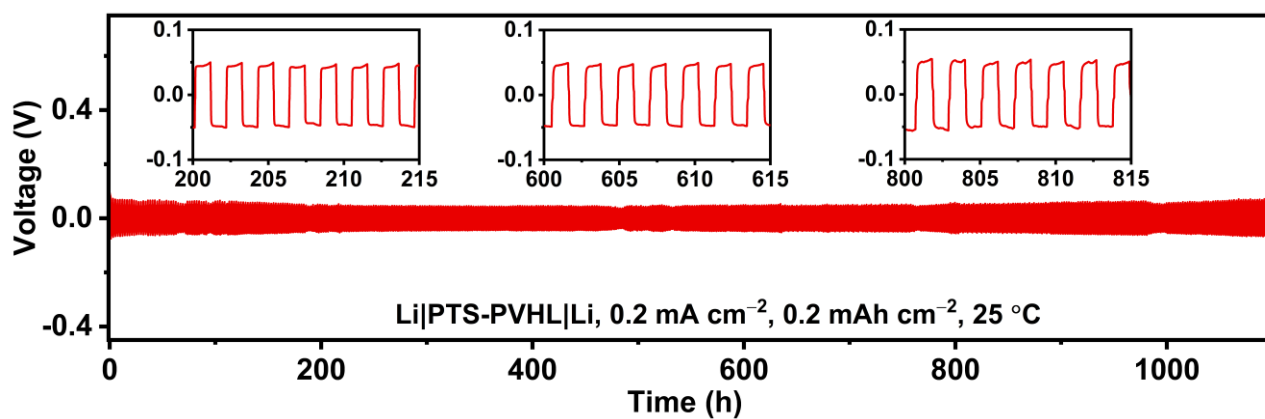


**Supplementary Fig. 34** | **a**, Picture of electrolyte membrane heated on a 120 °C heating table. **b**, Comparison of Young's modulus of PTS-PVHL membrane at different temperatures. Source data are provided as a Source Data file. **c-h**, Young's modulus of PTS-PVHL membrane at different temperatures.

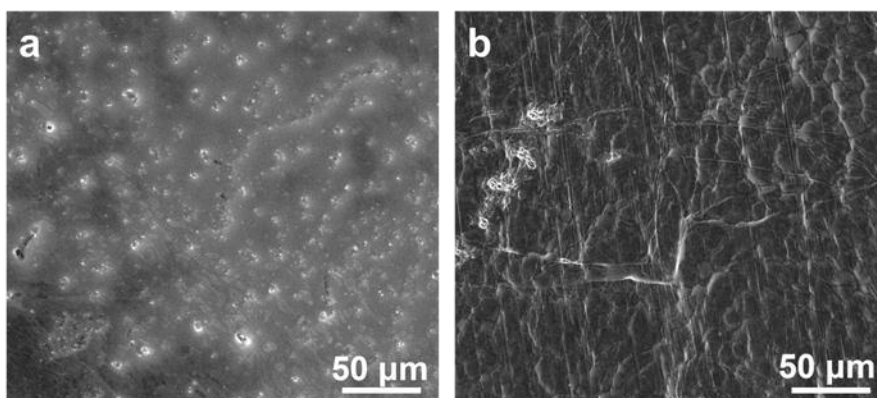
Note: The PTS-PVHL electrolyte exhibited favorable mechanical strength and good high-temperature thermal stability over a wide temperature range.



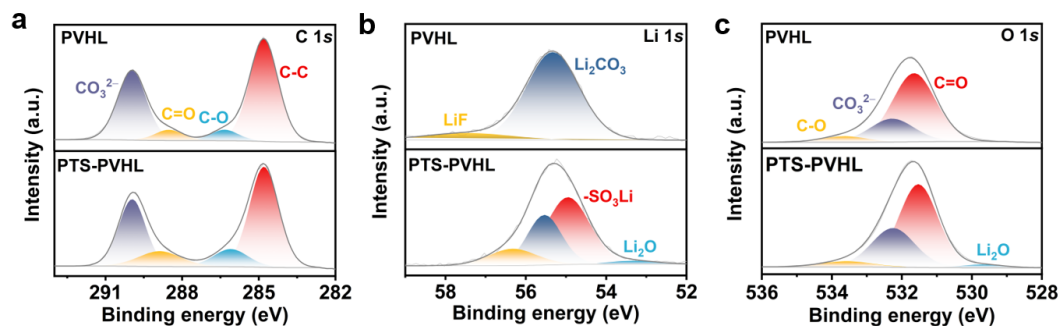
**Supplementary Fig. 35** | **a**, Tafel plots related to PTS-PVHL, PVHL, and PVH electrolytes at 25 °C. **b**, Voltage profiles of Li|PVHL|Li and Li|PTS-PVHL|Li symmetric cells upon galvanostatic plating/stripping at the current densities marked in the charts at 25 °C. Source data are provided as a Source Data file.



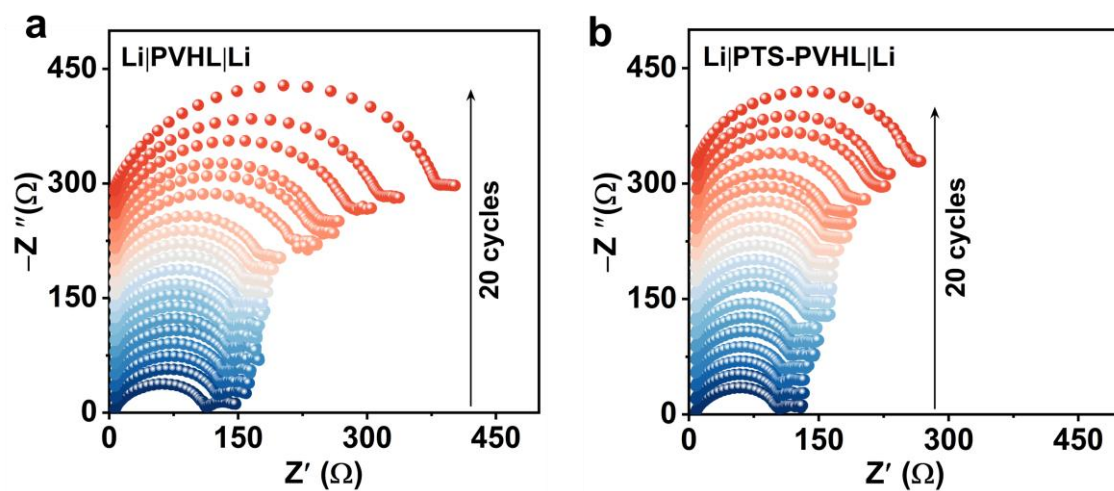
**Supplementary Fig. 36** | Voltage profiles of Li||Li symmetric cells with PTS-PVHL electrolyte, upon galvanostatic plating/stripping at 0.2 mA cm<sup>-2</sup>, 0.2 mAh cm<sup>-2</sup> at 25 °C. The 3 insets show enlarged voltage profiles for 200-215, 600-615, and 800-815 hours. Source data are provided as a Source Data file.



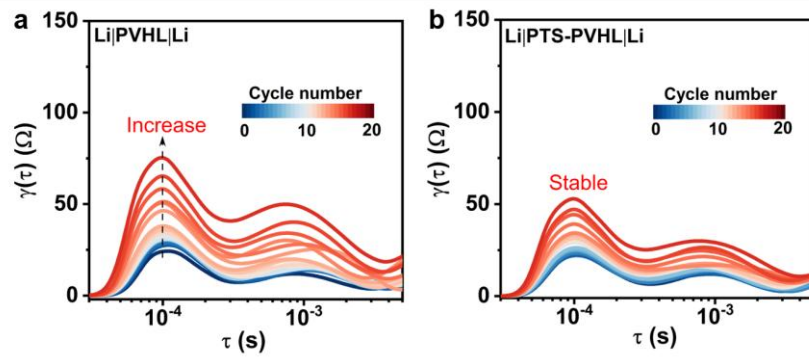
**Supplementary Fig. 37** | SEM images of the cycled Li metal for the Li||Li symmetric cells with (a) PTS-PVHL and (b) PVHL electrolytes (Li||Li symmetric cell,  $0.1 \text{ mA cm}^{-2}$ ,  $0.1 \text{ mAh cm}^{-2}$ , 100 cycles) at  $25^\circ\text{C}$ .



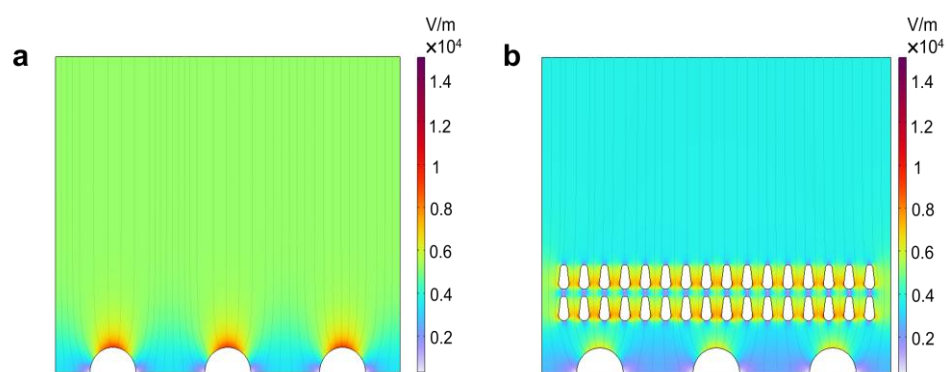
**Supplementary Fig. 38** | X-rays photoelectron spectra (XPS) of (a) C 1s, (b) Li 1s, and (c) O 1s on the Li metal surface after plating/stripping of Li||Li symmetric cells for PVHL and PTS-PVHL (Li||Li symmetric cell,  $0.1 \text{ mA cm}^{-2}$ ,  $0.1 \text{ mAh cm}^{-2}$ , 100 cycles) at  $25^\circ\text{C}$ . Source data are provided as a Source Data file.



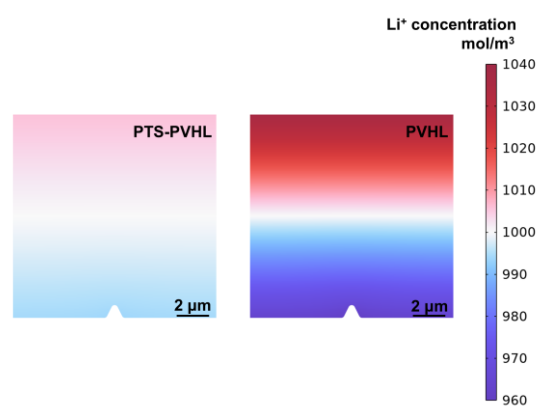
**Supplementary Fig. 39** | Serial impedance spectra presented as Nyquist plots reflecting the first 20 cycles of (a) Li|PVHL|Li and (b) Li|PTS-PVHL|Li symmetric cells upon galvanostatic plating/stripping at  $0.2 \text{ mA cm}^{-2}$  and  $0.2 \text{ mAh cm}^{-2}$  at  $25^\circ\text{C}$ . The spectra were collected at the end of each cycle. Source data are provided as a Source Data file.



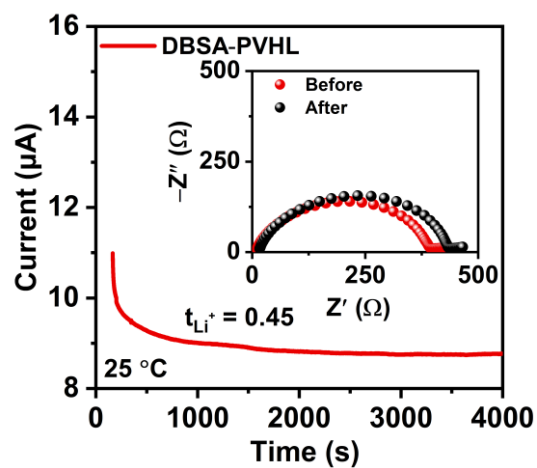
**Supplementary Fig. 40** | Time-dependent DRT curves of (a) Li|PVHL|Li and (b) Li|PTS-PVHL|Li cells. Source data are provided as a Source Data file.



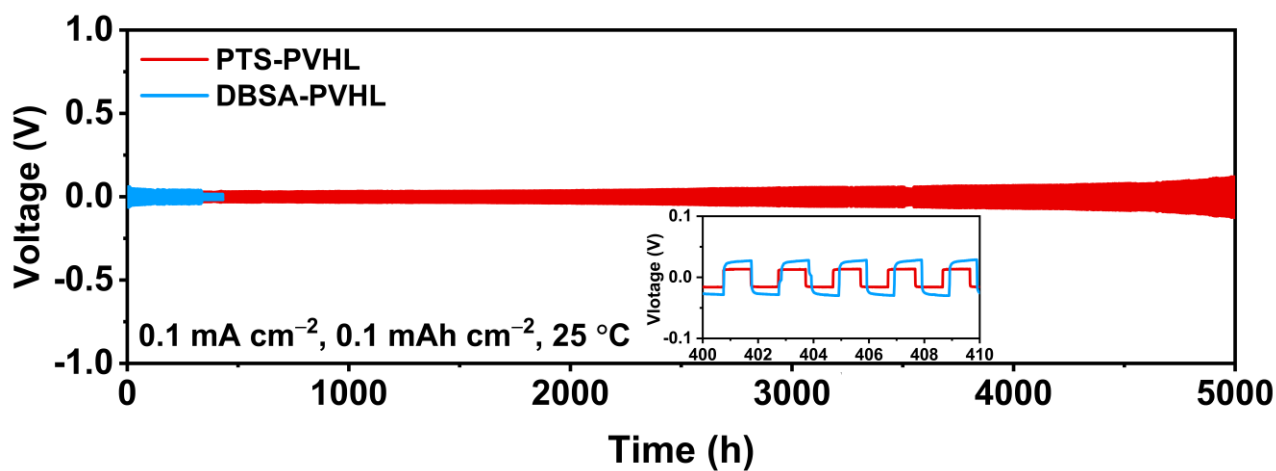
**Supplementary Fig. 41 | a, b, COMSOL simulations of electric field distribution at the Li/PVHL interface and Li/PTS-PVHL interface.**



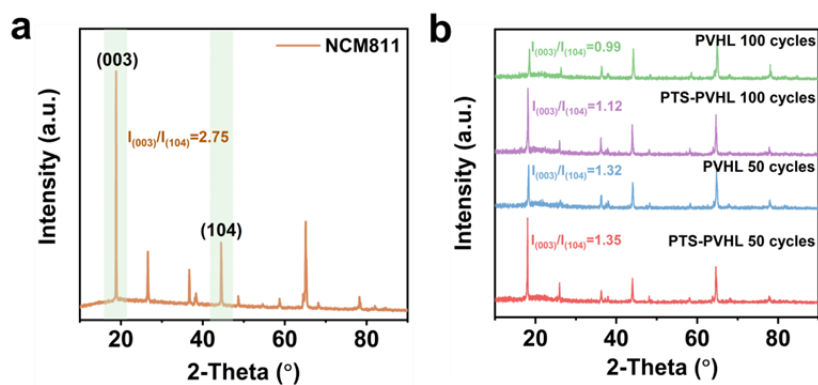
**Supplementary Fig. 42** | COMSOL Multiphysics finite-element method simulation (FEMS) of the  $\text{Li}^+$  concentration distribution based on PTS-PVHL and PVHL.



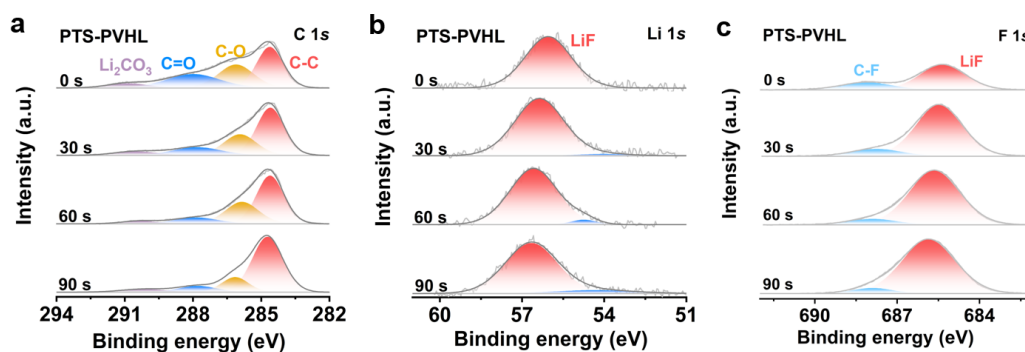
**Supplementary Fig. 43** | Polarization curve of Li|DBSA-PVHL|Li symmetrical cell at 25 °C. The illustration shows impedance spectra of symmetric cells before and after polarization. Source data are provided as a Source Data file.



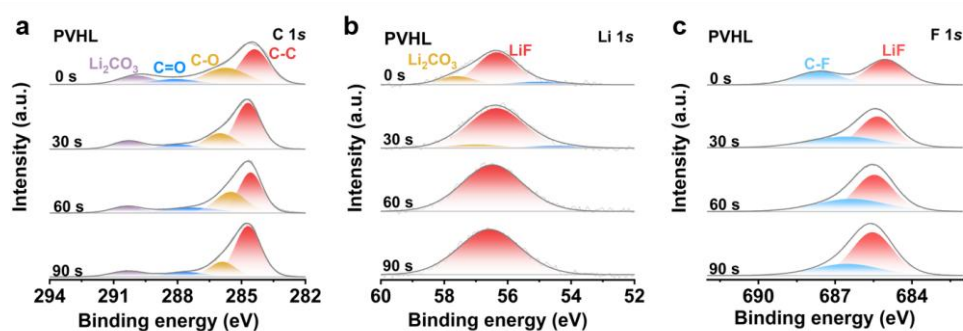
**Supplementary Fig. 44** | Comparison between symmetric Li||Li cells containing PTS-PVHL and DBSA-PVHL electrolytes through their voltage profiles measured during their galvanostatic plating/stripping at  $0.1 \text{ mA cm}^{-2}$  and  $0.1 \text{ mAh cm}^{-2}$  at  $25^\circ\text{C}$ . Source data are provided as a Source Data file.



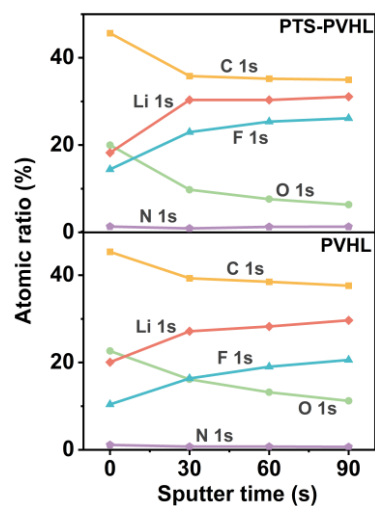
**Supplementary Fig. 45** | **a**, XRD pattern of NCM811 before cycling. **b**, XRD patterns of Li|PTS-PVHL|NCM811 and Li|PVHL|NCM811 cells after 50 and 100 cycles (2.8 V-4.3 V, 1 C/200 mA g<sup>-1</sup>, 25 °C), respectively. Source data are provided as a Source Data file.



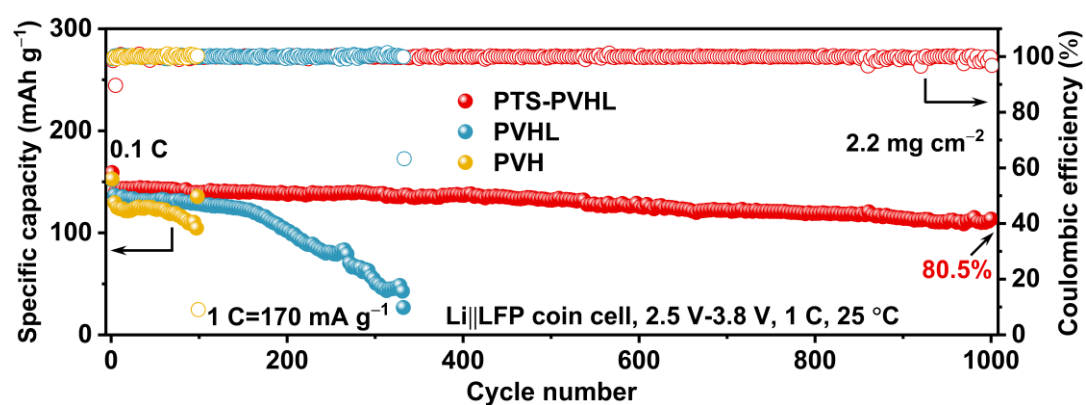
**Supplementary Fig. 46** | XPS depth profiles of NCM811 positive electrodes harvested from Li||NCM811 cells using PTS-PVHL electrolyte after 20 cycles at 1 C/200 mA g<sup>-1</sup> (2.8 V-4.3 V, 25 °C) of (a) C 1s, (b) Li 1s, (c) F 1s. Source data are provided as a Source Data file.



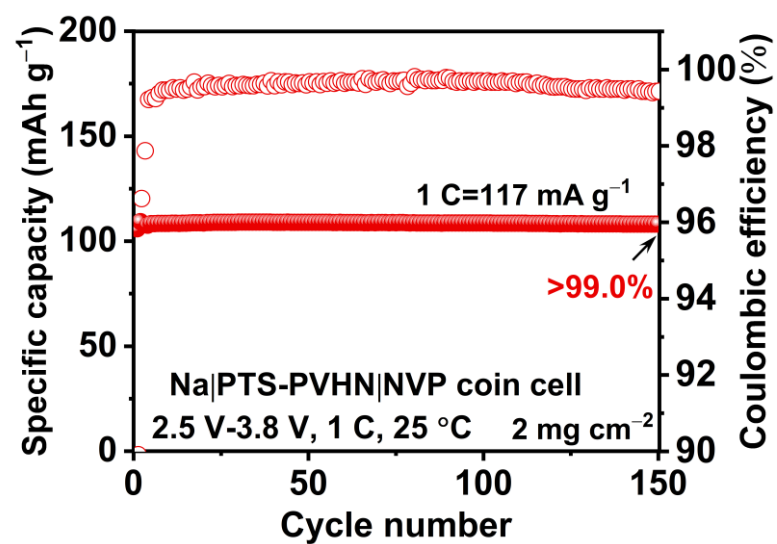
**Supplementary Fig. 47** | XPS depth profiles of NCM811 positive electrodes harvested from Li||NCM811 cells using PVHL electrolyte after 20 cycles at 1 C/200 mA g<sup>-1</sup> (2.8 V-4.3 V, 25 °C) of (a) C 1s, (b) Li 1s, (c) F 1s. Source data are provided as a Source Data file.



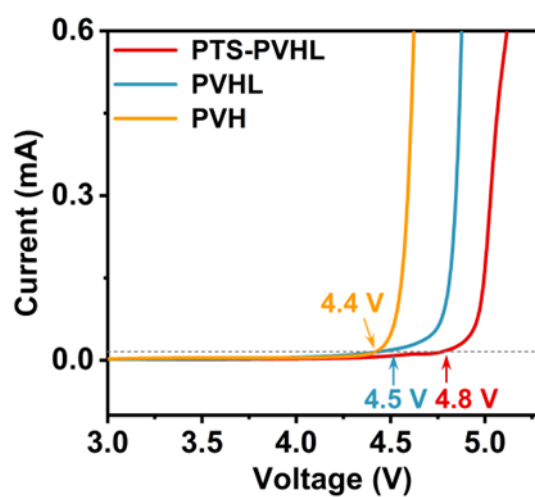
**Supplementary Fig. 48** | Quantified atomic ratios of the NCM811 positive electrode-electrolyte interface formed in PTS-PVHL and PVHL at varying sputter times (Li||NCM811 cell, 1 C/200 mA g<sup>-1</sup>, 2.8 V-4.3 V, 20 cycles, 25 °C). Source data are provided as a Source Data file.



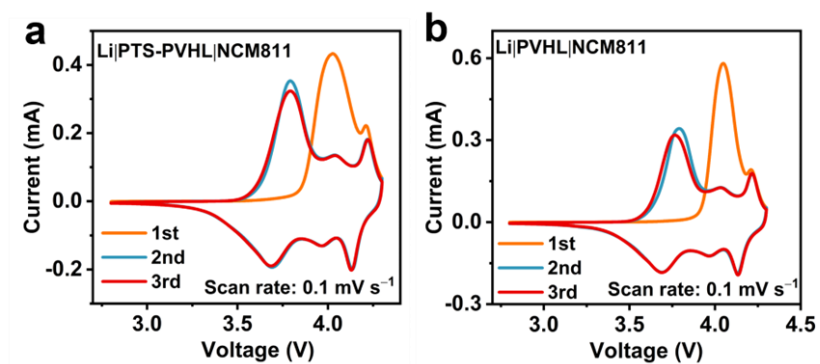
**Supplementary Fig. 49** | Cycling performance of Li||LFP cells with PVH, PVHL, and PTS-PVHL electrolytes at 1 C (1 C=170 mA g<sup>-1</sup>) between 2.5 V-3.8 V at 25 °C. Source data are provided as a Source Data file.



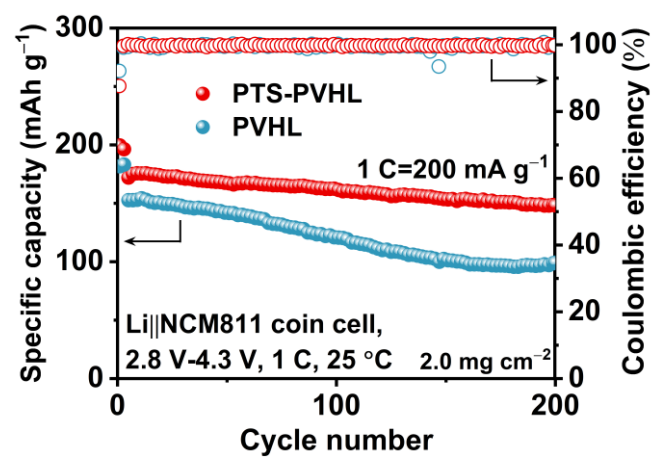
**Supplementary Fig. 50** | Cycling performance of Na|PTS-PVHN|NVP at 1 C and 2.5-3.8 V at 25 °C. Source data are provided as a Source Data file.



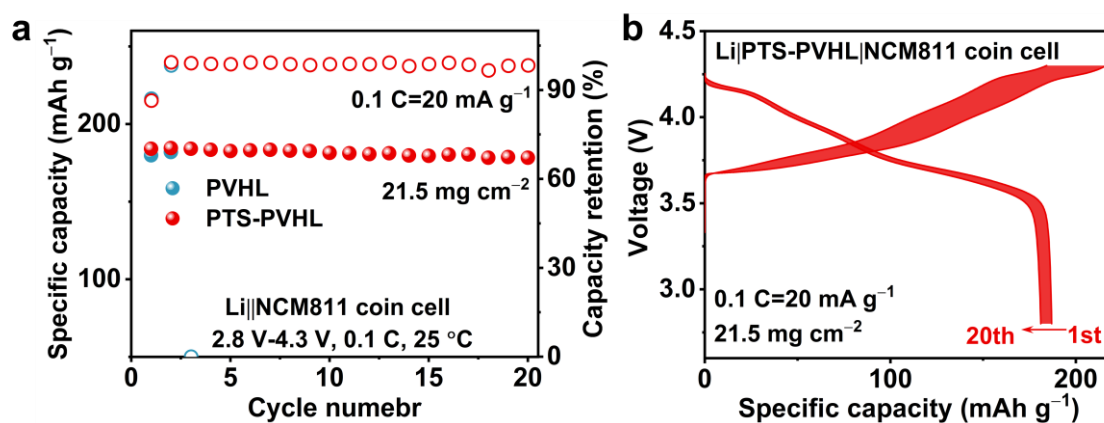
**Supplementary Fig. 51** | LSV curves related to PVH, PVHL, and PTS-PVHL electrolytes at 25 °C. Source data are provided as a Source Data file.



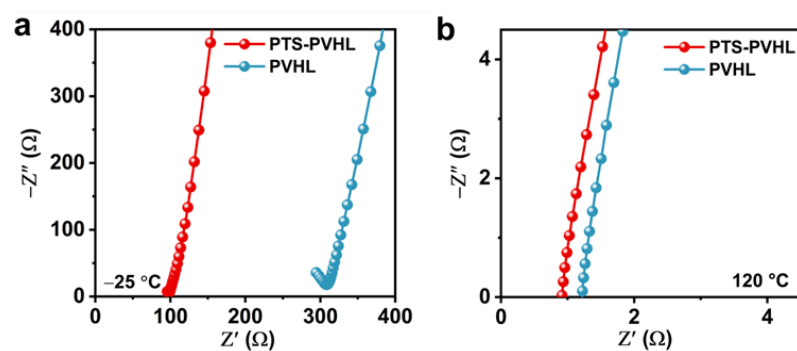
**Supplementary Fig. 52** | CV curves of (a) Li|PTS-PVHL|NCM811 and (b) Li|PVHL|NCM811 cells in the voltage range of 2.8 V-4.3 V and 25 °C. Source data are provided as a Source Data file.



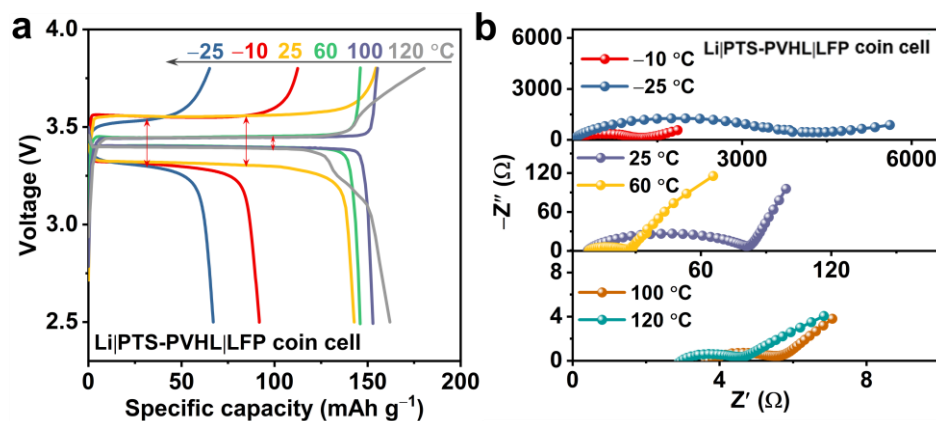
**Supplementary Fig. 53** | Cycling performance of Li||NCM811 based on PTS-PVHL and PVHL electrolytes at 2.8 V-4.3 V and 1 C at  $25^\circ\text{C}$ . Source data are provided as a Source Data file.



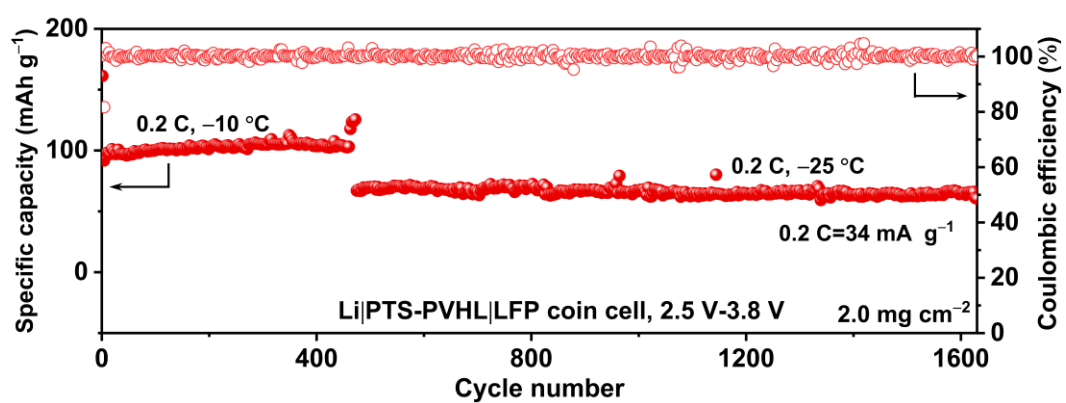
**Supplementary Fig. 54** | (a) Cycling performance of Li||NCM811 full cells with PVHL and PTS-PVHL electrolytes at 2.8 V-4.3 V and 0.1 C with high positive electrodes loading (21.5 mg cm<sup>-2</sup>) at 25 °C. (b) Charge and discharge voltage profiles of Li|PTS-PVHL|NCM811 cell at 25 °C. Source data are provided as a Source Data file.



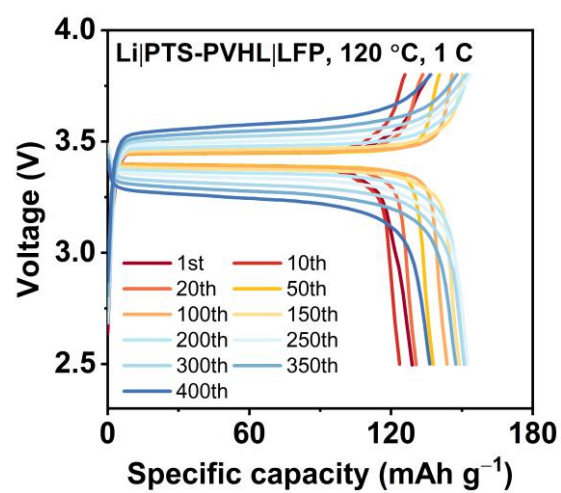
**Supplementary Fig. 55** | Impedance spectra (Nyquist plots) of S||S symmetrical cells with PTS-PVHL and PVHL at (a)  $-25\text{ }^{\circ}\text{C}$  and (b)  $120\text{ }^{\circ}\text{C}$ . Source data are provided as a Source Data file.



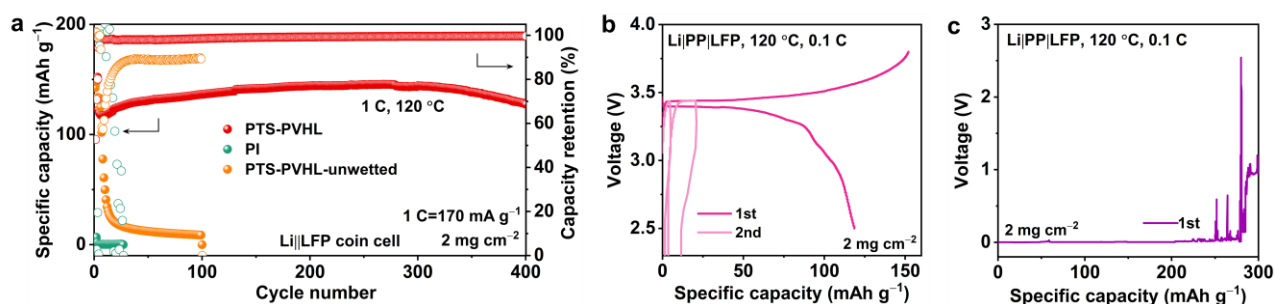
**Supplementary Fig. 56** | **a**, Voltage-capacity curves of Li|PTS-PVHL|LFP cell at different temperatures. **b**, EIS of Li|PTS-PVHL|LFP cell at different temperatures. Source data are provided as a Source Data file.



**Supplementary Fig. 57** | Cycling performance of Li|PTS-PVHL|LFP cells at  $-10\text{ }^{\circ}\text{C}$  to  $-25\text{ }^{\circ}\text{C}$  and  $0.2\text{ C}$ . Source data are provided as a Source Data file.

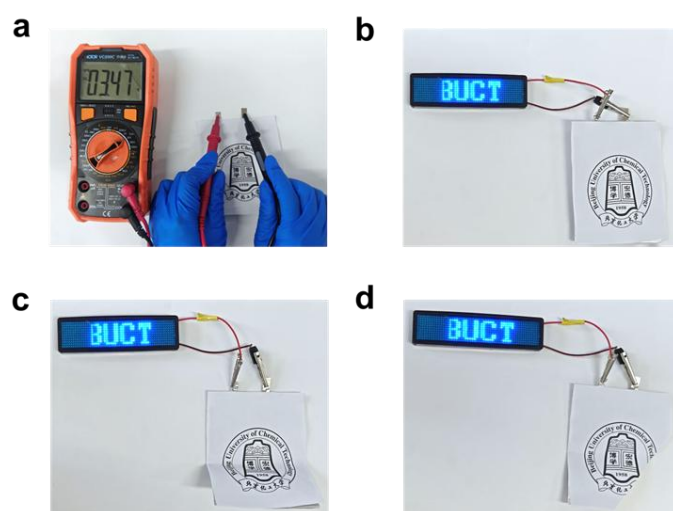


**Supplementary Fig. 58** | Voltage-capacity curves of Li|PTS-PVHL|LFP cell at 120 °C. Source data are provided as a Source Data file.



**Supplementary Fig. 59** | **a**, Cycling performance of Li|PTS-PVHL|LFP, Li|PI|LFP cells and Li|PTS-PVHL|LFP cell without interface wetting at 120 °C and 2.5-3.8 V. **b**, Voltage capacity profile of Li|PP|LFP full cell with 2.5 μL liquid electrolyte at 120 °C and 2.5-3.8 V. **c**, Voltage capacity profile of Li|PP|LFP full cell with 50 μL liquid electrolyte at 120 °C and 2.5-3.8 V. Source data are provided as a Source Data file.

Note: Thermally stable polyimide (PI, thickness: 20 μm, porosity: 68-75%, average pore size: 0.6-1.2 μm, Jiangxi Xiancai Nanofiber Technology Co., Ltd.) separators fail to sustain normal operation of assembled full cells at 120 °C with 5 μL of liquid electrolyte. Conventional polypropylene (PP, thickness: 25 μm, porosity: 55%, average pore size: 64 nm, Celgard 2500, Canrd New Energy Technology Co., Ltd) separators likewise could not support cell operation with only 2.5 μL of liquid electrolyte. Even under a conventional electrolyte amount of 50 μL, the PP-based cell exhibited severe overcharging in the first cycle, followed by rapid cell failure. Additionally, PTS-PVHL cells assembled without interfacial liquid electrolyte could operate initially but suffered rapid capacity fading. This result indicates that the trace liquid electrolyte mainly improves interfacial wetting and solid-solid contact, rather than serving as the primary ion-conducting phase. For coin-cell assembly, one circular separator with a diameter of 16 mm was employed in each cell.



**Supplementary Fig. 60** | **a**, Open-circuit voltage of Li metal pouch cell. Pictures of Li|PTS-PVHL|NCM811 pouch cell in **b**, normal state, **c**, folded, and **d**, cut to light the light pan.

**Supplementary Table 1 | Li<sup>+</sup> ion diffusivity of inorganic ceramic oxide solid electrolytes and different coating materials.**

| Sample                                           | Li ion diffusivity (cm <sup>2</sup> s <sup>-1</sup> ) | Ref. |
|--------------------------------------------------|-------------------------------------------------------|------|
| LLZTO                                            | 7.0×10 <sup>-8</sup>                                  | 1    |
| LATP                                             | 5.0×10 <sup>-8</sup>                                  | 2    |
| LLZO                                             | 2.0×10 <sup>-10</sup>                                 | 1    |
| LiSiO <sub>2</sub>                               | 2.58×10 <sup>-11</sup>                                | 3    |
| Li <sub>0.6</sub> TiO <sub>2</sub>               | 1.3×10 <sup>-11</sup>                                 | 4    |
| LiAlO <sub>2</sub>                               | 1.0×10 <sup>-11</sup>                                 | 5    |
| Li <sub>3</sub> PO <sub>4</sub>                  | 6.0×10 <sup>-13</sup>                                 | 6    |
| Li <sub>0.2</sub> Al <sub>2</sub> O <sub>3</sub> | 1.1×10 <sup>-14</sup>                                 | 7    |
| Li <sub>2</sub> ZrO <sub>3</sub>                 | 1×10 <sup>-18</sup>                                   | 8    |
| LiNbO <sub>3</sub>                               | 3.8×10 <sup>-23</sup>                                 | 9    |

**Supplementary Table 2 | Comparison of Li||Li symmetrical cells performance with different composite polymer electrolytes.**

| Electrolytes  | Current density<br>(mA cm <sup>-2</sup> ) | Areal capacity<br>(mAh cm <sup>-2</sup> ) | Cycle<br>time (h) | Ref.      |
|---------------|-------------------------------------------|-------------------------------------------|-------------------|-----------|
| PTS-PVHL      | 0.1                                       | 0.1                                       | 5000              | This work |
| PTS-PVHL      | 0.2                                       | 0.2                                       | 1100              | This work |
| PHLT          | 0.1                                       | 0.1                                       | 1400              | 10        |
| L-Li10/PVDF   | 0.1                                       | 0.1                                       | 2000              | 11        |
| PVDF/LLZTO-C  | 0.1                                       | 0.1                                       | 1000              | 12        |
| P-CPE         | 0.1                                       | 0.1                                       | 950               | 13        |
| PVBL          | 0.1                                       | 0.1                                       | 1900              | 14        |
| PTC ion-SPE   | 0.1                                       | 0.1                                       | 1500              | 15        |
| PVDF@PEO      | 0.1                                       | 0.1                                       | 1150              | 16        |
| PVDF/PI/LLZTO | 0.1                                       | 0.1                                       | 1000              | 17        |
| PNPU-PVDF-HFP | 0.1                                       | 0.1                                       | 1000              | 18        |
| PNNO-5        | 0.1                                       | 0.1                                       | 2800              | 19        |
| PLL-15        | 0.1                                       | 0.1                                       | 800               | 20        |
| PVDF-PZT      | 0.1                                       | 0.1                                       | 1900              | 21        |

**Supplementary Table 3 | Comparison of physiochemical parameters and the electrochemical performance of LMBs with the state-of-the-art SPEs-based electrolytes in the literature.**

| Electrolytes      | Cell type | Positive electrode | Rate (C) | Cycle number | Capacity retention (%) | Temperature (°C) | Mass loading (mg cm <sup>-2</sup> ) | Current density (mA g <sup>-1</sup> ) | Ref |
|-------------------|-----------|--------------------|----------|--------------|------------------------|------------------|-------------------------------------|---------------------------------------|-----|
| PHLT              | Coin cell | LFP                | 2        | 750          | 80.0                   | 25               | 1.2                                 | 340                                   | 10  |
| L-Li10/<br>ASPE12 | Coin cell | LFP                | 0.2      | 700          | 53                     | 25               | 2                                   | 34                                    | 11  |
| PHLP-15           | Coin cell | LFP                | 1        | 600          | 80.5                   | 25               | ~2-3                                | 170                                   | 22  |
| L-Li/ASPE12       | Coin cell | LFP                | 0.2      | 200          | 99                     | -20              | 2                                   | 34                                    | 11  |
| PLSTO             | Coin cell | LFP                | 1        | 130          | 88.7                   | 25               | 4                                   | 170                                   | 23  |
| H-PEO             | Coin cell | LFP                | 1        | 400          | 87.5                   | 65               | 2.5                                 | 174                                   | 24  |
| DSICE             | Coin cell | LFP                | 0.2      | 400          | 80                     | 25               | 1.2                                 | 34                                    | 25  |
| PTM4              | Coin cell | LFP                | 1        | 1000         | 81.1%                  | 25               | ~1-2                                | 170                                   | 26  |
|                   | Coin cell |                    |          | 500          | 81.3                   | 60               |                                     | 170                                   |     |
| TfOH-LLZTO        | Coin cell | LFP                | 1        | 500          | 81                     | 25               | 3.1                                 | 170                                   | 27  |
| LL-g-PMT20        | Coin cell | LFP                | 0.5      | 500          | 71                     | 25               | 1.9                                 | 85                                    | 28  |
| DLHSE             | Coin cell | LFP                | 0.2      | 140          | 91                     | 25               | 2                                   | 34                                    | 29  |

|                          |           |        |                |      |       |     |      |     |           |
|--------------------------|-----------|--------|----------------|------|-------|-----|------|-----|-----------|
| HTIT                     | Coin cell | LFP    | 1              | 800  | 90    | 30  | 3    | 170 | 30        |
| Li-MPSE                  | Coin cell | LFP    | 0.5            | 200  | 99.7  | 30  | 2    | 85  | 31        |
| F-Mo <sub>2</sub> C-LCPP | Coin cell | LFP    | 2              | 500  | 51.6  | 25  | 0.98 | 340 | 32        |
| PVDF/PCL/LA              | Coin cell | LFP    | 1              | 500  | 76    | 60  | 2    | 170 | 33        |
| AMSE                     | Coin cell | LFP    | 3              | 500  | 99    | 100 | 3    | 510 | 34        |
| GZ-62-QSSE               | Coin cell | LFP    | 1              | 600  | 93    | 80  | 2.5  | 170 | 35        |
| TPDOL                    | Coin cell | LFP    | 1              | 150  | 97.81 | 60  | 3    | 170 | 36        |
| TPPSE                    | Coin cell | LFP    | 0.2            | 100  | 96.6  | 60  | 2    | 34  | 37        |
| PTS-PVHL                 | Coin cell | LFP    | 1              | 1000 | 80.5  | 25  | ~2-3 | 170 | This work |
|                          | Coin cell | LFP    | 1              | 400  | 99.9  | 120 |      | 170 |           |
|                          | Coin cell | NCM811 | 0.2<br>(4.5 V) | 450  | 82.5  | -25 |      | 40  |           |

## Supplementary Note 1: Calculation method for desolvation energy

For molecular desolvation calculations, all simulations were implemented in Gaussian 09 with the B3LYP hybrid functional and zero-damping DFT-D3 dispersion correction. All molecular models adopted closed-shell electronic states without spin polarization, and explicit charge states were assigned for ionic species. Geometric optimization and frequency analysis were conducted at the B3LYP-D3/6-31G level to acquire stable optimized structures and confirm energy-minimum configurations without imaginary frequencies. Subsequently, high-precision single-point energy calculations were performed at the B3LYP-D3(BJ)/6-311+G level to obtain accurate electronic wave functions and energies. The triple-zeta basis set was adopted for single-point calculations to improve energy correction reliability. The Gibbs free energy of desolvation ( $\Delta G$ ), including entropy contributions and thermal corrections, was calculated as:  $\Delta G = G_C + G_D - G_A - G_B$ , among them,  $G_A/G_B$  and  $G_C/G_D$  are the energies of reactants and products in the desolvation reaction, respectively. The final  $\Delta G$  values were derived via the Shermo 1.6 program, which integrates thermal corrections from 6-31G-level frequency calculations and high-precision single-point energies from the 6-311+G basis set.

Binding energy calculations were carried out using the DMol<sup>3</sup> module in Materials Studio. The GGA-PBE exchange-correlation functional combined with Grimme's DFT-D3 van-der-Waals correction and DNP basis set was employed. All systems adopted closed-shell electronic states with customized charge assignments for ionic structures. The geometry optimization convergence thresholds were set to a total energy of  $2 \times 10^{-5}$  Ha and a force convergence criterion of 0.004 Ha/Å were set in the calculation. The binding energy ( $E_b$ ) was calculated by the following equation:

$$E = E_{A+B} - (E_A + E_B)$$

where  $E_A$ ,  $E_B$ , and  $E_{\text{total}}$  are the energy of the isolate A, B, and A-B complex, respectively.

## **Supplementary Note 2: Calculation method for Li<sup>+</sup> ion chain migration**

All calculations for Li<sup>+</sup> ion chain migration behavior were performed using Gaussian 16 software. Geometry optimizations were carried out with the B3LYP hybrid functional and the 6-31G(d) basis set, incorporating Grimme's D3 dispersion correction with Becke-Johnson (BJ) damping to account for weak intermolecular interactions. All simulated models adopted closed-shell electronic states without spin polarization, and explicit charge states were assigned for lithium-containing ionic species. Harmonic vibrational frequency calculations were conducted following geometry optimization to verify that all optimized structures corresponded to stable energy minimum points without imaginary frequencies. High-precision single-point energy calculations for migration energy analysis were performed at the B3LYP/6-311G(d,p) level to acquire accurate electronic energies. All molecular geometric configurations were visualized and constructed via GaussView 6.1.1. A flexible dimer scan method implemented in Gaussian 16 was utilized to simulate the continuous migration process of Li<sup>+</sup> ions. The scanning pathway started at a Li-N bond length of 2.0 Å and terminated at a Li-O bond length of 1.9 Å, with a fixed step size of 0.2 Å for each structural relaxation. The electronic energy of each scanned conformation was calculated at the B3LYP/6-311G(d,p) theoretical level. Finally, the energy variation profile as a function of Li<sup>+</sup> migration distance was obtained and plotted to characterize the ion migration behavior.

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