

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

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

This work introduces a cationic chain-anchored monolayer (CCM) strategy to engineer stable ion transport pathways within PVDF-HFP/garnet electrolytes. The lithium ionic conductivity and activation energy were evaluated as a function of the alkyl chain length of pyridinium trifluoromethanesulfonate (PTS), and an optimized material capable of stabilizing the performance of LLZTO oxide solid electrolytes was developed. Although advanced characterization indicates that PTS-coated LLZTO exhibits excellent electrochemical performance, several technical issues should be addressed.

1. After prolonged cycling, in what chemical or structural state does PTS remain? Under high-voltage charging conditions, does PTS participate in electrochemical reactions or undergo degradation?
2. A more in-depth discussion is required regarding the electrolyte decomposition behavior in cells using PTS@LLZTO compared to pristine LLZTO (Fig. S17). If PTS does not directly participate in electrochemical reactions, what is the underlying mechanism by which it suppresses electrolyte decomposition?
3. The Li symmetric cell testing conditions shown in Figure 3d and S33 (0.1 mA cm<sup>-2</sup> and 0.1 mAh cm<sup>-2</sup>) are insufficient to properly evaluate lithium dendrite formation and interfacial stability (see Joule, 2022, 6, 1770–1781). To convincingly demonstrate the superiority of the developed electrolyte, symmetric cell testing at a current density of 1.0 mA cm<sup>-2</sup> with an areal capacity of 3.0 mAh cm<sup>-2</sup> is required.
4. It is difficult to clearly identify the electrochemical testing conditions throughout the manuscript. For example, what are the electrode loading and current density used in Figure 5a? If Figure 5c was evaluated at 120 °C, what is the testing temperature for Figure 5d? For clarity and reproducibility, detailed information such as including electrode loading, testing temperature, and current density should be provided for all data in both the main text and the Supporting Information.
5. The performance evaluation conditions in Figure 5f are not sufficiently described. A graph that includes electrode loading information should be added to the Supporting Information to further substantiate the reported performance.
6. In the electrochemical testing section, it is stated that 2.5  $\mu$ L of a carbonate-based liquid electrolyte was added to the cell. The authors claim that this small amount does not affect the intrinsic properties of the materials. If this is the case, cell performance without any liquid electrolyte should also be demonstrated. Many studies add a small amount of liquid electrolyte as a wetting agent or initiator; however, such systems should more appropriately be classified as quasi-solid-state or hybrid systems. Furthermore, 2.5  $\mu$ L cannot reasonably be considered a negligible amount.

Reviewer #2

(Remarks to the Author)

This manuscript presents a comprehensive study on a cationic chain-anchored monolayer strategy to enhance interfacial stability and ion transport in solid-state Li-metal batteries over a wide temperature range. The integration of experimental characterization with multiscale simulations is commendable, and the electrochemical performance—particularly under extreme temperatures—is impressive. However, several aspects of the computational methodology and data consistency require clarification to ensure reproducibility and to strengthen the physical interpretation of the results. Addressing the points below would significantly improve the rigor and transparency of the study.

1. Please provide detailed information on the AIMD simulation settings and the equation used for binding energy calculations. Specifically, the preparation of the simulation cell, ensemble (NVT/NPT), temperature, time step, and total

simulation time should be clearly stated to ensure reproducibility. In addition, although AIMD is mentioned in the Supplementary Information, corresponding AIMD-derived results are not presented in the main manuscript or SI. Please clarify how AIMD contributes to the conclusions and provide the relevant results.

2. The reported Li binding energies are on the order of ~4 eV, indicating very strong interactions. Please clarify the physical interpretation of such large binding energies and explain how Li-ion diffusion remains feasible under these conditions. A discussion connecting binding energy to migration barrier or dynamic transport behavior would help reconcile this apparent contradiction.

3. The desolvation reaction energy is denoted as  $\Delta G$ , which conventionally refers to Gibbs free energy. However, Supplementary Note 2 does not clearly specify whether entropic contributions and thermal corrections were included, or whether  $\Delta G$  corresponds effectively to electronic energy differences. Please clarify whether vibrational frequency calculations and thermal corrections were incorporated to compute true Gibbs free energies.

4. Although RDF and coordination number calculations are described in Supplementary Note 5, the corresponding RDF plots and CN results are not presented in the manuscript or SI. Please provide the calculated RDF curves and CN analysis to support the discussion of ion coordination structure.

5. In Figure 4c, the MSD plot starts from a non-zero value, and the MSD curve for PVHL appears noticeably slanted. This may indicate insufficient equilibration, particularly given that the reported equilibration time is only 100 ps. Please clarify whether a longer equilibration period was tested and confirm that the diffusion analysis was performed after complete system equilibration.

6. The manuscript employs multiple cathodes (LFP, NCM811, and LCO) under different testing conditions. While this demonstrates broad applicability, the varying cathode types, loadings, and voltage windows make it difficult to directly compare electrochemical performance. Please clarify the rationale for selecting different cathodes and clearly specify the testing conditions to avoid confusion.

### Reviewer #3

#### (Remarks to the Author)

This manuscript reports a cationic chain-anchored monolayer (CCM) strategy to regulate ion transport in PVDF-HFP/garnet composite electrolytes, enabling wide-temperature operation (-25 to 120 °C) in solid-state lithium-metal batteries. The work combines interfacial chemistry design with multi-modal characterization (IR, ssNMR, DEMS, etc.) and demonstrates promising electrochemical performance. The topic is timely and relevant to the development of wide-temperature SSLMBs. However, several key issues regarding mechanistic clarity, experimental rigor, and data presentation need to be addressed before the manuscript can be considered for publication.

1. A key highlight of this work is the claimed operation over an ultrawide temperature range (-25 to 120 °C). While the results are promising, the current evidence is not yet fully convincing. The ionic conductivity at -25 °C is only 0.028 mS cm<sup>-1</sup>. Despite this, the cells show good cycling performance. Systematic low-temperature polarization analysis is missing. High temperature: the mechanical stability of the polymer matrix at 120 °C is not sufficiently discussed. Potential risks of softening or dimensional instability are not evaluated. It is recommended that the authors provide: Full-temperature EIS analysis. Temperature-dependent polarization data. Mechanical modulus vs. temperature. Additional discussion on high-temperature safety and stability.

2. At present, the article only presents the full battery test results of PTS-PVHL assembly, and does not provide the corresponding full battery performance data of PVHL system. It is suggested to supplement the full battery test results of the control group to improve the comparative demonstration.

3. The authors mentioned in the article that alkyl chains have a solvent repellent effect. Please elaborate on the intrinsic reasons why alkyl chains exhibit solvent repellent properties, as well as the advantages of electrolytes with solvent repellent effects.

4. Can the proposed "cationic chain-anchored monolayer" strategy be extended to other battery systems?

5. It is recommended that the authors provide additional necessary explanations for the excellent rate capability and long-term cycling performance in order to better highlight the advancement of the design.

6. The manuscript claims the formation of a "single-ion-conducting CCM" in the Abstract. However, the current evidence appears insufficient to fully support this statement. The reported Li<sup>+</sup> transference number ( $t_{Li^+} = 0.78$ , Fig. 3b) is relatively high but does not reach the typical level expected for true single-ion conductors. Direct evidence of suppressed anion mobility is lacking. No concentration-gradient analysis or more rigorous validation is provided. Suggestions: The authors are encouraged to adopt more cautious wording (e.g., single-ion-like conduction), or provide stronger supporting evidence, such as PFG-NMR measurements or a more rigorous Bruce-Vincent analysis.

7. All abbreviations (e.g., PVHL, CCM) should be defined at first appearance.

Version 1:

Reviewer comments:

Reviewer #1

#### (Remarks to the Author)

Although the authors provided additional data and explanations, the major concerns remain unresolved. Therefore, I cannot

support publication of the manuscript in its current form.

1. Based on the experimental section, the cathodes do not contain the composite electrolyte. If so, how is  $\text{Li}^+$  transported within the cathode? If  $\text{Li}^+$  transport relies on the liquid electrolyte added at the cathode/electrolyte interface, why should this system be considered a solid-state battery?

2. The authors argue that 2.5  $\mu\text{l}$  of liquid electrolyte has little influence on cell performance. However, cells without liquid electrolyte cannot operate (Figure r14). Does this not indicate that the liquid electrolyte is essential for cell operation?

3. The electrochemical performance also remains unconvincing. According to Figure r7, stable cycling is only achieved at 0.5  $\text{mA cm}^{-2}$  and 0.5  $\text{mAh cm}^{-2}$  with considerable polarization. The cells fail under 1.0  $\text{mA cm}^{-2}$  and 3.0  $\text{mAh cm}^{-2}$ . What practical advantage is provided by the PTS modification under these conditions?

4. The full-cell performance was evaluated using a cathode loading of only 2  $\text{mg cm}^{-2}$ , corresponding to  $\sim 0.4 \text{ mAh cm}^{-2}$ . This is far below practical conditions. How do the authors justify the relevance of these results?

5. The emphasis on operation at 120  $^{\circ}\text{C}$  is also questionable. Most lithium-ion batteries operate between 10 and 60  $^{\circ}\text{C}$ . Why is performance at 120  $^{\circ}\text{C}$  considered a key metric in this work?

6. Approximately 3.1 wt% DMF remains in the membrane, and additional liquid electrolyte is introduced during cell assembly. Is there any direct evidence that  $\text{Li}^+$  transport occurs primarily through the solid electrolyte rather than through residual liquid phases?

Reviewer #2

(Remarks to the Author)

The manuscript has been thoroughly revised and is ready for publication in Nature Communications.

Reviewer #3

(Remarks to the Author)

Accept without change

Version 2:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

All reviewer comments have been addressed.

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# Response Letter

## Responses to Reviewer 1

**Reviewer 1:** This work introduces a cationic chain-anchored monolayer (CCM) strategy to engineer stable ion transport pathways within PVDF-HFP/garnet electrolytes. The lithium ionic conductivity and activation energy were evaluated as a function of the alkyl chain length of pyridinium trifluoromethanesulfonate (PTS), and an optimized material capable of stabilizing the performance of LLZTO oxide solid electrolytes was developed. Although advanced characterization indicates that PTS-coated LLZTO exhibits excellent electrochemical performance, several technical issues should be addressed.

**Response:** We sincerely thank the reviewer for the positive assessment of our work and for the constructive comments. We have carefully addressed all the suggestions and revised the manuscript accordingly to improve its clarity and rigor.

**Question 1:** After prolonged cycling, in what chemical or structural state does PTS remain? Under high-voltage charging conditions, does PTS participate in electrochemical reactions or undergo degradation?

**Response:** Thank you for your insightful and constructive comments. To address this important issue, we systematically analyzed the electrodes and electrolytes after prolonged cycling using multiple characterization techniques, because the chemical and structural state of PTS after cycling was crucial for evaluating the stability of the modified material and determining whether PTS participates in the electrochemical reactions.

(1) To determine whether PTS participated in electrochemical reactions or underwent degradation under high-voltage charging conditions. First, we performed X-ray photoelectron spectroscopy (XPS) analysis on the surfaces of the Li metal anode and NCM811 cathode of 4.3 V Li||NCM811 full cells after different cycling (after 3 cycling activation, 5th, and 10th cycle) to track the interfacial chemical evolution. Comparison of the high-resolution C 1s XPS spectra of the solid electrolyte interphase (SEI) on Li metal revealed no significant difference in the organic C–C component between the PVHL and PTS-PVHL electrolytes (Figure r1). The N 1s spectrum of the activated PVHL system showed only the characteristic LiTFSI signal, suggesting that the organic electrolyte preferentially decomposed on the Li-metal anode rather than LiTFSI. In the PTS-PVHL system, the content of NO<sub>x</sub> component in SEI remained relatively stable under different cycle numbers. After 10 cycles, the N/S atomic ratio of SEI showed a decreasing trend (Figure r3a). It confirmed that the NO<sub>x</sub> species in the N 1s spectrum originate from the decomposition of LiTFSI, and the PTS-PVHL electrolyte showed more complete LiTFSI decomposition. Further analysis from the cathode electrolyte interface (CEI)

showed that the relative content of C-C organic components in the PVHL system CEI was significantly higher than that in PTS-PVHL, indicating that more solvent molecules underwent oxidative decomposition in the CEI for the PVHL system (Figure r2). For the PTS-PVHL system, the C 1s spectra collected at different cycles showed that the C-C component remained nearly unchanged, indicating that the electrolyte did not undergo continuous decomposition. Although there were slight fluctuations in the proportion of NO<sub>x</sub> in its N 1s spectra, the overall S element content remained basically unchanged. The N/S ratio first increased slightly with the cycle and then tended to stabilize (Figure r3b). In summary, the SEI and CEI compositional results did not provide direct evidence for whether PTS undergoes interfacial decomposition. They instead confirm the stable interphase chemistry established in the PTS-PVHL system.

(2) Second, we further conducted electrochemical impedance spectroscopy (EIS) on the full cell during high-voltage charging. The results showed that the overall cell impedance did not change significantly throughout the charging process. To gain deeper insight, we employed distribution of relaxation time (DRT) analysis to deconvolute the impedance spectra (Figure r4). The DRT results clearly showed that, for the PTS-PVHL-based full cell, the R<sub>SEI</sub> remained nearly constant starting from 3.8 V during high-voltage charging, revealing no obvious decomposition under high-voltage cycling. In contrast, both R<sub>SEI</sub> and charge transfer resistance (R<sub>CT</sub>) of the PVHL-based full cell increased sharply, implying continuous growth of the interfacial film and degraded reaction kinetics under high voltage. This indicated that the charge transfer process at the electrode/electrolyte interface of the PTS-PVHL-based cell remained stable, without kinetic deterioration induced by interfacial side reactions. These findings provided strong electrochemical evidence for the stable interfacial behavior enabled by PTS under high-voltage charging conditions.

Therefore, we have added Figures r1, r2, and r4 as Supplementary Figs. 24 and 25 (in the revised Supporting Information), and the following description to the revised manuscript (Page 9):

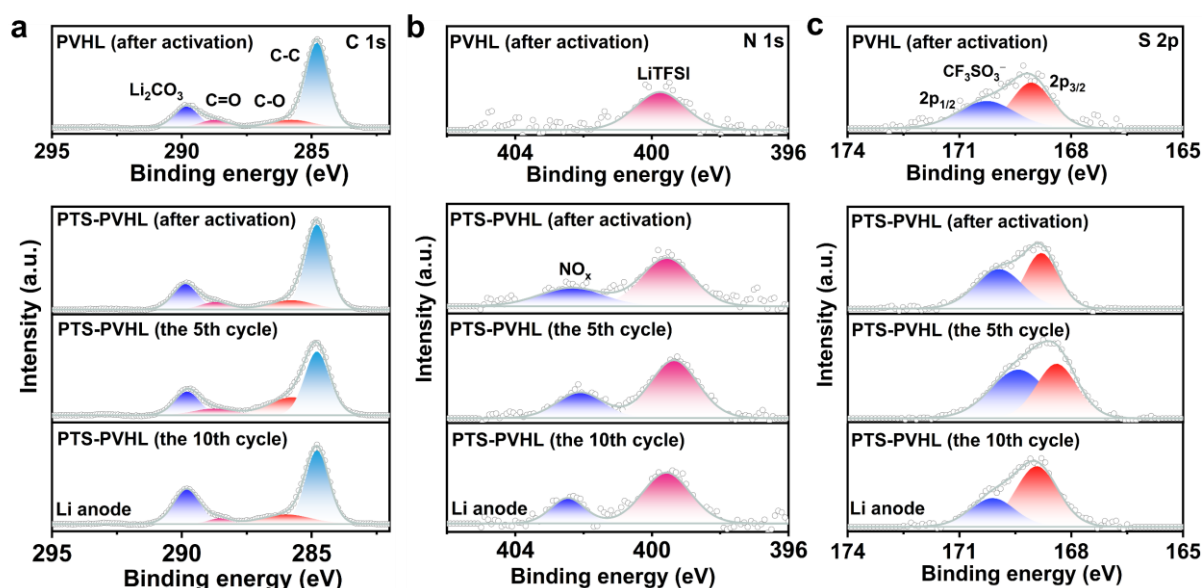
Its durability was further supported by post-cycling XPS analysis and in situ EIS measurements of the full cell. Thus, the solvent-repulsion effect favorably maintains the structural integrity of ion-transport channels within the PTS-PVHL. In contrast, electrolyte decomposition at the composite-phase interfaces in PVHL consumes mobile Li<sup>+</sup> and obstructs effective ion transport.

(3) Third, according to Figure 2i of the manuscript, the Li<sup>+</sup> coordination environment showed no evident change before and after cycling. This result indicated that the Li<sup>+</sup> transport pathways in PTS-PVHL were not blocked and provided further evidence for the stability of the PTS modified layer (Figure r5, 2D NMR).

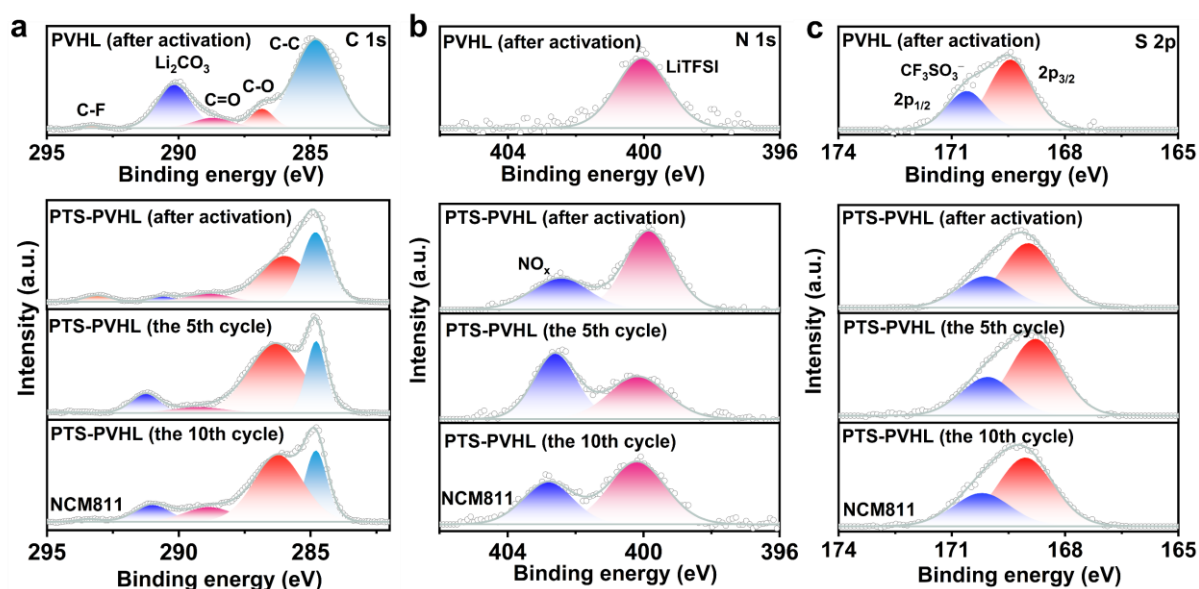
(4) Finally, to further evaluate the stability of the membrane after high-voltage cycling, Raman spectroscopy analysis was conducted (Figure r6). If the PTS modification layer were unstable, obvious spectral changes would be expected in the membrane harvested after cycling. In contrast, the Raman spectrum after cycling remained highly similar to that of the pristine electrolyte, while the solvent-repelling layer was still clear and recognizable. These results indicated that no obvious chemical degradation or side reaction occurs during prolonged cycling under high-voltage conditions, further confirmed the structural and chemical stability of the PTS-modified system.

Therefore, we have added Figure r6 as Supplementary Fig. 21 (in the revised Supporting Information), and the following description to the revised manuscript (Page 9):

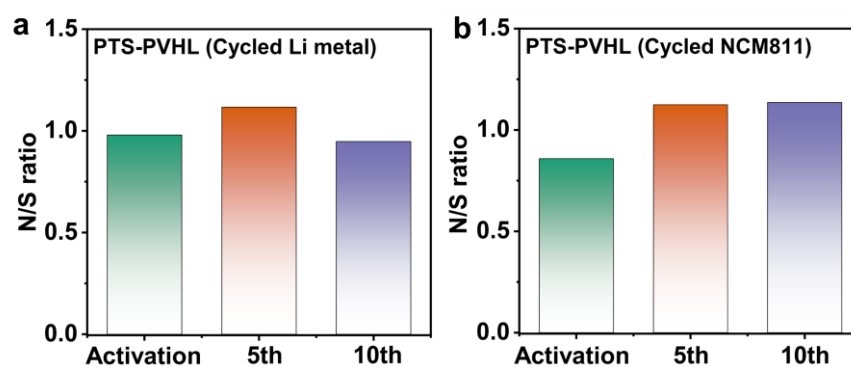
Even after full-cell cycling, the PTS-PVHL electrolyte membrane retained a homogeneous lithium-salt distribution, confirming its structural and compositional stability.



**Figure r1:** XPS profiles of (a) C 1s, (b) N 1s, and (c) S 2p for Li metal anodes with PVHL and PTS-PVHL after 3 activation cycles, and PTS-PVHL after 5 and 10 cycles within 2.8-4.3 V.

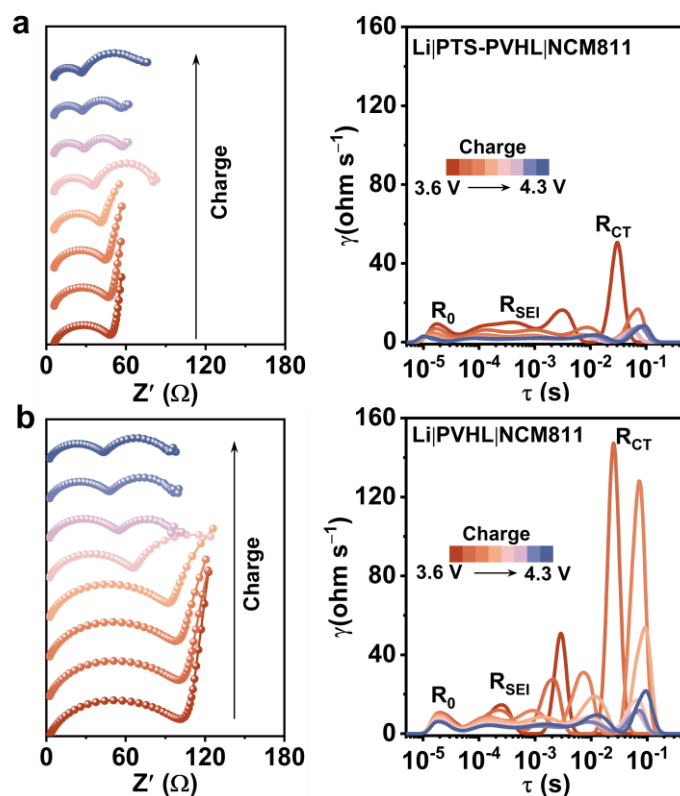


**Figure r2:** XPS profiles of (a) C 1s, (b) N 1s, and (c) S 2p for NCM811 cathodes with PVHL and PTS-PVHL after 3 activation cycles, and PTS-PVHL after 5 and 10 cycles within 2.8-4.3 V.



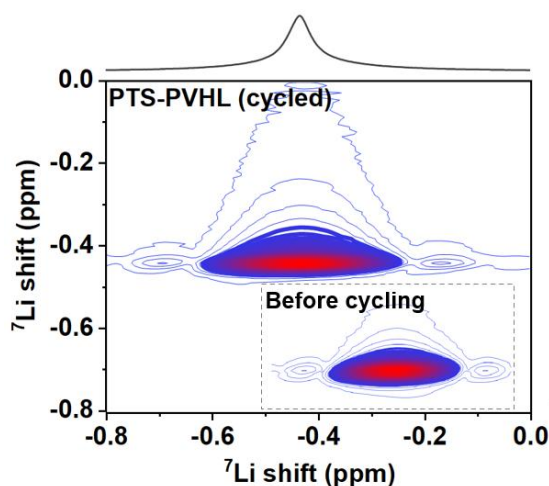
**Figure r3:** The N/S atomic ratios of (a) Li metal anode and (b) NCM811 cathode at different cycles of PTS-PVHL.

Note: For SEI, the decrease in the N/S ratio with increasing cycles indicates that the  $\text{NO}_x$  species mainly originate from the decomposition of anions. Meanwhile, the contents of organic components and sulfur-containing species in the CEI remain stable throughout cycling, demonstrating that the electrode interface maintains favorable structural stability after activation.

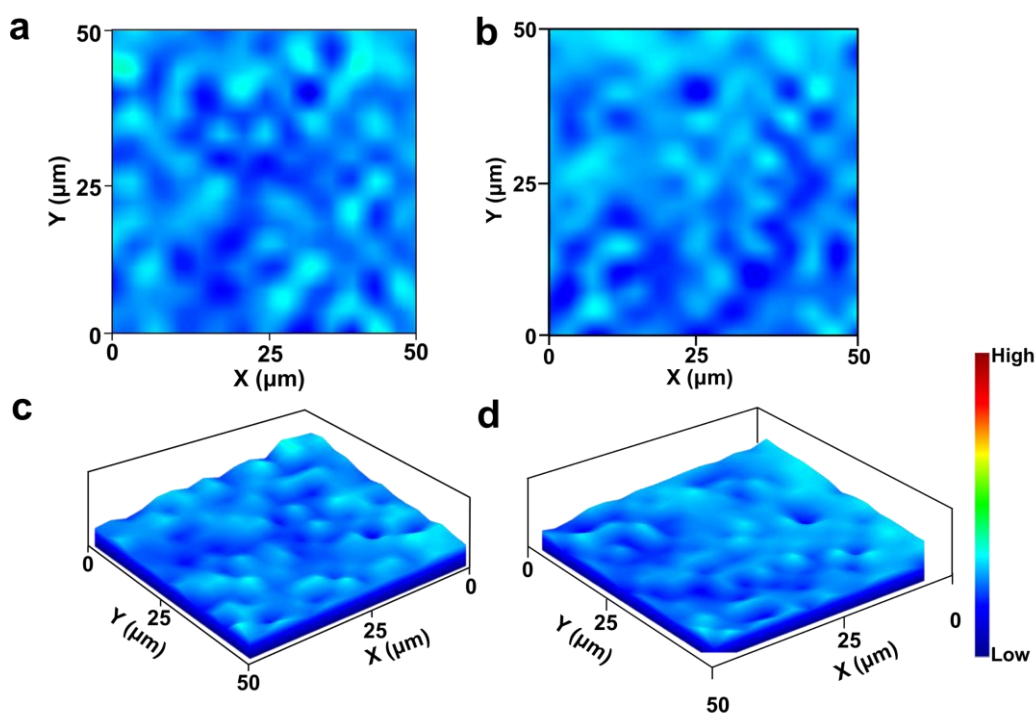


**Figure r4:** In situ EIS and DRT of (a) Li|PTS-PVHL|NCM811 and (b) Li|PVHL|NCM811 full cells.

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 remarkable 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.



**Figure r5:** 2D  $^7\text{Li}$ - $^7\text{Li}$  EXSY spectra of PTS-PVHL after cycling (The inset is before cell cycling).



**Figure r6:** 2D Raman mapping of PTS-PVHL membrane in the range of  $730\text{--}770\text{ cm}^{-1}$ : (a) before and (b) after high-voltage cycling. 3D Raman mapping of PTS-PVHL membrane in the range of  $730\text{--}770\text{ cm}^{-1}$ : (c) before and (d) after high-voltage cycling.

Note: Lithium salts remain uniformly distributed within the solvent-repellent electrolyte layer before and after cycling, confirming the robust stability of the PTS-PVHL electrolyte architecture and composition.

**Question 2:** A more in-depth discussion is required regarding the electrolyte decomposition behavior in cells using PTS@LLZTO compared to pristine LLZTO (Fig. S17). If PTS does not directly participate in electrochemical reactions, what is the underlying mechanism by which it

suppresses electrolyte decomposition?

**Response:** We sincerely appreciate the reviewer's valuable comments. For the decomposition behavior of electrolytes, in the pristine LLZTO/PVDF composite electrolyte system, alkaline impurities (e.g., LiOH and Li<sub>2</sub>CO<sub>3</sub>) inevitably remain on the LLZTO surface. These impurities acted as strong catalytic sites that directly attack the C-F bonds in PVDF chains, triggering persistent dehydrofluorination reactions and inducing the formation of conjugated C=C defects within the PVDF matrix. Consequently, the cell interfacial impedance increased progressively with cycling, indicating that the pristine LLZTO system undergoes uncontrollable and continuous interfacial side reactions. In sharp contrast, in the PTS@LLZTO system, the PTS formed a uniform monolayer coating on the LLZTO surface via in-situ acid-base neutralization, which eliminated the surface alkaline residues. Meanwhile, the ultrathin nature of this monolayer ensured that the Li<sup>+</sup> conduction channels remain unobstructed. More critically, the PTS modification layer effectively blocked the direct electron transfer from lithium metal to the LLZTO surface, suppressing the reductive degradation of LLZTO. This maintained a dense and stable interfacial structure, thus eliminating sustained electrolyte decomposition. Furthermore, the PTS modification significantly enhanced the interfacial affinity between the LLZTO and PVDF phases, promoting intimate interfacial contact, substantially reducing interfacial defects, and eliminating localized micro-regions that are prone to electrolyte accumulation and subsequent decomposition. In summary, the PTS monolayer modification elevated the overall chemical/physical stability of the electrolyte interface through multiple synergistic mechanisms, resulting in forming a stable and efficient composite solid electrolyte.

In this work, we provided direct evidence that the PTS modification layer can significantly suppress electrolyte decomposition on the surface of the nanofillers. We selected a LiPF<sub>6</sub>-based electrolyte to accelerate the electrolyte decomposition at the inorganic filler/electrolyte interface because of its lower thermodynamic stability compared with LiTFSI. This design provided a clear comparison between PTS@LLZTO and pristine LLZTO. Pristine LLZTO exhibited substantial formation of La-F species, whereas almost no La-F species were detected for PTS@LLZTO. Based on the interfacial decomposition mechanism of LLZO proposed by Huang et al., the pristine LLZTO surface underwent Li<sup>+</sup>/H<sup>+</sup> exchange, exposing abundant La active sites in the LiPF<sub>6</sub> system (Chem, 2022, 8, 1-16). These exposed sites were then attacked by HF generated from LiPF<sub>6</sub> hydrolysis, leading to the formation of an inert LaF<sub>3</sub>-rich layer. Because LaF<sub>3</sub> possesses extremely low ionic conductivity (<10<sup>-8</sup> S cm<sup>-1</sup>), and its porous structure cannot prevent the continued penetration of HF and H<sup>+</sup>. Thus, the interfacial impedance increases continuously, interfacial mechanical integrity deteriorates, and La active

sites on the LLZTO surface are irreversibly consumed, ultimately compromising long-term cell stability. In contrast, PTS@LLZTO exhibited a pronounced interfacial regulation effect. Importantly, the PTS modification layer preserved the stability of the organic/inorganic composite phase within the electrolyte membrane. This observation demonstrates that the stability of the interphase in composite polymer electrolytes is crucial to the overall stability of the battery system, rather than merely influencing the mechanical properties of the membrane and the  $\text{Li}^+$  transport pathways. From another perspective, our findings further revealed that the high- and low-temperature stability of full cells based on composite electrolyte systems was also strongly affected by the stability of the electrolyte composite phase.

Therefore, we have added the following description to the revised manuscript and Supporting Information:

Therefore, the introduction of PTS markedly improves the organic-inorganic interfacial compatibility within the composite electrolyte, further stabilizing the electrolyte-electrode interfaces. (In the revised manuscript, Page 9)

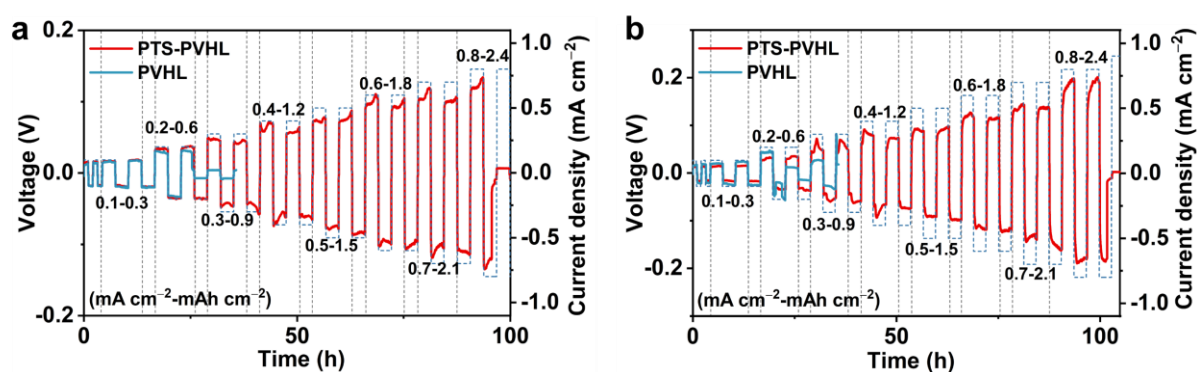
The PTS alkyl chain acts as a nonpolar hydrocarbon segment, enabling repulsion toward most polar organic species. Combined with the cell impedance and interfacial chemistry analyses, these results indicate that PTS-modified LLZTO constructs homogeneous and interconnected  $\text{Li}^+$ -transport pathways within the composite phase. The solvent-phobic nature of PTS further stabilizes these pathways, thereby reducing electrolyte consumption. (In the revised Supporting Information)

**Question 3:** The Li symmetric cell testing conditions shown in Figure 3d and S33 ( $0.1 \text{ mA cm}^{-2}$  and  $0.1 \text{ mAh cm}^{-2}$ ) are insufficient to properly evaluate lithium dendrite formation and interfacial stability (see Joule, 2022, 6, 1770–1781). To convincingly demonstrate the superiority of the developed electrolyte, symmetric cell testing at a current density of  $1.0 \text{ mA cm}^{-2}$  with an areal capacity of  $3.0 \text{ mAh cm}^{-2}$  is required.

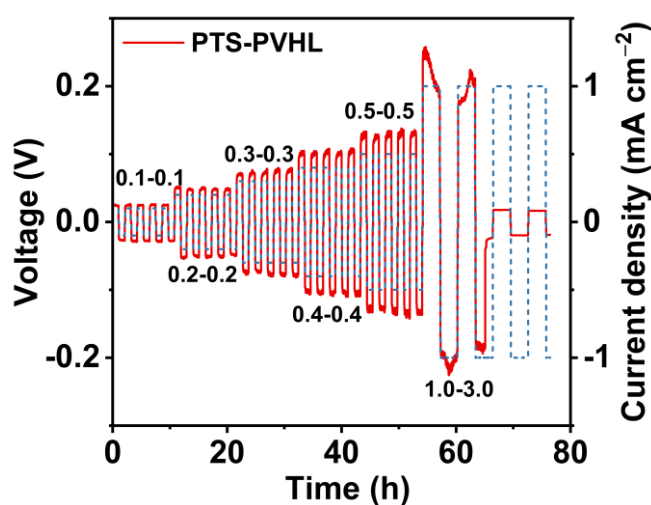
**Response:** We thank the reviewer for the valuable comments and constructive suggestions regarding the testing conditions for Li||Li symmetric cells. We fully agree that a systematic assessment of lithium dendrite growth and electrode/electrolyte interfacial stability under more demanding conditions is essential for convincingly demonstrating the advantages of the developed electrolyte.

In response, we performed additional Li||Li symmetric cell tests at higher current densities and areal capacities. As the reviewer correctly pointed out, we encountered the same issue as that reported in the Joule reference recommended by the reviewer, namely that the cell remained prone to soft short circuit under such harsh testing conditions. It is difficult to achieve long-

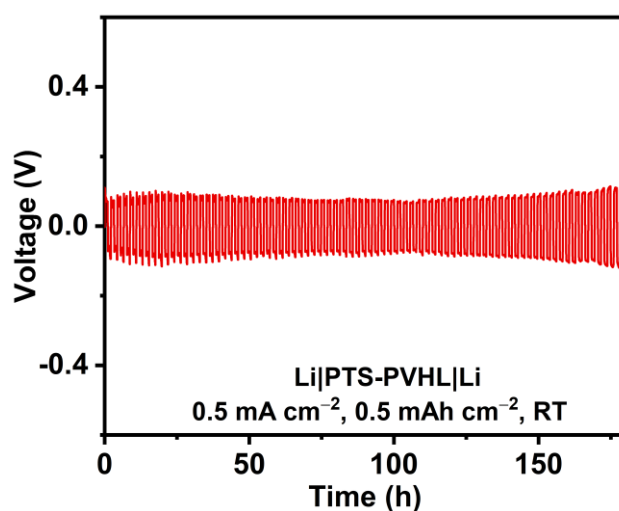
term stable cycling under harsh conditions of  $1.0 \text{ mA cm}^{-2}$  and  $3.0 \text{ mAh cm}^{-2}$  for polymer-based electrolytes (Figures r7 and r8), and most reported systems still struggle to meet this requirement (Table r1). In our supplementary experiments, the electrolyte system sustained only a few cycles under these stringent conditions before a soft short circuit occurred. We attribute this behavior primarily to the intrinsic limitations of the current polymer electrolyte system, particularly the still-insufficient interfacial ion-transport efficiency, mechanical robustness, and dendrite-suppression capability under high  $\text{Li}^+$  flux and deep stripping/plating conditions. Although cells are prone to short circuits at high current densities, supplementary experiments have shown that the performance of symmetrical cells is still superior to that of the control sample. In addition, the  $\text{Li}||\text{Li}$  symmetric cell can also cycle stably at higher current densities of  $0.5 \text{ mA cm}^{-2}$  and  $0.5 \text{ mAh cm}^{-2}$  (Figure r9).



**Figure r7:** (a, b) Cycling of  $\text{Li}|\text{PVHL}|\text{Li}$  and  $\text{Li}|\text{PTS-PVHL}|\text{Li}$  symmetric cells.



**Figure r8:** Cycling of  $\text{Li}|\text{PTS-PVHL}|\text{Li}$  symmetric cells.



**Figure r9:** Galvanostatic cycling stability of Li||Li symmetric cells at current density of 0.5 mA cm<sup>-2</sup> with capacity of 0.5 mAh cm<sup>-2</sup>.

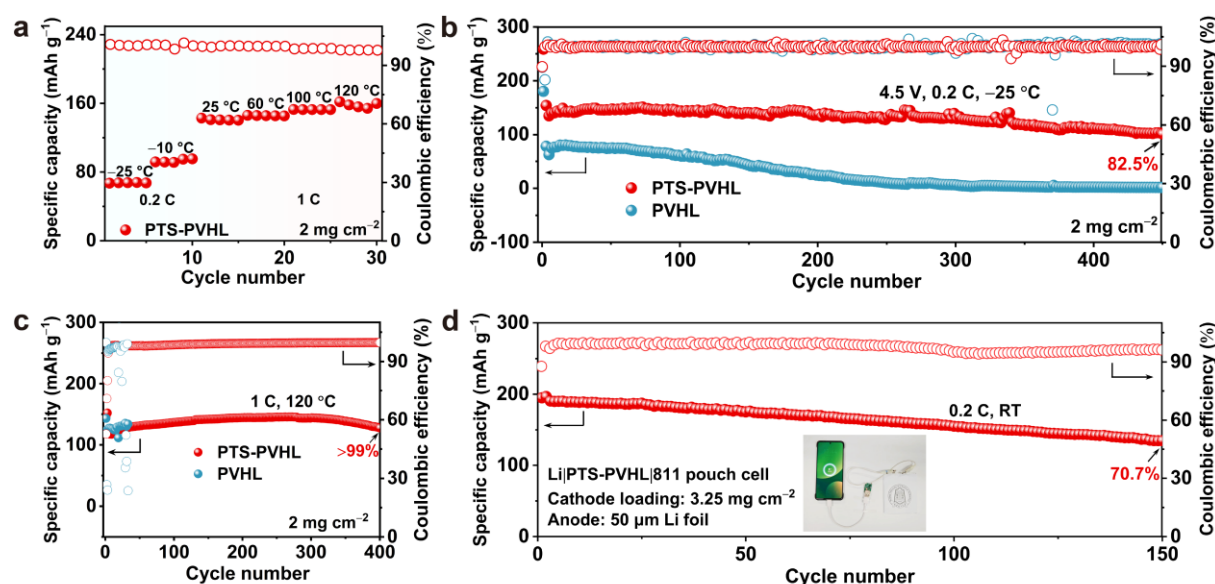
**Table r1** Comparison of Li||Li symmetrical cells performance with different composite polymer electrolytes.

| Ref.                                 | Current density<br>(mA cm <sup>-2</sup> ) | Areal capacity<br>(mAh cm <sup>-2</sup> ) | Cycle<br>time (h) |
|--------------------------------------|-------------------------------------------|-------------------------------------------|-------------------|
| J.Am.Chem.Soc.2025,147,25896–25909   | 0.2                                       | 0.2                                       | 1500              |
| Adv. Mater.2025,e13427               | 0.1                                       | 0.1                                       | 3000              |
| Angew. Chem. Int. Ed.2026,65,e17142  | 0.2                                       | 0.1                                       | 2000              |
| Angew. Chem. Int. Ed.2026,0,e8139928 | 0.1                                       | 0.1                                       | 700               |
| Nat. Nanotech.2023,18,602–610        | 0.1                                       | 0.1                                       | 1900              |
|                                      | 1                                         | 1                                         | 300               |
| Nat. Commun.2026,17,376              | 0.1                                       | 0.1                                       | 1300              |
| J.Am.Chem.Soc.2025,147,25940–25949   | 0.1                                       | 0.1                                       | 1300              |
| Adv. Mater.2025, e12960              | 0.1                                       | 0.1                                       | 4000              |
| Adv. Mater.2025,0,e19284             | 1                                         | 1                                         | 1000              |
| Nat. Commun.2025,16,3626             | 0.5                                       | 0.25                                      | 1500              |
|                                      | 1                                         | 0.5                                       | 1200              |
| Adv. Mater. 2025, 2415966            | 0.2                                       | 0.2                                       | 2400              |
| This work                            | 0.1                                       | 0.1                                       | 5000              |
|                                      | 0.2                                       | 0.2                                       | 1200              |
|                                      | 0.5                                       | 0.5                                       | 180               |

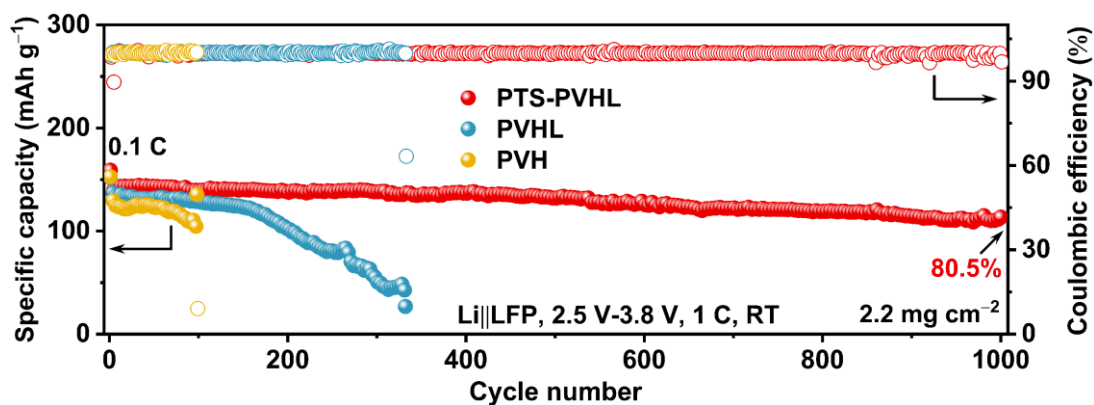
**Question 4:** It is difficult to clearly identify the electrochemical testing conditions throughout the manuscript. For example, what are the electrode loading and current density used in Figure 5a? If Figure 5c was evaluated at 120 °C, what is the testing temperature for Figure 5d? For clarity and reproducibility, detailed information such as including electrode loading, testing temperature, and current density should be provided for all data in both the main text and the Supporting Information.

**Response:** Thank you for your valuable suggestion. We have specified the areal loading and current density as 2 mg cm<sup>-2</sup>, 0.2 C, and 1 C, respectively, in Figure 5a, and clarified that the test temperature in Figure 5d was room temperature. For improved clarity and reproducibility, the corresponding details, including areal loading, test temperature, and current density (Figures r10-r13), have been added to the manuscript and the figures in the Supporting Information.

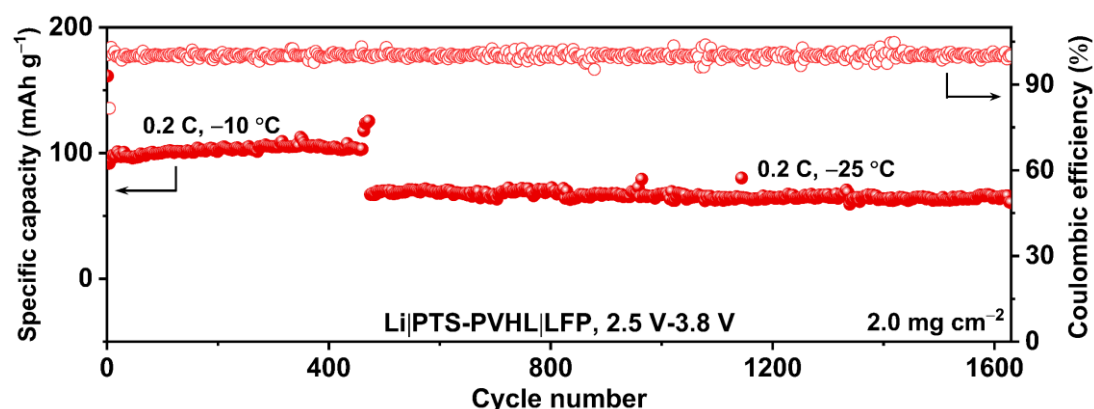
Therefore, we have revised Figure r10 as Fig. 5 (in the revised manuscript), and Figures r11-r13 as Supplementary Figs. 50, 51, and 54 (in the revised Supporting Information).



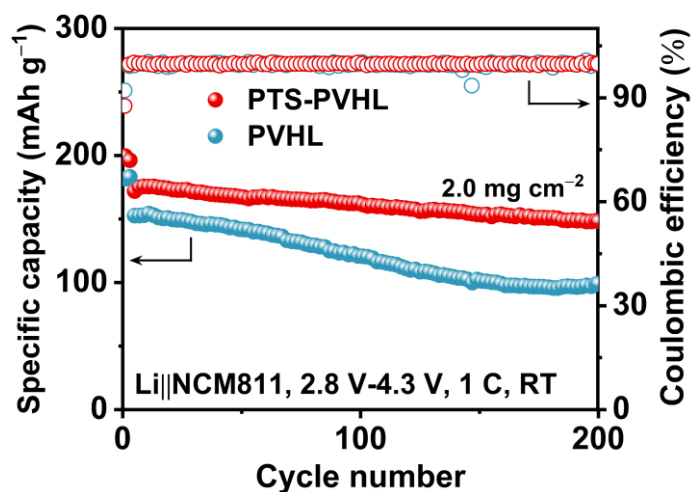
**Figure r10:** (a) Specific capacities and CEs of the Li|PTS-PVHL|LFP cells were evaluated over a temperature range from -25 °C to 120 °C. (b) Long-term cycling performance of Li|PTS-PVHL|NCM811 cells at 0.2 C between 2.8 V and 4.5 V at -25 °C. (c) Cycling performance of Li|PTS-PVHL|LFP cells at high temperature of 120 °C and 1 C. (d) Cycling performance of 50 μm Li|PTS-PVHL|NCM811 pouch cell at 0.2 C between 2.8 V-4.3 V (Inset: optical picture of pouch cell powering a mobile phone).



**Figure r11:** Cycling performance of Li||LFP cells with PVH, PVHL, and PTS-PVHL electrolytes at 1 C (1 C=170 mAh g<sup>-1</sup>) between 2.5 V-3.8 V.



**Figure r12:** cycling performance of Li|PTS-PVHL|LFP cells at -10 °C to -25 °C and 0.2 C.



**Figure r13:** Cycling performance of Li||NCM811 (1 C=200 mAh g<sup>-1</sup>) based on PTS-PVHL and PVHL electrolytes at 2.8 V-4.3 V and 1 C.

**Question 5:** The performance evaluation conditions in Figure 5f are not sufficiently described. A graph that includes electrode loading information should be added to the Supporting Information to further substantiate the reported performance.

**Response:** Thank you for your valuable suggestion. We have added the electrode loading

conditions to Supplementary Table 3 for the performance evaluation and further verified the reported performance. The corresponding revisions have been incorporated into the manuscript, as shown in the table below (Table r2).

Therefore, we have revised Table r2 as Supplementary Table 3 (in the revised Supporting Information).

**Table r2 Comparison of physiochemical parameters and the electrochemical performance of LMBs with the state-of-the-art SPEs-based electrolytes in the literature.**

| Electrolytes            | Cathode | Rate (C) | Cycle number | Capacity retention (%) | Temperature (°C) | Mass loading (mg cm <sup>-2</sup> ) | Ref |
|-------------------------|---------|----------|--------------|------------------------|------------------|-------------------------------------|-----|
| PHLT                    | LFP     | 2        | 750          | 80.0                   | 25               | 1.2                                 | 10  |
| L-Li10/PVDF             | LFP     | 0.2      | 700          | 53                     | 25               | 2                                   | 11  |
| PHLP-15                 | LFP     | 1        | 600          | 80.5                   | 25               | ~2-3                                | 22  |
| L-Li/ASPE12             | LFP     | 0.2      | 200          | 99                     | -20              | 2                                   | 11  |
| PLSTO                   | LFP     | 1        | 130          | 88.7                   | 25               | 4                                   | 23  |
| H-PEO                   | LFP     | 1        | 400          | 87.5                   | 65               | 2.5                                 | 24  |
| DSICE                   | LFP     | 0.2      | 400          | 80                     | 25               | 1.2                                 | 25  |
| PTM4                    | LFP     | 1        | 1000         | 81.1%                  | 25               | ~1-2                                | 26  |
|                         |         |          | 500          | 81.3                   | 60               |                                     |     |
| TfOH-LLZTO              | LFP     | 1        | 500          | 81                     | 25               | 3.1                                 | 27  |
| LL-g-PMT20              | LFP     | 0.5      | 500          | 71                     | 25               | 1.9                                 | 28  |
| DLHSE                   | LFP     | 0.2      | 140          | 91                     | 25               | 2                                   | 29  |
| HTIT                    | LFP     | 1        | 800          | 90                     | 30               | 3                                   | 30  |
| Li-MPSE                 | LFP     | 0.5      | 200          | 99.7                   | 30               | 2                                   | 31  |
| F-Mo <sub>2</sub> C-LCP | LFP     | 2        | 500          | 51.6                   | 25               | 0.98                                | 32  |
| PVDF/PCL/L              | LFP     | 1        | 500          | 76                     | 60               | 2                                   | 33  |
| AMSE                    | LFP     | 3        | 500          | 99                     | 100              | 3                                   | 34  |

|            |        |             |      |       |     |      |           |
|------------|--------|-------------|------|-------|-----|------|-----------|
| GZ-62-QSSE | LFP    | 1           | 600  | 93    | 80  | 2.5  | 35        |
| TPDOL      | LFP    | 1           | 150  | 97.81 | 60  | 3    | 36        |
| TPPSE      | LFP    | 0.2         | 100  | 96.6  | 60  | 2    | 37        |
| PTS-PVHL   | LFP    | 1           | 1000 | 80.5  | 25  | ~2-3 | This work |
|            | LFP    | 1           | 400  | 99.0  | 120 |      |           |
|            | NCM811 | 0.2 (4.5 V) | 450  | 82.5  | -25 |      |           |

**Question 6:** In the electrochemical testing section, it is stated that 2.5  $\mu\text{L}$  of a carbonate-based liquid electrolyte was added to the cell. The authors claim that this small amount does not affect the intrinsic properties of the materials. If this is the case, cell performance without any liquid electrolyte should also be demonstrated. Many studies add a small amount of liquid electrolyte as a wetting agent or initiator; however, such systems should more appropriately be classified as quasi-solid-state or hybrid systems. Furthermore, 2.5  $\mu\text{L}$  cannot reasonably be considered a negligible amount.

**Response:** We fully agree with the reviewer that the liquid electrolyte introduced into the solid-state electrolyte system, even at a low amount of 2.5  $\mu\text{L}$ , cannot be simply neglected, and its role must be clearly defined and quantitatively assessed. To address this important issue, we have strengthened the revised manuscript from the following three aspects:

(1) Our high-temperature tests confirmed that the small amount of electrolyte introduced into the system merely improved interfacial wettability and did not cause performance degradation of the batteries at elevated temperatures. In comparison, conventional liquid-electrolyte batteries still cannot operate stably under such high-temperature conditions, even when equipped with highly stable polyimide (PI) separators. Moreover, batteries assembled with unwetted dry electrolyte membranes can only achieve charge-discharge operation at low rates at high temperature, failing to work normally at higher current densities (Figure r14). To further clarify the role of interfacial wetting, comparative tests were performed using conventional polypropylene (PP) separators. When only a small amount of electrolyte (2.5  $\mu\text{L}$ ) was added, the full cell completed only one normal activation cycle at high temperature before overcharging occurred. By contrast, with a conventional electrolyte content of 50  $\mu\text{L}$ , severe overcharging appeared immediately in the first cycle under high temperature (120  $^{\circ}\text{C}$ ). These results fully demonstrated that pure liquid electrolyte cannot function stably at high temperature,

and appropriate interfacial wetting was indispensable for alleviating the inherent drawbacks of solid–solid contact.

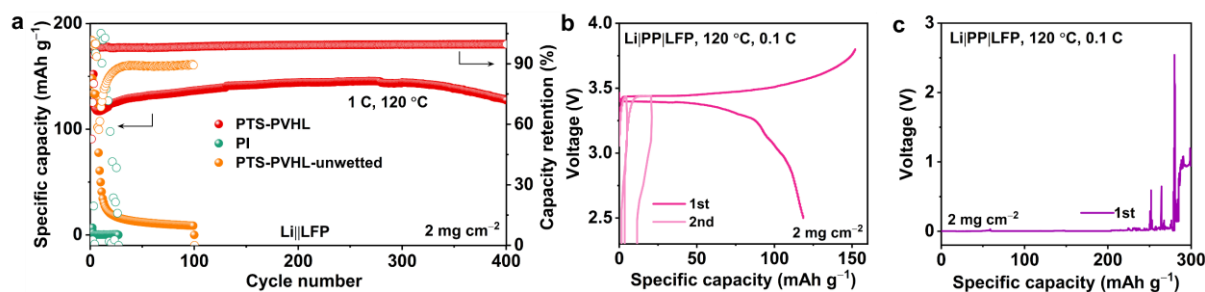
Therefore, we have added Figure r14 as Supplementary Fig. 59 (in the revised Supporting Information), and the following description to the revised manuscript (Page 18):

By contrast, cells based on conventional polypropylene (PP) separators or thermally stable polyimide (PI) separators failed rapidly under identical conditions. The comparative results indicate that PTS-PVHL sustains high-temperature operation by constructing efficient and stable solid-state ion-transport pathways (Supplementary Fig. 59).

(2) Unlike other works that exploit strong lithium-salt coordination to immobilize a considerable amount of solvents, our design was based on removing as much residual solvent as possible from the membrane during fabrication. Although residual solvent can enhance ionic conductivity, it adversely affected the high-temperature stability of the batteries. Thermogravimetric analysis (TGA) results showed that the residual DMF content in the final membrane was only 3.1 wt.% (Figure r15 and Table r3), which was at a low level. Therefore, our dry membrane contained only a very low amount of residual solvent.

(3) Regarding quasi-solid-state and hybrid battery systems, we noted that their liquid-electrolyte content is generally much higher, typically far exceeding 2.5  $\mu\text{L}$ . In addition, we have compiled the electrolyte amounts reported in recent studies, including lots of works described as solid-state batteries (Table r4).

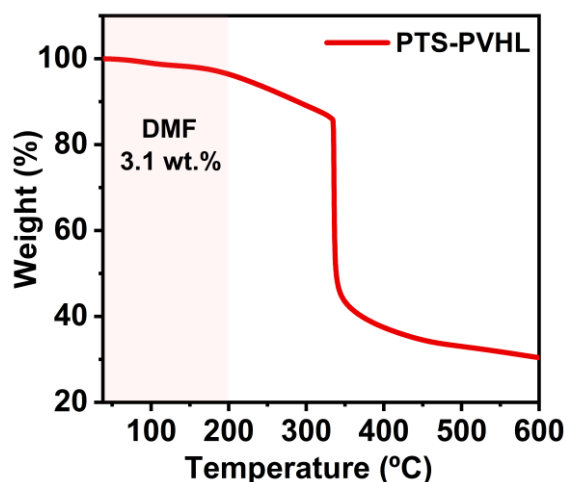
Based on these results, we define our battery system as a solid-state battery rather than an all-solid-state battery or a hybrid battery.



**Figure r14:** (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  $\mu\text{L}$  liquid electrolyte at 120 °C and 2.5-3.8 V. (c) Voltage capacity profile of Li|PP|LFP full cell with 50  $\mu\text{L}$  liquid electrolyte at 120 °C and 2.5-3.8 V.

Note: Thermally stable polyimide (PI) separators fail to sustain normal operation of assembled full cells at 120 °C with 5  $\mu\text{L}$  of liquid electrolyte. Conventional polypropylene (PP) separators likewise could not support cell operation with only 2.5  $\mu\text{L}$  of liquid electrolyte. Even under a

conventional electrolyte amount of 50  $\mu\text{L}$ , 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.



**Figure r15:** TGA curves of PTS-PVHL membrane.

**Table r3** Recent reports on PVDF-based polymer electrolytes on residual solvents.

| Ref.                                           | electrolytes    | Residual solvents (wt.%) |
|------------------------------------------------|-----------------|--------------------------|
| <i>Nat. Nanotechnol.</i> 2023, 18, 602–610     | PVBL            | 14.4                     |
| <i>Nature</i> 2025, 647, 86–92                 | PALA            | 15.7                     |
| <i>Adv. Mater.</i> 2024, 36, 2311195.          | PNNO-5          | 17                       |
| <i>ACS Nano</i> 2025, 19, 20084–20095          | md-PVDF         | 21.8                     |
| <i>Nat. Commun.</i> 2023, 14, 6296             | PVMS-15         | 12.46                    |
| <i>Adv. Mater.</i> 37, 2025, e13427            | Br-COF@PVDF-HFP | 20                       |
| <i>Adv. Funct. Mater.</i> 2026, 36, e25220     | PHWN            | 15                       |
| <i>Energy Storage Mater.</i> 2022, 51, 443–452 | PVDF-DMF-LiFSI  | 15                       |
| <i>Energy Storage Mater.</i> 2026, 84, 104835  | NCFB            | 17.5                     |
| <i>Adv. Funct. Mater.</i> 2026, 36, e18511     | PVDFHF+DOPO     | 13                       |
| This work                                      | PTS-PVHL        | 7.3                      |

**Table r4** Recent reports on PVDF-based polymer electrolytes incorporating interfacial wetting strategies.

| Ref.                                       | electrolytes          | Amount of electrolyte (μL) |
|--------------------------------------------|-----------------------|----------------------------|
| Nat. Commun. 2026, 17,376                  | L@FL <sub>35</sub> PH | 2                          |
| Adv. Mater. 2025, 0,e19284                 | PTLT-H                | 2.5                        |
| Adv. Mater. 2025, 37, 2419782              | PLSTO                 | 2                          |
| J.Am.Chem.Soc.2025,147,25896–25909         | PLF@COF316            | 5                          |
| Angew. Chem. Int. Ed. 2025, 64, e202505232 | LiPHB SICPEs          | 10                         |
| Nature 2025,647                            | PALA                  | 2                          |
| Adv. Funct. Mater. 2025, 35, 2424763       | BPLE-2                | A small amount             |
| Adv. Energy Mater. 2026, 16,e05438         | F/OH-ZIF-8@PVH        | 6                          |
| Small 2026, 22, e09917                     | PVSI-3                | 10                         |

## **Responses to Reviewer 2**

**Reviewer 2:** This manuscript presents a comprehensive study on a cationic chain-anchored monolayer strategy to enhance interfacial stability and ion transport in solid-state Li-metal batteries over a wide temperature range. The integration of experimental characterization with multiscale simulations is commendable, and the electrochemical performance—particularly under extreme temperatures—is impressive. However, several aspects of the computational methodology and data consistency require clarification to ensure reproducibility and to strengthen the physical interpretation of the results. Addressing the points below would significantly improve the rigor and transparency of the study.

**Response:** We sincerely thank the Reviewer for the positive assessment of our work and for the constructive suggestions. We have carefully addressed all comments in the revised manuscript.

**Question 1:** Please provide detailed information on the AIMD simulation settings and the equation used for binding energy calculations. Specifically, the preparation of the simulation cell, ensemble (NVT/NPT), temperature, time step, and total simulation time should be clearly stated to ensure reproducibility. In addition, although AIMD is mentioned in the Supplementary Information, corresponding AIMD-derived results are not presented in the main manuscript or SI. Please clarify how AIMD contributes to the conclusions and provide the relevant results.

**Response:** We thank the reviewer for the valuable comments. We sincerely appreciate the reviewer's critical comments regarding the simulation methodology. We acknowledge and deeply regret an error in the original manuscript where the term "AIMD" was inadvertently used during the description of Li<sup>+</sup> ion migration calculations. This was due to a terminology misapplication during drafting. We confirm that all results pertaining to Li<sup>+</sup> migration energetics were exclusively obtained using the transition state search (TSS) module within the Dmol<sup>3</sup> package of Materials Studio software, no Ab Initio Molecular Dynamics (AIMD) simulations were performed or contributed to the conclusions. Consequently, AIMD-derived results were neither included in the main text nor the Supporting Information. This terminology has been comprehensively corrected throughout the revised manuscript and Supporting Information.

Therefore, we have revised the following description in the revised Supporting Information: The methodology supporting these conclusions relies on static transition state calculations within Dmol, and we provide the complete computational settings below to ensure reproducibility, now detailed in our updated Supporting Information. All calculations were conducted using the GGA-PBE functional for exchange-correlation energy and the DNP 3.5 basis set (comparable to 6-31G in quantum chemistry). The Brillouin zone was sampled at the

Gamma point only. Prior to TSS, all structures underwent geometry optimization with convergence thresholds of  $1.0 \times 10^{-5}$  Ha for electronic energy and 0.002 Ha/Å for atomic forces. Transition states for  $\text{Li}^+$  migration paths were located using the Complete LST/QST algorithm, which involves an initial Linear Synchronous Transit (LST) path search followed by refinement via Quadratic Synchronous Transit (QST) and conjugate gradient minimization, with an atomic force convergence criterion of 0.004 Ha/Å. For all calculations, a  $3 \times 3 \times 1$  supercell with a vacuum layer thickness exceeding 15 Å was employed to mitigate periodic interactions, and a FINE integration grid was used in real space. The binding energy ( $E_{\text{bind}}$ ) of ions at specific sites was calculated as  $E_{\text{bind}} = E_{\text{total}} - (E_{\text{substrate}} + E_{\text{adsorbate}})$ , where  $E_{\text{total}}$  is the total energy of the adsorption complex,  $E_{\text{adsorbate}}$  is the energy of the pristine substrate, and  $E_{\text{adsorbate}}$  is the energy of the isolated ion. The migration energy barrier ( $\Delta E_a$ ) was determined from the energy difference between the identified transition state (TS) and the initial state (IS):  $\Delta E_a = E_{\text{TS}} - E_{\text{IS}}$ . In this part of the calculation, the  $\text{Li}^+$  diffusion energy barriers were calculated in PTS@LLZTO and  $\text{Li}_2\text{CO}_3$ @LLZTO, respectively. All energy values are referenced to 298 K for consistency in thermodynamic interpretation. We emphasize that this was a static calculation, such as ensemble (NVT/NPT), time step, and total simulation time are not applicable since molecular dynamics was not performed.

**Question 2:** The reported Li binding energies are on the order of ~4 eV, indicating very strong interactions. Please clarify the physical interpretation of such large binding energies and explain how Li-ion diffusion remains feasible under these conditions. A discussion connecting binding energy to migration barrier or dynamic transport behavior would help reconcile this apparent contradiction.

**Response:** Thank you for these important and professional suggestions. We appreciate the insightful comments provided by the reviewer regarding the calculated lithium ion binding energy of approximately 4 eV. This calculation was performed based on the following considerations:

- (1) This calculation only reflected the reduction in  $\text{Li}^+$ -TFSI<sup>-</sup> binding energy under competitive coordination with PTS, while the initial LiTFSI state was not considered as a solvated or dissociated configuration.
- (2) The subsequent desolvation-energy analysis of  $\text{Li}^+$ -TFSI<sup>-</sup> in the solvated state further demonstrated that PTS significantly lowered the  $\text{Li}^+$  desolvation energy. This behavior can be attributed to the dynamic competitive coordination of PTS, which created favorable pathways for  $\text{Li}^+$  migration.
- (3) The binding energy (~4 eV) calculated by DFT reflected the total energy difference of the

lowest energy configuration, while the activation energy of ion diffusion depended on the energy difference between the transition state and the ground state. The activation energy measured at variable temperature conductivity was only 0.092 eV.

(4) We have also observed significant  $\text{Li}^+$  binding energies (4.08 eV) in the reported literature (*Angew. Chem. Int. Ed.* 2025, 64, e202517359), further supporting our findings.

In summary, the dynamic exchange mechanism induced by competitive coordination environment is key to understanding the coexistence of high binding energy and rapid ion conduction.

Therefore, we have added the following description to the revised manuscript (Page 6):

We further evaluated the weakened  $\text{Li}^+$ -TFSI<sup>-</sup> binding induced by competitive coordination between  $\text{Li}^+$  and the cationic moieties of PTS. The results showed that  $\text{PTS}_4(\text{N}^+)$  exhibited the strongest binding affinity toward TFSI<sup>-</sup>, enabling competitive coordination with  $\text{Li}^+$  and thereby weakening the  $\text{Li}^+$ -TFSI<sup>-</sup> binding interaction. This finding confirms the intrinsic Li salt-dissociation capability of the CCM layer, even though the  $\text{Li}^+$ -TFSI<sup>-</sup> binding energy remains relatively high.

As a result, the CCM layer not only promotes lithium-salt dissociation but also provides  $\text{Li}^+$ -transport pathways, thereby facilitating solvated  $\text{Li}^+$  migration.

It further confirmed that, although PTS only slightly affected  $\text{Li}^+$ -TFSI<sup>-</sup> dissociation, its dynamic competitive coordination substantially lowered the migration barrier for solvated  $\text{Li}^+$  across the CCM layer and facilitates  $\text{Li}^+$  transport. Simulations of  $\text{Li}^+$  desolvation also indicated that PTS cations assisted  $\text{Li}^+$  in stripping its solvation shell.

**Question 3:** The desolvation reaction energy is denoted as  $\Delta G$ , which conventionally refers to Gibbs free energy. However, Supplementary Note 2 does not clearly specify whether entropic contributions and thermal corrections were included, or whether  $\Delta G$  corresponds effectively to electronic energy differences. Please clarify whether vibrational frequency calculations and thermal corrections were incorporated to compute true Gibbs free energies.

**Response:** Thank you very much for this important and professional comment. We fully agree that the desolvation reaction energy  $\Delta G$  should strictly incorporate entropic contributions and thermal corrections, rather than being simply represented by the electronic energy difference. We sincerely apologize for the ambiguous description of the  $\Delta G$  calculation method in the original Supplementary Note 2, which has led to misunderstanding.

In the revised manuscript (Supporting Information), we have supplemented and explicitly clarified the detailed calculation procedure for the desolvation Gibbs free energy  $\Delta G$ . In this work, the Shermo 1.6 program was employed to perform rigorous thermal and entropy

corrections. Structural optimization and vibrational frequency calculations for all configurations were carried out at the 6-31G\* basis set level. Subsequently, high-precision single-point energy calculations were performed using the triple-zeta 6-311+G basis set to guarantee the accuracy of electronic energies. On this basis, thermal corrections, entropic contributions, and zero-point energy corrections were integrated into the single-point electronic energy via Shermo 1.6, yielding the standard Gibbs free energy G that fully accounts for thermal and entropic effects.

Accordingly, the  $\Delta G$  defined in this work corresponds to the desolvation reaction Gibbs free energy that completely included entropic contributions and thermal corrections, rather than a pure electronic energy difference.

Therefore, we have added the following description to the revised Supporting Information:

The  $\Delta G$  includes entropy contribution and thermal correction. The  $\Delta G$  value was obtained using the Shermo 1.6 program by summing the corresponding thermal corrections obtained from the electron energy calculated using the 6-311+G basis set and the vibration frequency calculated using the 6-31G\* basis set. Use the triple zeta (3 zeta) basis set for single point energy calculation to provide better energy correction.

In addition, we also calculated the desolvation energies in the PTS-PVHL and PVHL electrolytes using two simplified representative solvation structures. The process from solvated  $\text{Li}^+$  to  $\text{LiTFSI}$  involved multiple steps including desolvation and anion participation, and the desolvation energy was calculated based on the binding energy of  $\text{Li}^+$  with the respective solvent or anion (Figure r16). The lower the calculated total desolvation energy in the PTS-PVHL electrolyte, the faster the desolvation process (*Adv. Energy Mater.* **2025**, *15*, 2404120).

Therefore, we have added Figure r16 as Supplementary Fig. 4 (in the revised Supporting Information), and the following description to the revised manuscript (Page 6):

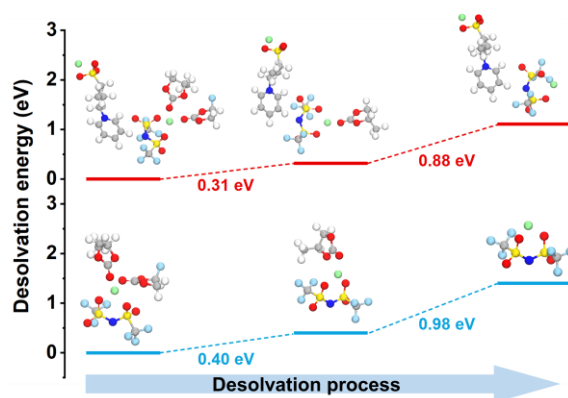
Simulations of  $\text{Li}^+$  desolvation also indicated that PTS cations assist  $\text{Li}^+$  in stripping its solvation shell.

Therefore, we have added the following description to the revised Supporting Information:

DFT calculations were performed using the Dmol3 code in Materials Studio software. Van der Waals correction of Grimme's DFT-D3 model1 was used, together with the GGA/PBE2-3 exchange-correlation functional and a DNP basis set. Next, an energy convergence criterion 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.



**Figure r16:** 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).

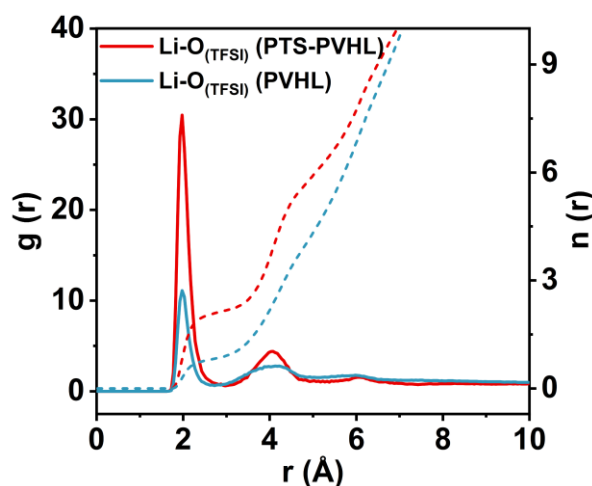
Note: In the pristine PVHL electrolyte system, the two-step desolvation energy barriers are 0.40 eV and 0.98 eV, while the corresponding barriers decreased to 0.31 eV and 0.88 eV in the PTS-modified PTS-PVHL electrolyte. The lower overall desolvation energy of the PTS-PVHL system clearly verifies that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

**Question 4:** Although RDF and coordination number calculations are described in Supplementary Note 5, the corresponding RDF plots and CN results are not presented in the manuscript or SI. Please provide the calculated RDF curves and CN analysis to support the discussion of ion coordination structure.

**Response:** Thank you for these important and professional suggestions. According to your suggestion, we have completed the calculation of the radial distribution function curve and coordination number analysis chart (Figure r17), and added them to the revised text and supplementary information, providing direct and sufficient support for the discussion of ion coordination structures in the manuscript.

Therefore, we have added Figure r17 as Supplementary Fig. 28 (in the revised Supporting Information), and the following description to the revised manuscript (Page 11).

Compared with PVHL, the radial distribution function and coordination analyses showed enhanced interaction between  $\text{TFSI}^-$  and  $\text{Li}^+$  in PTS-PVHL, demonstrating the increase of lithium-salt dissociation.



**Figure r17:** Radical distribution function (RDF) and coordination number (CN) for PVHL and PTS-PVHL electrolytes.

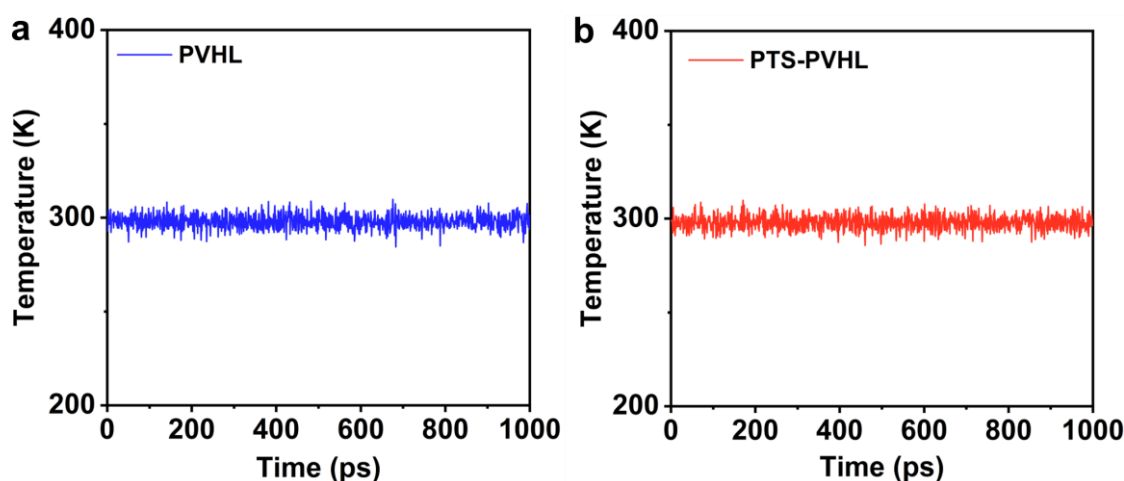
**Question 5:** In Figure 4c, the MSD plot starts from a non-zero value, and the MSD curve for PVHL appears noticeably slanted. This may indicate insufficient equilibration, particularly given that the reported equilibration time is only 100 ps. Please clarify whether a longer equilibration period was tested and confirm that the diffusion analysis was performed after complete system equilibration.

**Response:** Thank you for your important and professional suggestions. Regarding the MSD curves, the starting point is zero, and the slight deviation between the initial segment and the subsequent linear region is attributed to system oscillation or drift during the early stage of the trajectory, rather than insufficient convergence of the simulation. To address this, we will provide additional data demonstrating that the system has achieved full convergence (Figure r18). Importantly, all MSD analyses were performed based on the stable linear region of the curves, ensuring that this initial deviation does not affect the final calculated results. Such behavior was observed in published MD simulation studies (*Nat. Commun.* **2025**,16,3517). It should also be clarified that the molecular dynamics (MD) simulations were not limited to 100 ps. As described in the Computational Methods section, the simulation protocol involved an initial equilibration step using an NPT ensemble for 100 ps, followed by a production run in the NVT ensemble for 1 ns (Figure r19).

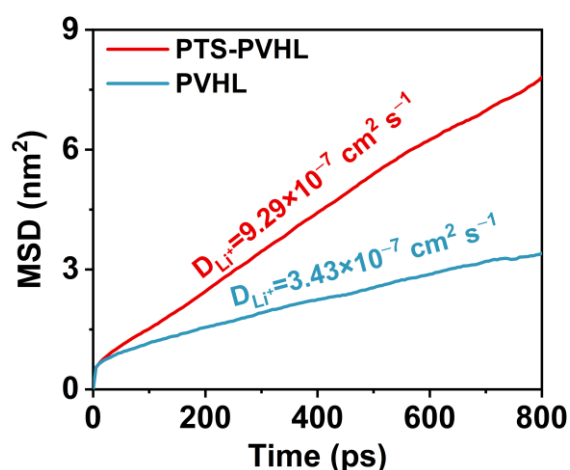
Therefore, all MSD calculations were conducted on well-equilibrated and stable systems.

Therefore, we have revised Figure r19 as Fig. 3c (in the revised manuscript), and the following description to the revised manuscript (Page 11).

From the MSD slope, the  $\text{Li}^+$  diffusion coefficient in PTS-PVHL was significantly higher than PVHL, indicating a marked enhancement of  $\text{Li}^+$  transporting because of the CCM modification.



**Figure r18:** Equilibration time of (a) PVHL and (b) PTS-PVHL.



**Figure r19:** Calculated mean square displacement (MSD) of  $\text{Li}^+$  in electrolytes.

**Question 6:** The manuscript employs multiple cathodes (LFP, NCM811, and LCO) under different testing conditions. While this demonstrates broad applicability, the varying cathode types, loadings, and voltage windows make it difficult to directly compare electrochemical performance. Please clarify the rationale for selecting different cathodes and clearly specify the testing conditions to avoid confusion.

**Response:** We thank the reviewer for the valuable comment. Three representative cathode materials were selected to evaluate the universality and compatibility of the designed electrolyte across different electrode systems. LFP was first used as a low-voltage cathode to decouple ion-transport and Li-metal interfacial effects from high-voltage oxidative degradation. Its highly stable olivine structure, limited volume fluctuation during cycling, and moderate voltage plateau ( $\sim 3.4$  V), together with an upper cut-off voltage below 4.0 V, make LFP suitable for probing the intrinsic ion-conduction capability of PTS-PVHL, Li-metal compatibility, dendrite suppression, and wide-temperature full-cell stability.

Therefore, we have added the following description to the revised manuscript (Page 16):

The full-cell performance of PTS-PVHL was first evaluated using LFP cathodes to verify the intrinsic homogeneity of its ion-transport pathways, thermal stability, and efficient Li<sup>+</sup> transport capability.

For high-voltage compatibility evaluation, LCO was selected as the cathode to assess the oxidative stability of PTS-PVHL. Compared with LFP, LCO operates at a higher potential and therefore imposes a more stringent oxidative environment on the electrolyte. When charged above 4.2 V, LCO undergoes pronounced H1-H2 phase evolution, which is highly sensitive to electrolyte oxidation, interfacial side reactions, and lattice instability. Therefore, stable cycling in LCO-based full cells can provide direct evidence that PTS-PVHL can withstand high-voltage operation while maintaining a stable cathode-electrolyte interface.

To further assess the applicability of PTS-PVHL in high-energy-density full cells, high-Ni NCM811 was employed as a stringent cathode model. Owing to its high Ni content, NCM811 is prone to structural degradation, including Li/Ni mixing, lattice strain, and oxygen release. These issues are further intensified above 4.3 V, where highly oxidizing Ni<sup>4+</sup> species promote electrolyte decomposition and cathode-electrolyte interfacial degradation. Therefore, NCM811 was used to verify the oxidative stability, interfacial compatibility, and practical viability of PTS-PVHL under high-voltage and harsh operating conditions.

Therefore, we have added the following description to the revised manuscript (Page 16):

To assess high-voltage and high-energy-density cell performance, NCM811 cathodes were employed.

For a clear electrochemical evaluation, we have explicitly stated the following voltage ranges in the revised manuscript (Page 23):

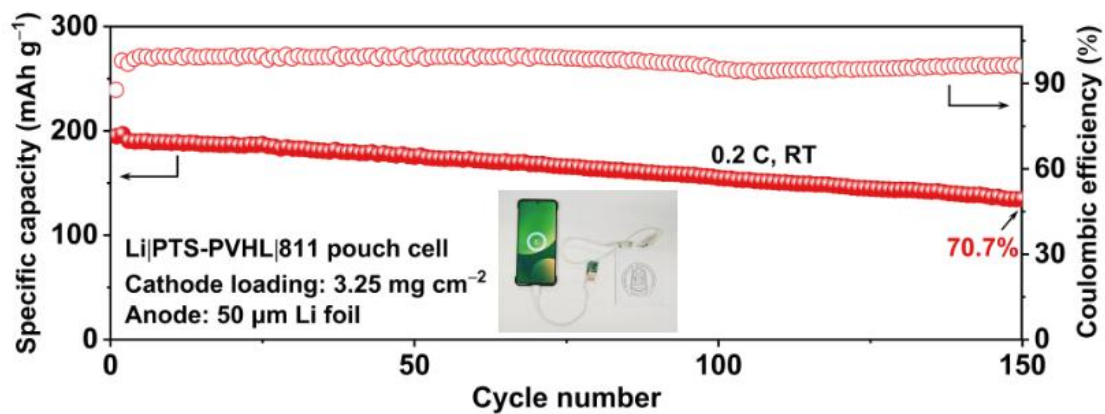
LFP full cells were tested within 2.5-3.8 V to demonstrate long-term cycling stability, whereas NCM811 full cells were examined at higher voltage ranges of 2.8-4.3 V or 2.8-4.5 V to assess high-voltage stability.

In addition, electrochemical tests using NCM811-based pouch cells (Figure r20) were added to further validate the practical potential of this electrolyte system and to minimize possible misunderstanding regarding the selection of cathode materials. The corresponding revisions have been incorporated into the revised manuscript.

Therefore, we have added Figure r20 as Fig. 5d (in the revised manuscript), and the following description to the revised manuscript (Page 19).

To further validate the practical applicability of the PTS-PVHL electrolyte, single-layer pouch cells were assembled using 50 μm Li anode and NCM811 cathode with a mass loading of 3.25 mg cm<sup>-2</sup>. As shown in Fig. 5d, the Li|PTS-PVHL|NCM811 pouch cells delivered an initial

capacity around  $190.5 \text{ mAh g}^{-1}$  at  $0.2 \text{ C}$  with a capacity retention of  $70.7\%$  after 150 cycles, demonstrating its exceptional cycling stability.



**Figure r20:** Cycling performance of  $50 \text{ }\mu\text{m}$  Li|PTS-PVHL|NCM811 pouch cell at  $0.2 \text{ C}$  between  $2.8 \text{ V}$ - $4.3 \text{ V}$  (Inset: optical picture of pouch cell powering a mobile phone).

### **Responses to Reviewer 3**

**Reviewer 3:** This manuscript reports a cationic chain-anchored monolayer (CCM) strategy to regulate ion transport in PVDF-HFP/garnet composite electrolytes, enabling wide-temperature operation (−25 to 120 °C) in solid-state lithium-metal batteries. The work combines interfacial chemistry design with multi-modal characterization (IR, ssNMR, DEMS, etc.) and demonstrates promising electrochemical performance. The topic is timely and relevant to the development of wide-temperature SSLMBs. However, several key issues regarding mechanistic clarity, experimental rigor, and data presentation need to be addressed before the manuscript can be considered for publication.

**Response:** We sincerely thank the Reviewer for the positive recognition of our work and for the constructive suggestions. We have carefully addressed all the comments in the revised manuscript. Our point-by-point responses are provided below.

**Question 1:** A key highlight of this work is the claimed operation over an ultrawide temperature range (−25 to 120 °C). While the results are promising, the current evidence is not yet fully convincing. The ionic conductivity at −25 °C is only 0.028 mS cm<sup>−1</sup>. Despite this, the cells show good cycling performance. Systematic low-temperature polarization analysis is missing. High temperature: the mechanical stability of the polymer matrix at 120 °C is not sufficiently discussed. Potential risks of softening or dimensional instability are not evaluated. It is recommended that the authors provide: Full-temperature EIS analysis. Temperature-dependent polarization data Mechanical modulus vs. temperature. Additional discussion on high-temperature safety and stability.

**Response:** We appreciate the important and professional suggestions provided by the Reviewers. We fully agree that wide-temperature operability and stability, particularly low-temperature functionality and high-temperature durability, cannot be sufficiently verified by electrochemical cycling data alone. This consideration is one of the key focuses of our work. Although only a trace amount of liquid electrolyte was introduced to improve interfacial wetting, it did not compromise the structural stability of the membrane at elevated temperatures. Notably, the high-temperature electrochemical performance of this system surpassed that of the conventional liquid-electrolyte cells, indicating that the membrane-dominated electrolyte architecture remained effective under harsh thermal conditions. Therefore, this system should not be simply regarded as a conventional quasi-solid-state battery, in which liquid-electrolyte instability often becomes severe at high temperatures. At low temperature, the electrolyte still enabled cell operation despite an ionic conductivity of only 0.028 mS cm<sup>−1</sup> at −25 °C, which we attribute to the retained continuous ion-transport pathways and the high Li<sup>+</sup> transference

number.

In response to the Reviewer's suggestion, we have added temperature-dependent EIS analysis, temperature-related polarization data, and thermal stability characterization of the solid electrolyte membrane to the Supporting Information.

(1) The added voltage-capacity curves provide a systematic assessment of the discharge behavior of Li|PTS-PVHL|LFP cells across a broad temperature range from  $-25\text{ }^{\circ}\text{C}$  to  $120\text{ }^{\circ}\text{C}$ . The cells maintain the typical flat LFP discharge plateau at  $\sim 3.40\text{ V}$  from  $-25\text{ }^{\circ}\text{C}$  to  $60\text{ }^{\circ}\text{C}$  with limited polarization, demonstrating efficient  $\text{Li}^{+}$  transport and favorable electrode-electrolyte interfacial compatibility. Even at  $100\text{ }^{\circ}\text{C}$ , the voltage plateau decreases only slightly, suggesting that the PTS-PVHL electrolyte can preserve effective ion conduction and stable interfacial contact at elevated temperature. Even under  $120\text{ }^{\circ}\text{C}$ , the cell retains the characteristic voltage plateau of LFP charge-discharge curves, and the ohmic polarization does not increase appreciably (Figure r21). Compared with the lower-temperature profiles (less than  $120\text{ }^{\circ}\text{C}$ ), the abnormal evolution observed at the later stage of the charge/discharge plateau is likely associated with temperature-modulated concentration polarization. But the overlapping charge-discharge profiles over different cycles at  $120\text{ }^{\circ}\text{C}$  further demonstrate the high reversibility of the electrochemical process (Figure r22).

(2) Full-temperature EIS analysis shows that both bulk and interfacial impedance decrease markedly as the temperature increases from  $-25\text{ }^{\circ}\text{C}$  to  $120\text{ }^{\circ}\text{C}$  (Figure r23). The impedance increases sharply at low temperatures ( $-25\text{ }^{\circ}\text{C}$  and  $-10\text{ }^{\circ}\text{C}$ ), while it decreases substantially at elevated temperatures above  $60\text{ }^{\circ}\text{C}$ , demonstrating the strong temperature dependence of ion transport in the electrolyte bulk and charge-transfer kinetics at the electrode-electrolyte interfaces. Notably, the impedance retained at high temperatures also confirms that the solid electrolyte membrane does not melt, collapse, or induce internal short circuiting under full-cell operation. In addition, the temperature-dependent polarization profiles further support the EIS results, confirming that the PTS-PVHL electrolyte maintains stable ion-conduction pathways and robust electrode-electrolyte interfaces under both low- and high-temperature conditions. These results verify the excellent interfacial stability and ion-transport capability of the designed electrolyte over a wide temperature range, providing important electrochemical evidence for its application in wide-temperature energy-storage devices.

Therefore, we have added Figures r21 and r23 as Supplementary Fig. 56 (in the revised Supporting Information), and the following description to the revised manuscript (Page 18):

Temperature-dependent impedance spectra and voltage profiles verified that the cell remained operational across different temperatures.

(3) Thermal stability tests were performed on the two electrolyte membranes at 120 °C. The reference PVHL membrane showed slight shrinkage, whereas PTS-PVHL exhibited no obvious dimensional deformation (Figure r24). This result directly confirms the superior high-temperature dimensional stability of PTS-PVHL, which supports its stable electrochemical performance under elevated-temperature conditions.

(4) In addition, we measured the Young's modulus of PTS-PVHL at different temperatures to further evaluate its thermomechanical properties. Before each measurement, the PTS-PVHL electrolyte was maintained at the target temperature for more than 6 h to ensure thermal equilibrium. The Young's modulus of the PVDF-based polymer electrolyte shows clear temperature dependence. Because the glass transition temperature ( $T_g$ ) of PVDF is approximately  $-35$  to  $-20$  °C, room temperature (25 °C) is well above its  $T_g$ . Under this condition, enhanced segmental motion gives rise to a moderate Young's modulus of 2.84 GPa. At  $-25$  °C, the restricted chain mobility leads to a significantly higher modulus of 4.25 GPa. As the temperature increases above room temperature, polymer chain motion is further activated, and the modulus gradually decreases. Nevertheless, PTS-PVHL still maintains considerable mechanical strength at elevated temperatures, confirming its robust thermomechanical stability under wide-temperature operating conditions (Figures r25 and r26).

Therefore, we have added Figures r24-26 as Supplementary Fig. 35 (in the revised Supporting Information), and the following description to the revised manuscript (Page 11):

Further investigations indicated that the PTS-PVHL membrane provided other key prerequisites for wide-temperature operation, including excellent homogeneity, mechanical robustness, and thermal stability, indicating its potential compatibility with lithium metal.

(5) Surface XPS characterization of the cathode and anode in full cells further verifies the excellent interfacial stability of electrodes at a high temperature of 120 °C (Figure r27). No obvious accumulation of organic components was observed on the surface of both electrodes after high-temperature cycling, demonstrating that the PTS-PVHL composite electrolyte can maintain a stable interfacial chemical environment under high-temperature operating conditions. Even when high-nickel NCM811 is employed as the cathode material (Figure r28), the content and distribution of organic components on the electrode surface after cycling remain nearly unchanged, which fully confirms the superior interfacial structural stability of this system under high-temperature conditions and compatibility with high-nickel cathodes.

Therefore, we have added Figure r28 as Supplementary Fig. 25 (in the revised Supporting Information), and the following description to the revised manuscript (Page 9):

Its durability was further supported by post-cycling XPS analysis and in situ EIS measurements

of the full cell.

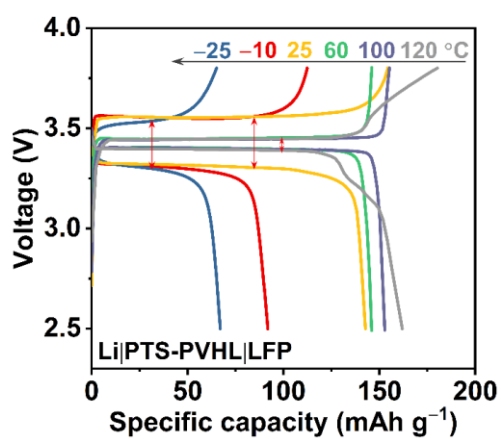


Figure r21: Voltage-capacity curves of Li|PTS-PVHL|LFP cell at different temperatures.

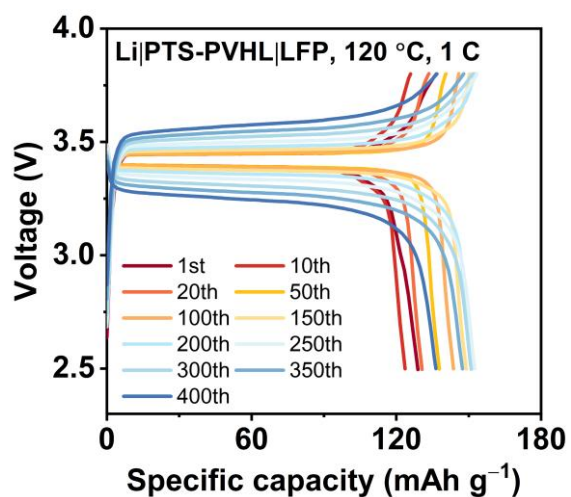


Figure r22: Voltage-capacity curves of Li|PTS-PVHL|LFP cell at 120 °C.

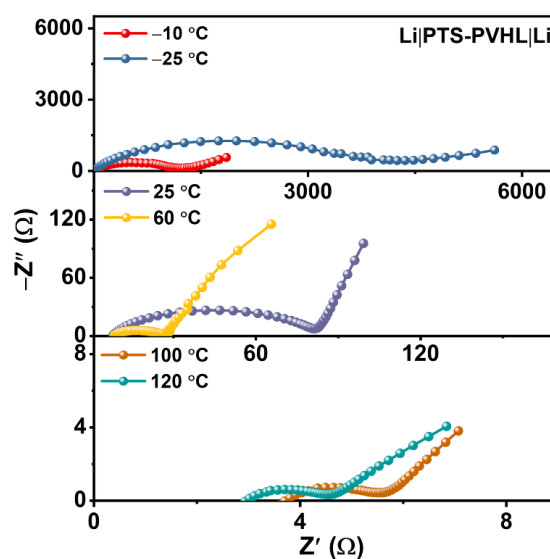
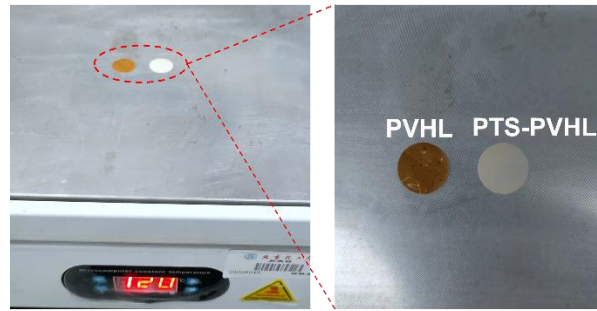
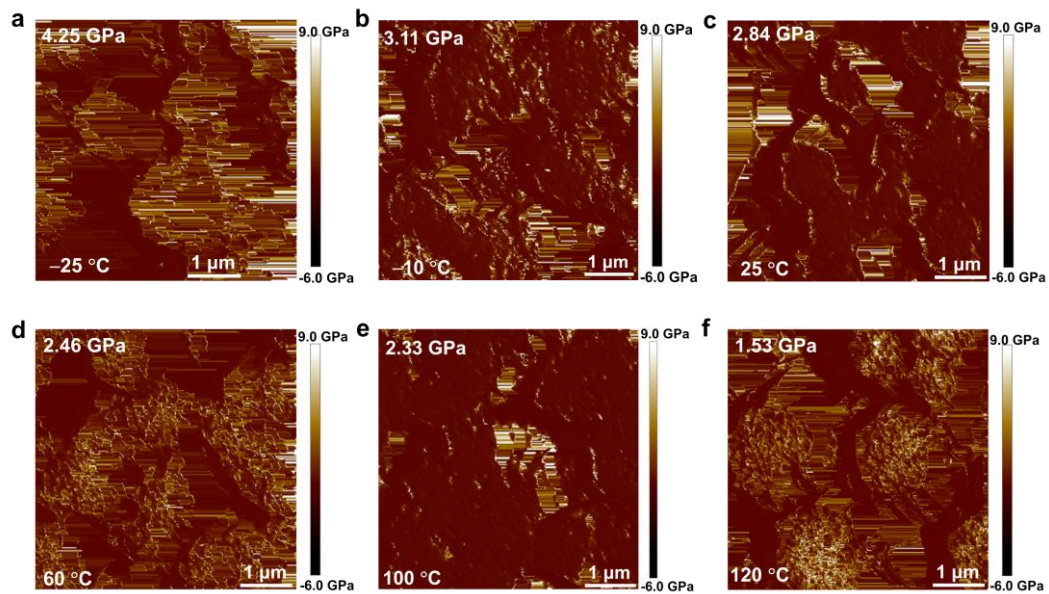


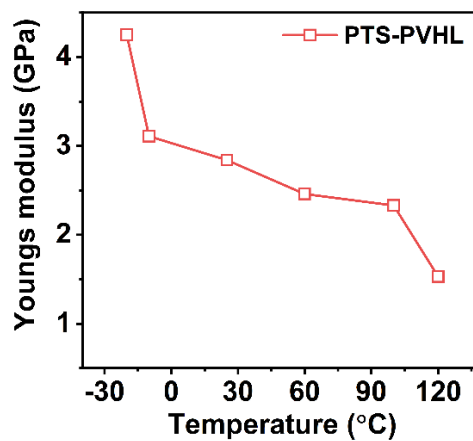
Figure r23: EIS of Li|PTS-PVHL|LFP cell at different temperatures.



**Figure r24:** Picture of electrolyte membrane heated on a 120 °C heating table.

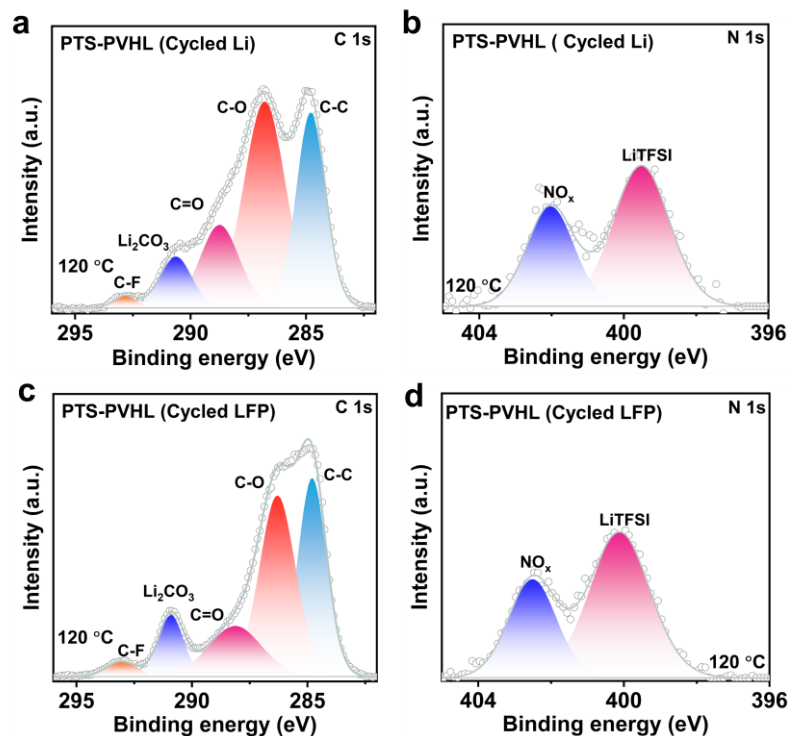


**Figure r25:** Young's modulus of PTS-PVHL membrane at different temperatures.

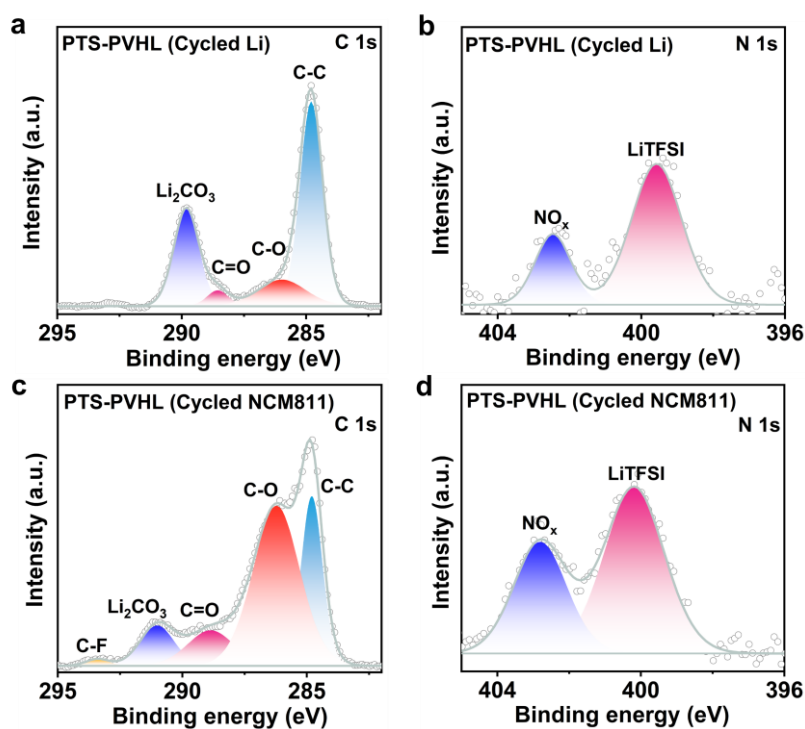


**Figure r26:** Comparison of Young's modulus of electrolytes at different temperatures.

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



**Figure r27:** XPS profiles of (a) C 1s and (b) N 1s of cycled Li metal anode of PTS-PVHL. XPS profiles of (c) C 1s and (d) N 1s of cycled LFP cathode of PTS-PVHL.



**Figure r28:** XPS profiles of (a) C 1s and (b) N 1s of cycled Li metal anode of PTS-PVHL. XPS profiles of (c) C 1s and (d) N 1s of cycled NCM811 cathode of PTS-PVHL.

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 CEI remain stable throughout cycling, demonstrating that the electrode interface maintains favorable structural stability after activation.

**Question 2:** At present, the article only presents the full battery test results of PTS-PVHL assembly, and does not provide the corresponding full battery performance data of PVHL system. It is suggested to supplement the full battery test results of the control group to improve the comparative demonstration.

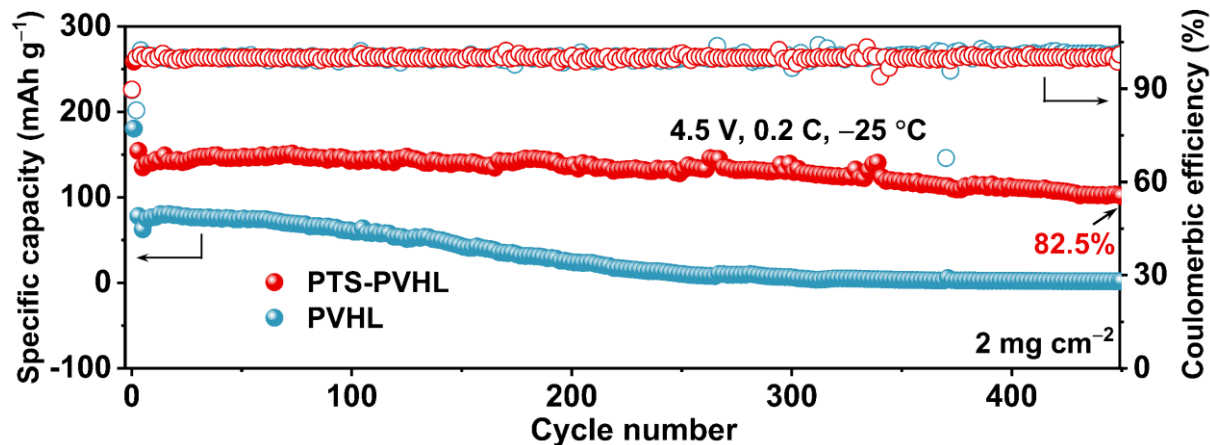
**Response:** Thank you for these important and professional suggestions. To provide a more intuitive comparison of the full-cell electrochemical performance, we have supplemented the corresponding data for the control PVHL electrolyte. As shown in the revised figure (Figures r29 and r30), PTS-PVHL delivers markedly better electrochemical performance than PVHL under wide-temperature testing conditions. These results further confirm that the cation-chain-anchored monolayer electrolyte exhibits superior overall performance.

Therefore, we have added Figure r29 as Fig. 5b (in the revised manuscript), and the following description to the revised manuscript (Page 18):

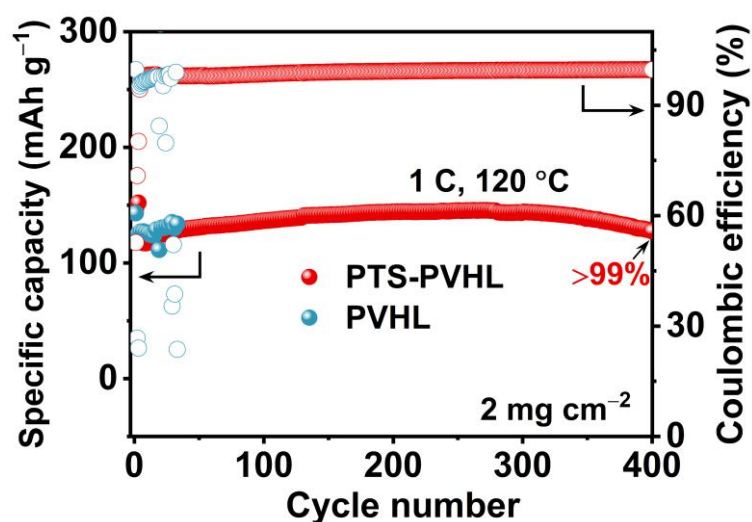
Therefore, we further evaluated high-voltage NCM811|PTS-PVHL|Li cells under ultralow-temperature conditions at 4.5 V. Li|PTS-PVHL|NCM811 (4.5 V) cells delivered a discharge capacity of 130 mAh g<sup>-1</sup> after 450 cycles at -25 °C, with 82.5% capacity retention, whereas the capacity of Li|PVHL|NCM811 full cell decayed to zero after 200 cycles.

Therefore, we have added Figure r30 as Fig. 5c (in the revised manuscript), and the following description to the revised manuscript (Page 18):

During prolonged high-temperature cycling, Li|PTS-PVHL|LFP cells sustained stable operation at 120 °C for over 400 cycles at 1 C, with a capacity retention of >99%. In sharp contrast, the Li|PVHL|LFP full cell suffered from overcharging after only 30 cycles.



**Figure r29:** Long-term cycling performance of Li|PTS-PVHL|NCM811 cells at 0.2 C between 2.8 V and 4.5 V at -25 °C.



**Figure r30:** Cycling performance of Li|PTS-PVHL|LFP cells at high temperature of 120 °C and 1 C.

**Question 3:** The authors mentioned in the article that alkyl chains have a solvent repellent effect. Please elaborate on the intrinsic reasons why alkyl chains exhibit solvent repellent properties, as well as the advantages of electrolytes with solvent repellent effects.

**Response:** We thank the Reviewer for the valuable comment. The intrinsic solvent-repellent effect of alkyl chains can be attributed to the thermodynamic mismatch in intermolecular interactions. Alkyl chains consist mainly of non-polar C–C and C–H bonds, with a highly symmetric electron distribution and no permanent dipole moment. Therefore, they cannot form strong dipole-dipole interactions or hydrogen bonds with polar solvent molecules. When alkyl chains are exposed to a polar solvent, surrounding solvent molecules must be rearranged. This unfavorable thermodynamic cost drives the system to minimize direct contact between the alkyl chains and the polar solvent, giving rise to solvent-repellent behavior (Angew. Chem. Int. Ed. 2026, 65, e20071). In addition, by appropriately increasing the length of the non-polar alkyl segments, enhanced steric hindrance and surfactant-like characteristics can be introduced, which further assist the desolvation of solvated Li<sup>+</sup> at the interface (Angew. Chem. Int. Ed. 2025, 64, e202506056).

Solid-state electrolytes with solvent-repellent properties offer several advantages. First, our results demonstrate that the solvent-repellent effect on the surface of the inorganic composite phase is critical for the overall stability of the cell, especially at elevated temperatures. Previous studies have mainly focused on stabilizing the electrode interfaces, whereas our findings reveal that electrolyte corrosion can also occur on the surface of the inorganic composite phase. This corrosion may generate ionically inactive regions on the composite surface and produce side products that deteriorate overall cell performance by

aggravating interfacial side reactions, particularly under high-temperature conditions. Second, the use of an ionic-liquid modification layer can mitigate the ion-transport limitation caused by solvent exclusion, which is attributed to ionic-liquid-mediated  $\text{Li}^+$  transport while retaining the solvent-repellent effect. In addition, desolvation analysis indicates that this solvent-repellent ionic-liquid layer facilitates the desolvation of solvated  $\text{Li}^+$ , thereby enabling rapid  $\text{Li}^+$  transport within the composite electrolyte.

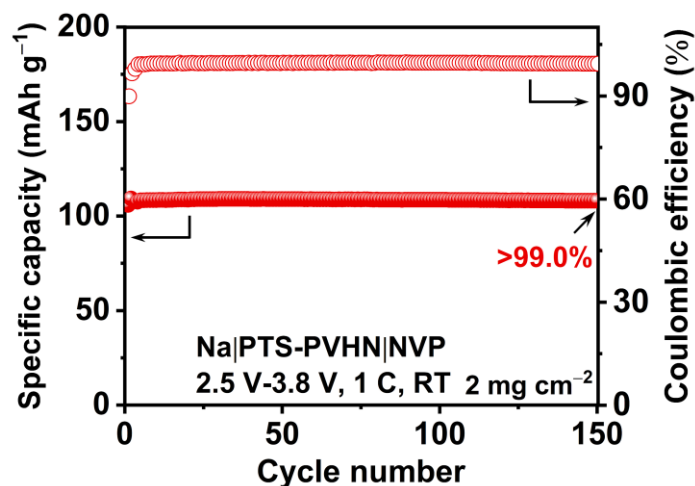
Therefore, we have added the following description to the revised Supporting Information: The alkyl chain in PTS is a nonpolar hydrocarbon skeleton, while carbonate-based electrolyte solvents are highly polar molecules. The significant polarity difference between them prevents the formation of stable 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.

**Question 4:** Can the proposed "cationic chain-anchored monolayer" strategy be extended to other battery systems?

**Response:** Thank you for these important and professional suggestions. We have further expanded the application of the cationic chain anchoring monolayer strategy mentioned above to sodium metal battery systems. Firstly, surface modification of  $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$  (NZSP) nanofillers was carried out using the same acidic ionic liquid, and then a composite solid electrolyte membrane for sodium metal batteries was prepared using the same film-forming process as before, named PTS-PVHN. Subsequently, the electrolyte was assembled into sodium-metal full cells using a sodium-metal anode and a  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  (NVP) cathode to evaluate its electrochemical performance. As shown in the corresponding figure (Figure r31), the assembled sodium-metal full cells exhibit excellent cycling performance, confirming that the cation-chain-anchoring strategy is not only applicable to lithium-metal battery systems but also shows good adaptability and universality in sodium-metal batteries.

Therefore, we have added Figure r31 as Supplementary Fig. 51 (in the revised Supporting Information), and the following description to the revised manuscript (Page 16):

Additionally, the effectiveness of this CCM improvement was further confirmed in sodium metal cells, which exhibited excellent cycling stability in full cells (Supplementary Fig. 51).



**Figure r31:** Cycling performance of Na|PTS-PVHN|NVP at 1 C and 2.5-3.8 V.

**Question 5:** It is recommended that the authors provide additional necessary explanations for the excellent rate capability and long-term cycling performance in order to better highlight the advancement of the design.

**Response:** Thank you for these important and professional suggestions. The excellent rate capability and wide-temperature long-term cycling performance originate from the unique solvophobic yet Li<sup>+</sup>-conductive cation-chain-anchored monolayer formed by PTS on the LLZTO surface. The reasons are as follows. We have also revised the manuscript accordingly to emphasize the rationale and advantages of this design.

(1) Surface functionalization of the inorganic composite phase, particularly with organic modifiers, improves organic-inorganic interfacial compatibility and promotes the formation of a uniform, mechanically robust composite membrane. This contributes to stable dendrite inhibition under high-rate and long-cycle conditions.

(2) The solvophobic characteristic prevents electrolyte decomposition on the surface of the inorganic nanofillers, constructing effective and stable ion-transport pathways at the organic-inorganic composite interface. The homogeneous distribution of the modified PTS-LLZTO nanofillers further provides abundant interfacial ion-transport channels throughout the composite electrolyte membrane.

(3) The self-assembled monolayer formed by the organic ionic-liquid modification exhibits single-ion-like conducting behavior. This feature not only enables efficient Li<sup>+</sup> transport along

the interfacial ion-transport pathways but also guides  $\text{Li}^+$  migration through the  $\text{Li}^+$ -conductive active fillers. As a result, rapid and efficient ion transport is achieved, supporting high-rate capability and stable long-term cycling.

Therefore, to highlight this design, we have added the following description to the revised manuscript (Page 18):

The wide-temperature stability can arise from PTS-enabled organic-inorganic interfacial compatibility, which forms homogeneous and mechanically robust CSEs and suppresses Li dendrite growth under high-rate and long-cycle conditions. The solvent-phobic PTS layer further limits electrolyte decomposition on composite nanofiller surfaces, while uniformly distributed PTS@LLZTO provides continuous  $\text{Li}^+$ -transport pathways. Combined with single-ion-like interfacial conduction, this CCM design can accelerate  $\text{Li}^+$  migration and enhance rate capability and cycling stability.

**Question 6:** The manuscript claims the formation of a “single-ion-conducting CCM” in the Abstract. However, the current evidence appears insufficient to fully support this statement. The reported  $\text{Li}^+$  transference number ( $t_{\text{Li}^+} = 0.78$ , Fig. 3b) is relatively high but does not reach the typical level expected for true single-ion conductors. Direct evidence of suppressed anion mobility is lacking. No concentration-gradient analysis or more rigorous validation is provided. Suggestions: The authors are encouraged to adopt more cautious wording (e.g., single-ion-like conduction), or provide stronger supporting evidence, such as PFG-NMR measurements or a more rigorous Bruce–Vincent analysis.

**Response:** We sincerely thank the Reviewer for the valuable and constructive comment. We fully agree that the original description of “single-ion-conducting CCM” in the Abstract was not sufficiently supported by the current experimental evidence. We greatly appreciate the Reviewer’s professional suggestion to either adopt more cautious wording or provide stronger supporting evidence.

In response to this comment, we have revised the manuscript accordingly.

(1) All statements related to “single-ion-conducting CCM” have been changed to more accurate and conservative wording throughout the manuscript. Specifically, in the Abstract, Results, and Conclusion sections, we adopted the Reviewer’s suggested term “single-ion-like conducting behavior” to describe the system. This revision avoids overstatement and aligns the description more closely with the experimental results, including the high  $\text{Li}^+$  transference number of 0.78 (Figure 3b).

Therefore, we have revised the following description to the revised manuscript (Page 1 and Page 19):

We demonstrate that an in-situ formed single-ion-like conducting CCM, featuring solvent-phobic chain-tethered cationic channels, establishes robust and efficient ion transport pathways in the composite electrolyte interface.

We thereby design and demonstrate the anchoring CCM to provide durable ion-conduction pathways via its solvent-phobic chain and enables rapid single-ion-like conduction through its salt-philic cationic center.

(2) We agree with the Reviewer that a high  $\text{Li}^+$  transference number alone is insufficient to definitively confirm single-ion conduction. To provide a more comprehensive understanding of ion-transport behavior in the composite solid electrolyte, we have added simulated  $\text{Li}^+$  concentration distribution results based on our transport model. The simulation shows a pronounced  $\text{Li}^+$  concentration gradient in the PVHL electrolyte, whereas the  $\text{Li}^+$  concentration distribution in PTS-PVHL is substantially more uniform. This result indicates reduced concentration polarization and suppressed anion migration, supporting the single-ion-like conducting behavior of PTS-PVHL (Figure r32).

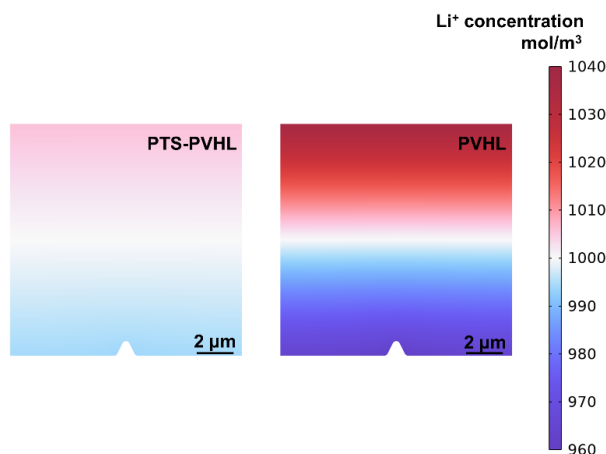
Therefore, we have added Figure r32 as Supplementary Fig. 43 (in the revised Supporting Information), and the following description to the revised manuscript (Page 12):

The  $\text{Li}^+$  concentration distribution further revealed a pronounced  $\text{Li}^+$  concentration gradient in PVHL, whereas PTS-PVHL showed a uniform  $\text{Li}^+$  distribution (Supplementary Fig. 43). These results indicated that PTS-PVHL effectively alleviates concentration polarization and suppresses anion migration.

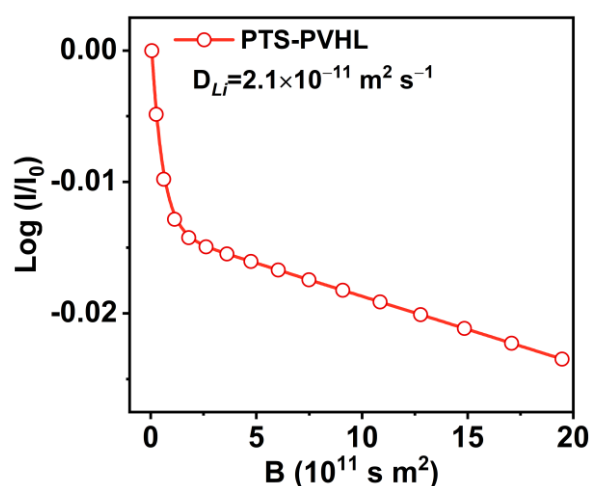
(3) Furthermore, to provide stronger supporting evidence, we performed pulsed-field gradient nuclear magnetic resonance (PFG-NMR) measurements on PTS-PVHL electrolytes. The result showed that the PTS-PVHL had a high  $\text{Li}^+$  diffusion coefficient (Figure r33). This result further supported the high  $\text{Li}^+$  transference number of PTS-PVHL and provided more direct evidence for its single-ion-like conducting behavior.

Therefore, we have added Figure r33 as Supplementary Fig. 29 (in the revised Supporting Information), and the following description to the revised manuscript (Page 11):

$\text{Li}^+$  self-diffusion coefficients of electrolyte was also measured by pulsed field gradient nuclear magnetic resonance (PFG-NMR) technology<sup>31</sup>. The result showed that the self-diffusion coefficient of  $\text{Li}^+$  in PTS-PVHL was up to  $2.1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$  (Supplementary Fig. 29). This result was consistent with the MD simulation results.



**Figure r32:** COMSOL Multiphysics finite-element method (FEMS) simulation of the  $\text{Li}^+$  concentration distribution based on PTS-PVHL and PVHL.



**Figure r33:** Diffusion plots of  $^7\text{Li}$  in the PTS-PVHL electrolyte measured by PFG-NMR.

**Question 7:** All abbreviations (e.g., PVHL, CCM) should be defined at first appearance.

**Response:** Thank you for your valuable suggestion. We have defined each abbreviation at its first occurrence and revised the manuscript accordingly.

Therefore, we have revised the following description to the revised manuscript:

Here, we report a cationic chain-anchored monolayer (CCM) strategy for engineering stable ion transport pathways within PVDF-HFP/garnet electrolytes. (Page 1)

Specifically, the  $\text{Li}||\text{LiFePO}_4$  (LFP) cells delivered over 400 stable cycles at 120 °C with >99% capacity retention, demonstrating outstanding thermal tolerance and interfacial stability. (Page 3)

Assembled high-voltage  $\text{Li}||\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  (NCM811) cells attained remarkable performance at -25 °C, maintaining 82.5% of their initial capacity after 450 cycles upon

charging to 4.5 V. (Page 3)

Synchrotron-based IR mapping revealed a gradual spatial distribution of the characteristic TFSI<sup>-</sup> bands at 1180 and 1350 cm<sup>-1</sup> in the PVDF-HFP/LLZTO (PVHL) CSE. (Page 8)

Compared with PVDF-HFP (PVH) and PVHL, quantitative analysis revealed that PTS-PVHL exhibited the highest proportion of solvent-separated ion pairs. (Page 8)

Accordingly, the morphology of cycled Li metal anodes and the chemical composition of the solid electrolyte interphase (SEI) were conducted to correlate interfacial evolution with electrolyte performance. (Page 11)

Scanning electron microscope (SEM) results revealed that the Li metal surface retained a smooth and dense morphology after 200 h of cycling in Li|PTS-PVHL|Li cell. (Page 11)

Structural stability was further evidenced by changes in the X-ray diffraction (XRD) peak intensity ratio of  $I_{(003)}/I_{(104)}$ . (Page 14)

# Response Letter

## Responses to Reviewer 1

Although the authors provided additional data and explanations, the major concerns remain unresolved. Therefore, I cannot support publication of the manuscript in its current form.

■ We sincerely thank the reviewer for the professional evaluation of our manuscript. We fully acknowledge that the concerns raised by the reviewer were not sufficiently addressed in the previous version. In response, we have made our best efforts to further improve the manuscript by supplementing targeted experimental evidence, strengthening the mechanistic interpretation, and carefully revising the relevant descriptions and core sections. Importantly, these revisions do not change the central findings of our work. Instead, the newly added results and expanded discussion further clarify and support our core conclusion that multiphase compatibility is critical for the stable operation of composite electrolytes, particularly under extreme high- and low-temperature conditions. We hope that these additional experiments, mechanistic analyses and revisions to the relevant sections can address the reviewer's concerns. All newly added results and corresponding changes have been highlighted in the revised manuscript for ease of checking. We are grateful for the reviewer's insightful suggestions, which have helped us improve the accuracy, clarity and scientific depth of this work. We believe that the revised manuscript now conveys our findings more precisely to readers and may provide useful guidance for the future design of composite-electrolyte-based batteries.

**Question 1:** Based on the experimental section, the cathodes do not contain the composite electrolyte. If so, how is  $\text{Li}^+$  transported within the cathode? If  $\text{Li}^+$  transport relies on the liquid electrolyte added at the cathode/electrolyte interface, why should this system be considered a solid-state battery?

■ Thank you for your insightful and constructive comments. We fully agree with the reviewer's concerns regarding  $\text{Li}^+$  transport within the cathode and the inappropriate description of our cell as a solid-state system. Limited ionic transport and insufficient electrolyte-electrode contact within porous cathodes remain common challenges in solid-state batteries, making interfacial wetting important for establishing effective ion-transport pathways. Based on our experimental results and recent studies and reviews, we have revised the relevant terminology throughout the manuscript to describe the system more accurately as a quasi-solid/solid-state battery using a composite polymer electrolyte (CPE). These revisions also clarify that the central aim of this work is to improve the wide-temperature stability of CPEs. Our detailed response is provided below.

(1) The issue raised by the reviewer represents a common challenge for polymer-based

electrolytes, including solid polymer electrolytes and composite polymer electrolytes. In liquid-free polymer-based electrolytes,  $\text{Li}^+$  transport is limited by polymer-segment motion and polymer crystallinity, making room-temperature cell operation difficult. A widely adopted strategy is therefore to introduce a limited amount of plasticizer or interfacial wetting component into the polymer-based electrolyte. However, interfacial wetting alone does not guarantee stable cell operation at either low or high temperatures. This point is also supported by our experiments. With the same interfacial wetting electrolyte, the unmodified PVDF-HFP/LLZTO composite polymer electrolyte could not deliver stable cell operation and even failed to operate under low- and high-temperature conditions. This indicates that the wetting electrolyte improves interfacial contact with the CPE, whereas the intrinsic properties of the CPE remain critical to the full cell performance.

(2) In practice, polymer-based electrolyte systems still strongly depend on the careful control of residual solvents. In recent reported works, the residual solvent content can exceed 15 wt%, which is even higher than the amount of our wetting electrolyte (7.3 wt%). Such dependence on residual solvents may substantially limit practical cathode loading and wide-temperature stability. In addition, for some cells using composite cathode configurations, stable operation at high cathode loading still relies on the presence of residual solvent or liquid-like components to maintain sufficient ion transport within the cathode (*Energy Environ. Sci.* 2024, 17, 344–353; *Angew. Chem. Int. Ed.* 2021, 60, 24668–24675).

(3) Previous studies have mainly focused on the electrode/electrolyte interface and have generally attributed performance degradation to electrode/electrolyte interface instability. Our results indicate that the situation is more complex. In addition to the electrode/electrolyte interface, the interfaces between different composite phases within the CPE are also critical. Composite-phase interfaces that can stabilize solvated  $\text{Li}^+$  and support  $\text{Li}^+$  migration are essential for constructing multiple  $\text{Li}^+$  transport pathways in CPEs.

(4) We acknowledge that interfacial wetting can alter ion-transport behaviour, particularly when the cathode is not configured as a composite cathode. However, our experimental results, including solid-state NMR analysis, demonstrate that  $\text{Li}^+$  transport in the composite system is mainly governed by the polymer network. Moreover, our small amount of wetting electrolyte is primarily accommodated within the porous cathode. Only a trace fraction enters the polymer membrane, corresponding to an ultra-lean electrolyte condition. Our subsequent characterizations further show that this fraction is predominantly coordinated with the polymer matrix and exists in a confined, bound state rather than as a mobile liquid phase. Recent studies have also highlighted the role of trace liquid-electrolyte addition and interfacial wetting in

polymer-based batteries (*Energy Environ. Sci.* 2025, 18, 1612; *Nat. Commun.* 2023, 14, 4884).

In response, we have comprehensively revised the terminology throughout the manuscript. All mentions of “solid-state electrolyte” and “solid-state battery” have been removed, and the term “composite polymer electrolyte” (CPE) is now used consistently and accurately to define our electrolyte system. Detailed revisions are provided below.

“Cationic Chain-Anchored Monolayer Enables Stable Ion Transport in **Composite Polymer Electrolytes** for Li-Metal Batteries from –25 to 120 °C.” (Page 1 in the revised manuscript)

“Here, we report a cationic chain-anchored monolayer (CCM) strategy for engineering stable ion transport pathways within PVDF-HFP/garnet **composite polymer electrolytes (CPE)**.” (Page 1 in the revised manuscript)

“**Keywords:** **Composite polymer electrolyte**, Li metal batteries, monolayer, ion transport, wide temperature range.” (Page 1 in the revised manuscript)

“Our work offers a new avenue for achieving high-performance **quasi-solid/solid-state** LMBs with stable long-term cycling under extreme temperature conditions.” (Page 1 in the revised manuscript)

“polymer electrolytes including poly(ethylene oxide) and poly(vinylidene fluoride) (PVDF) have been extensively developed, **composite polymer electrolytes (CPEs)** are increasingly favored for practical SSLMBs that require wide-temperature operation because they combine adequate ionic conductivity with mechanical flexibility, interfacial compliance, and scalable processability.” (Page 2 in the revised manuscript)

“Considerable efforts have been devoted to optimizing phase compatibility in the **CPEs** to achieve continuous and efficient ion transport pathways<sup>14</sup>. However, **CPE-based** LMBs remain vulnerable to safety hazards and performance failure under non-ambient conditions.” (Page 2 in the revised manuscript)

“This work delivers insight into the kinetic design and thermodynamic stability of ion-conducting pathways across a wide-temperature range, offering practical guidelines for **quasi-solid/solid-state** battery implementation.” (Page 3 in the revised manuscript)

“In this work, we propose a cationic chain-anchored monolayer (CCM) that self-assembles on inorganic Li<sup>+</sup>-conducting fillers within **CPEs**.” (Page 3 in the revised manuscript)

“Assembled **CPE-based** LMBs exhibit exceptional electrochemical stability under both elevated/high and sub-zero temperatures.” (Page 3 in the revised manuscript)

“Design principles of Li<sup>+</sup> transport pathways in **CPEs**.” (Page 3 in the revised manuscript)

“Therefore, the CCM design impacts both the cathode structure and the CEI stability in **CPE-based** LMBs.” (Page 15 in the revised manuscript)

“The wide-temperature stability can arise from PTS-enabled organic-inorganic interfacial compatibility, which forms homogeneous and mechanically robust CPEs and suppresses Li dendrite growth under high-rate and long-cycle conditions.” (Page 18 in the revised manuscript)

“The organic-inorganic interphase in CPEs is identified as a dominant origin of accelerated degradation at elevated temperatures.” (Page 19 in the revised manuscript)

“in quasi-solid/solid-state electrolyte systems, offering valuable design guidance for structural and kinetic engineering of ion-conducting pathways towards practical battery development.” (Page 19 in the revised manuscript)

**Question 2:** The authors argue that 2.5  $\mu\text{L}$  of liquid electrolyte has little influence on cell performance. However, cells without liquid electrolyte cannot operate (Figure r14). Does this not indicate that the liquid electrolyte is essential for cell operation?

■ We greatly appreciate the reviewer’s careful evaluation of this critical issue. This question is closely related to the concern regarding the addition of a small amount of liquid electrolyte (Q1). As discussed in detail in our response above, the use of interfacial wetting components or residual solvent assistance is still common in current polymer-based and composite electrolyte systems, especially when practical porous cathodes are used. Therefore, we have revised the relevant terminology throughout the manuscript to describe the system more accurately as a quasi-solid/solid-state battery using a composite polymer electrolyte (CPE).

To avoid any possible overstatement or ambiguity, we have removed all descriptions suggesting that “2.5  $\mu\text{L}$  of liquid electrolyte has little influence on cell performance”. In the revised manuscript, we now describe the added 2.5  $\mu\text{L}$  liquid electrolyte only as an interfacial wetting component. Detailed revisions are provided below.

“The coin cells were made with LFP/NCM811 electrodes and Li metal electrodes, and 2.5  $\mu\text{L}$  interface wetting liquid electrolyte (1.0 M LiTFSI and 0.1 M LiDFOB in FEC/PC (1:1, wt.%) was dropped on the interface between the composite solid electrolytes and these cathodes to ensure sufficient electrodes’ wetting. The wetting electrolyte enables the use of conventional electrodes without complex composite-cathode fabrication, while reducing contact resistance between the CPE and porous cathode.” (Page 22 in the revised manuscript)

**Question 3:** The electrochemical performance also remains unconvincing. According to Figure r7, stable cycling is only achieved at 0.5  $\text{mA cm}^{-2}$  and 0.5  $\text{mAh cm}^{-2}$  with considerable polarization. The cells fail under 1.0  $\text{mA cm}^{-2}$  and 3.0  $\text{mAh cm}^{-2}$ . What practical advantage is provided by the PTS modification under these conditions?

■ Thank you for your comments. We fully acknowledge that the cycling performance reflects

the current limitations of the PTS-modified electrolyte system in terms of rate capability and areal-capacity tolerance. We would like to respond to this concern in the following aspects.

(1) We agree that stable lithium stripping/plating at  $1.0 \text{ mA cm}^{-2}$  and  $3.0 \text{ mAh cm}^{-2}$  is highly relevant to practical lithium-metal batteries, but it remains a major challenge across the broader lithium-metal-battery field, including liquid-electrolyte, polymer-based electrolyte and inorganic solid-electrolyte systems. Under such demanding conditions, stable long-term operation is difficult in Li metal batteries, because of Li-metal compatibility, interfacial stability, and local  $\text{Li}^+$ -flux regulation. For polymer-based electrolyte systems in particular, the challenge is further intensified by intrinsically limited  $\text{Li}^+$  transport kinetics and the strong dependence on residual solvent, plasticizer or interfacial wetting components.

(2) To date, only a limited number of representative polymer-based electrolyte systems have reported stable lithium stripping/plating at approximately  $1.0 \text{ mA cm}^{-2}$  and  $1.0 \text{ mAh cm}^{-2}$ . It should be noted, however, that these systems still relied on considerable amount of residual solvents, with the residual solvent content reaching over 15 wt% (*Angew. Chem. Int. Ed.* 2024, 63, e202401428; *J. Am. Chem. Soc.* 2026, 148, 11540-11550; *J. Am. Chem. Soc.* 2026, 148, 25685-25695; *Nat. Nanotech.* 2023, 18, 602-610). One representative polymer-based electrolyte system reported in *Nature Communications*, the residual solvent content reached over 18 wt% (*Nat. Commun.* 2025, 16, 3517). In another representative polymer-based electrolyte system reported in *Nature Energy*, stable cycling was also achieved at  $1.0 \text{ mA cm}^{-2}$  and  $1.0 \text{ mAh cm}^{-2}$ , but the residual solvent content was similarly as high as approximately 18 wt% (*Nat. Energy* 2024, 9, 386). In addition, a recent breakthrough study reported remarkable current-density tolerance in a polymer-based electrolyte system. Nevertheless, this system also contained approximately 15.7 wt% residual solvent, and an additional interfacial wetting electrolyte was used in the high-loading cathode configuration (*Nature* 2025, 637, 123–129). These representative examples further support the reviewer's important comment that stable high-rate and high-areal-capacity operation remains a critical challenge for polymer-based electrolyte systems, especially when residual solvent content, cathode loading, and interfacial wetting are taken into account.

(3) We would like to clarify that the primary objective of this work is not to overstate extreme cycling performance, but to provide a mechanistic investigation into composite-interface chemistry. The stable cycling achieved at  $0.5 \text{ mA cm}^{-2}$  and  $0.5 \text{ mAh cm}^{-2}$  should therefore be regarded as evidence of improved  $\text{Li}^+$ -flux uniformity and enhanced interfacial stability, rather than as a benchmark for high-rate or high-areal-capacity applications.

(4) To place our results in a broader context, we have systematically summarized recent state-

of-the-art symmetric-cell performance in polymer-based lithium-metal battery systems, as presented in the Table r1. This comparison shows that stable long-term cycling at current densities  $\geq 1.0 \text{ mA cm}^{-2}$  with areal capacities  $\geq 3.0 \text{ mAh cm}^{-2}$  remains a significant challenge for polymer-based electrolyte systems. Even many advanced composites or interfacial modified electrolytes cannot maintain stable cycling under such stringent conditions. Based on this comparison, our PTS modification provides a meaningful step towards the practical implementation of composite polymer electrolytes. More importantly, this work identifies the critical role of composite-phase interfaces in determining the overall cell performance and demonstrates that targeted interfacial modification can effectively regulate  $\text{Li}^+$  flux, improve interfacial compatibility and enhance cycling stability. Therefore, the proposed interfacial design strategy may provide useful guidance for advancing composite polymer electrolytes towards practical lithium-metal battery applications.

Table r1 Comparison of the cycling performance of polymer-based electrolytes in symmetric batteries recently reported.

| Ref.                                            | Current density<br>( $\text{mA cm}^{-2}$ ) | Areal capacity<br>( $\text{mAh cm}^{-2}$ ) | Cycle time<br>(h) |
|-------------------------------------------------|--------------------------------------------|--------------------------------------------|-------------------|
| <i>Adv. Mater.</i> 2026, 0, e73393              | 0.1                                        | 0.1                                        | 6000              |
| <i>Sci. Adv.</i> 2026, 12, eaed5972             | 0.1                                        | 0.1                                        | 2500              |
| <i>Angew. Chem. Int. Ed.</i> 2026, 65, e15515   | 0.2                                        | 0.2                                        | 4000              |
| <i>J. Am. Chem. Soc.</i> 2026, 148, 8784–8794   | 0.2                                        | 0.2                                        | 2000              |
| <i>J. Am. Chem. Soc.</i> 2025, 147, 27611–27623 | 0.3                                        | 0.3                                        | 1000              |
| <i>J. Am. Chem. Soc.</i> 2026, 148, 17356–17371 | 0.1                                        | 0.1                                        | 2800              |
| <i>Nat. Commun.</i> 2026, 17:376                | 0.1                                        | 0.1                                        | 1300              |
| <i>Sci. Adv.</i> 2026, 12, eadz1014             | 1                                          | 1                                          | 2800              |
| <i>J. Am. Chem. Soc.</i> 2025, 147, 14554–14563 | 0.05                                       | 0.05                                       | 1700              |
| <i>Angew. Chem. Int. Ed.</i> 2025, e202517153   | 0.1                                        | 0.1                                        | 1000              |
| Nat. Commun. 2026, 10.1038/s41467-026-74573-0   | 0.1                                        | 0.1                                        | 7800              |
| <i>Adv. Mater.</i> 2025, e13427                 | 0.1                                        | 0.1                                        | 3000              |
| <i>Nat. Nanotech.</i> 2023, 18, 602–610         | 0.1                                        | 0.1                                        | 1900              |
| <i>Nat. Nanotech.</i> 2023, 18, 602–610         | 1                                          | 1                                          | 300               |
| <i>Nat. Commun.</i> 2025, 16, 3626              | 1                                          | 0.5                                        | 1200              |

|                                                 |      |       |      |
|-------------------------------------------------|------|-------|------|
| <i>J. Am. Chem. Soc.</i> 2026, 148, 21599–21610 | 1.2  | 1.2   | 2000 |
| <i>J. Am. Chem. Soc.</i> 2026, 148, 24852–24862 | 0.5  | 0.5   | 1800 |
| <i>J. Am. Chem. Soc.</i> 2026, 148, 11540–11550 | 0.2  | 0.2   | 6000 |
| <i>J. Am. Chem. Soc.</i> 2026, 148, 11540–11550 | 1    | 1     | 400  |
| <i>J. Am. Chem. Soc.</i> 2025, 147, 25940–25949 | 0.3  | 0.3   | 1000 |
| <i>Adv. Mater.</i> 2025, 37, 2510376            | 0.5  | 0.1   | 6000 |
| <i>Adv. Mater.</i> 2026, 0, e23369              | 0.8  | 0.8   | 1100 |
| <i>Adv. Mater.</i> 2025, 2415966                | 0.2  | 0.2   | 2400 |
| <i>Adv. Mater.</i> 2026, 0, e73748              | 0.2  | 0.2   | 2500 |
| <i>Adv. Mater.</i> 2025, 37, 2504419            | 1    | 1     | 900  |
| <i>Angew. Chem. Int. Ed.</i> 2026, 65, e8139928 | 0.1  | 0.1   | 800  |
| <i>Angew. Chem. Int. Ed.</i> 2026, 65, e1789437 | 0.05 | 0.025 | 1000 |
| <i>Nat. Nanotech.</i> 2022, 17: 768             | 1    | 1     | 400  |
| <i>Sci. Adv.</i> 2024, 10, eadl3925             | 0.1  | 0.1   | 1500 |
| <i>Nat. Energy</i> 2024, 9: 386                 | 0.5  | 0.5   | 1500 |
| <i>J. Am. Chem. Soc.</i> 2024, 146, 11371       | 1    | 1     | 600  |
| <i>Nat. Commun.</i> 2023, 14: 6296              | 1    | 1     | 500  |

**Question 4:** The full-cell performance was evaluated using a cathode loading of only 2 mg cm<sup>-2</sup>, corresponding to ~0.4 mAh cm<sup>-2</sup>. This is far below practical conditions. How do the authors justify the relevance of these results?

We sincerely appreciate the reviewer's constructive comments. We completely agree that high cathode mass loading is a critical metric for evaluating the practical application potential of our system. In the original manuscript, the low-loading full-cell tests were mainly designed to reveal the fundamental regulatory mechanism of PTS modification on interfacial stability and Li<sup>+</sup>-flux distribution. To better reflect realistic battery operating conditions, we have supplemented the additional full-cell cycling tests using high-loading cathodes of and 21.3 mg cm<sup>-2</sup> (Figure r1), with the corresponding to an areal capacity above 4.26 mAh cm<sup>-2</sup>. Under these practically relevant high-loading conditions, the PTS-modified samples still exhibited significantly cycling performance. These newly added results further extend our mechanistic conclusions to practical electrode configurations and verify the promising application potential of the PTS-modified composite polymer electrolyte for high-energy-density lithium-metal batteries. Therefore, we have added Figure r1 as Supplementary Figure 55 (in the revised

Supporting Information), and the following description to the revised manuscript (Page 17):

“The Li|PTS-PVHL|NCM811 cell assembled with high-loading NCM811 cathode ( $21.3 \text{ mg cm}^{-2}$ ) achieved stable cycling performance (Supplementary Fig. S5).

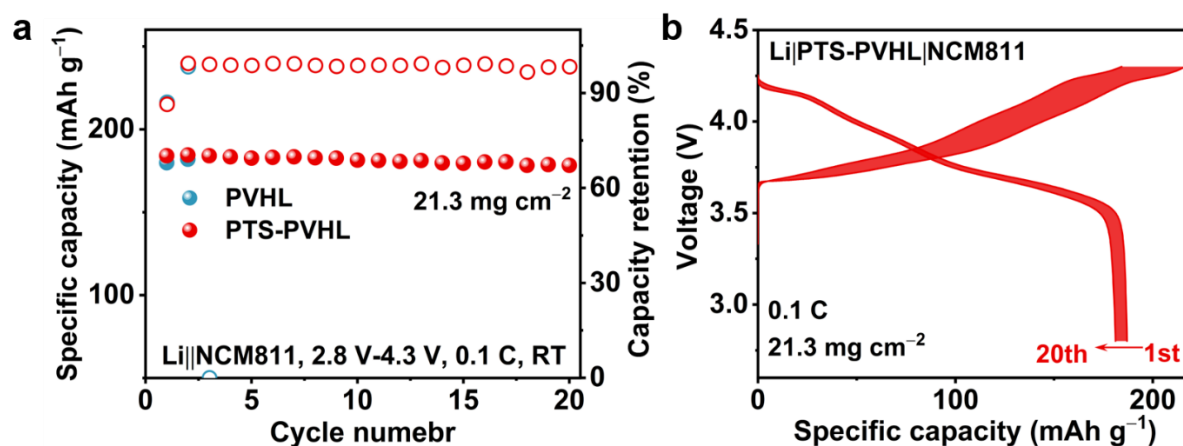


Figure r1. (a) Cycling performance of Li||NCM811 full cells with PVHL and PTS-PVHL electrolytes at 2.8 V-4.3 V and 0.1 C with high cathode loading ( $21.3 \text{ mg cm}^{-2}$ ). (b) Charge and discharge voltage profiles of Li|PTS-PVHL|NCM811 cell.

**Question 5:** The emphasis on operation at  $120^\circ\text{C}$  is also questionable. Most lithium-ion batteries operate between  $10$  and  $60^\circ\text{C}$ . Why is performance at  $120^\circ\text{C}$  considered a key metric in this work?

We agree that most commercial lithium-based batteries, particularly those used in consumer electronics, are generally operated within a moderate temperature window. Therefore, we fully understand the reviewer’s concern about the practical relevance of evaluating cell performance at  $120^\circ\text{C}$ . The primary objective of this work is to demonstrate durable battery operation over a wide temperature range, thereby supporting safer operation and potential use in demanding environments. We have addressed this concern in the following three aspects.

(1) The  $120^\circ\text{C}$  test in this work is not intended to replace performance evaluation under standard operating conditions. Instead, it is used to assess the thermal tolerance and safety margin of the proposed composite polymer electrolyte (CPE) under extreme conditions. To provide a more balanced and practically relevant evaluation, we have supplemented additional cycling tests at  $60^\circ\text{C}$  (Figure r2). The results show that the PTS-modified CPE-based lithium-metal cells can operate stably at  $60^\circ\text{C}$  with mild polarization and stable capacity retention, confirming their capability under a conventional elevated-temperature operating condition.

(2) The  $120^\circ\text{C}$  test was further included to evaluate the thermal tolerance of the electrolyte under abusive or extreme environmental conditions. This result indicates that the modified electrolyte can tolerate temperatures that would normally impose serious safety risks on

conventional liquid-electrolyte batteries, thereby providing an enlarged safety margin.

(3) High-temperature operation is also relevant to specialized energy-storage scenarios in which active thermal management is difficult or unavailable. Examples include downhole drilling and exploration, geothermal and oil/gas operations, aerospace and avionics systems, and industrial facilities exposed to tropical or desert climates. In these cases, batteries may experience temperatures far beyond the normal operating window of consumer electronics. Demonstrating stable operation at 120 °C therefore highlights the potential of the PTS-modified CPE for high-safety and extreme-environment applications.

Accordingly, we have revised the Introduction sections.

“Moreover, wide-temperature operation is essential for battery safety and applications in demanding environments, including petroleum exploration, polar operations, and aerospace systems. Quasi-solid and hybrid electrolytes have improved ion transport at ambient and subzero temperatures. However, durable operation across a broad temperature range remains challenging across quasi-solid and solid-state LMBs.” (Page 2 in the revised manuscript)

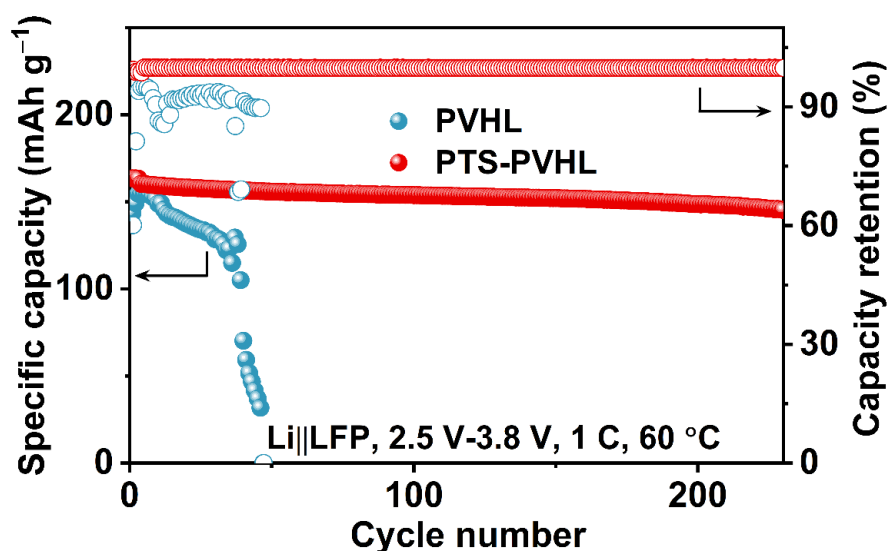


Figure r2. Cycling performance of Li||LFP full cells based on PVHL and PTS-PVHL electrolytes at 60 °C and 1 C.

**Question 6:** Approximately 3.1 wt% DMF remains in the membrane, and additional liquid electrolyte is introduced during cell assembly. Is there any direct evidence that Li<sup>+</sup> transport occurs primarily through the solid electrolyte rather than through residual liquid phases?

■ We sincerely appreciate the reviewer’s valuable comment. This concern is closely related to the issues of residual solvent and added wetting electrolyte discussed in our responses above (Q1-2), where we have provided detailed clarification of their roles in the composite polymer electrolyte (CPE)-based cell system. We would like to further respond to this concern from the

following three aspects.

(1) First, we have provided direct evidence from  $^7\text{Li}$ - $^7\text{Li}$  two-dimensional exchange solid-state NMR to clarify the  $\text{Li}^+$  transport mechanism. The results show that  $\text{Li}^+$  exchange is mainly associated with the continuous polymer-based network in the CPE. In the composite electrolyte, the strong signal peak located in the  $-0.2$  to  $-0.3$  ppm region is attributed to  $\text{Li}^+$  ions within the polymer matrix. Additionally, the weak signal near 0 ppm corresponds to  $\text{Li}^+$  ions in the LLZTO lattice (*Adv. Funct. Mater.* 2023, 33, 2303574; *Nat. Commun.* 2026, 17, 376; *Adv. Mater.* 2025, 2415966). For comparison, the pure liquid electrolyte (LE) exhibits a sharp peak at  $-0.77$  ppm (Figure r3). This specific chemical shift represents  $\text{Li}^+$  ions fully solvated by solvent molecules. In stark contrast, the dominant signal for our composite electrolyte shifts significantly to  $-0.2$  ppm and exhibits notable broadening. This substantial deviation from the liquid phase position ( $-0.77$  ppm) confirms a fundamental reconstruction of the  $\text{Li}^+$  coordination environment. Consequently, this evidence proves that ion transport occurs primarily through the interconnected polymer/LLZTO network.

(2) Second, the residual DMF content in our membrane is only approximately 3.1 wt%, which is much lower than that in many reported PVDF-based composite polymer electrolyte systems (Table r2). It is unlikely to form a continuous liquid-phase pathway that dominates long-range  $\text{Li}^+$  conduction. In addition, the PTS-modified CPE-based cells exhibit significantly better cycling stability, Li-metal compatibility and high-temperature tolerance than the corresponding liquid-electrolyte-based cells. These results further confirm that the stable cell performance cannot be simply attributed to the residual solvent or added wetting electrolyte.

(3) Third, to avoid ambiguity, we have revised the terminology and discussion throughout the manuscript. We now consistently use “composite polymer electrolyte” (CPE) to describe our electrolyte system and explicitly clarify that the small amount of added liquid electrolyte mainly serves as an interfacial wetting component.

(4) Compared with pure liquid electrolytes (LE), when the electrolyte is filled into the PTS-PVHL solid matrix, its microscopic solvation configuration undergoes a fundamental transformation. Specifically, the proportion of AGG clusters representing free liquid phase characteristics significantly decreased from 30.7% to 17.6%, and the proportion ofSSIP dependent on free solvents also decreased synchronously; on the contrary, the comparison of CIP contact ions with typical characteristics of solid electrolytes increased significantly from 27.3% to 47.9% (Figure r4). This change strongly confirms that PVDF-based polymers effectively “anchor” solvent molecules through strong coordination.

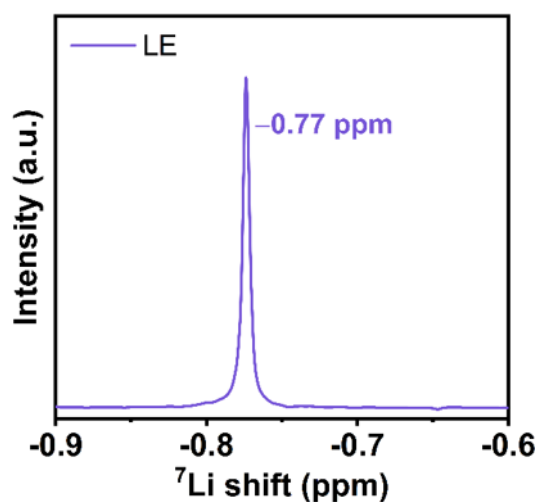


Figure r3.  $^7\text{Li}$  NMR of LE.

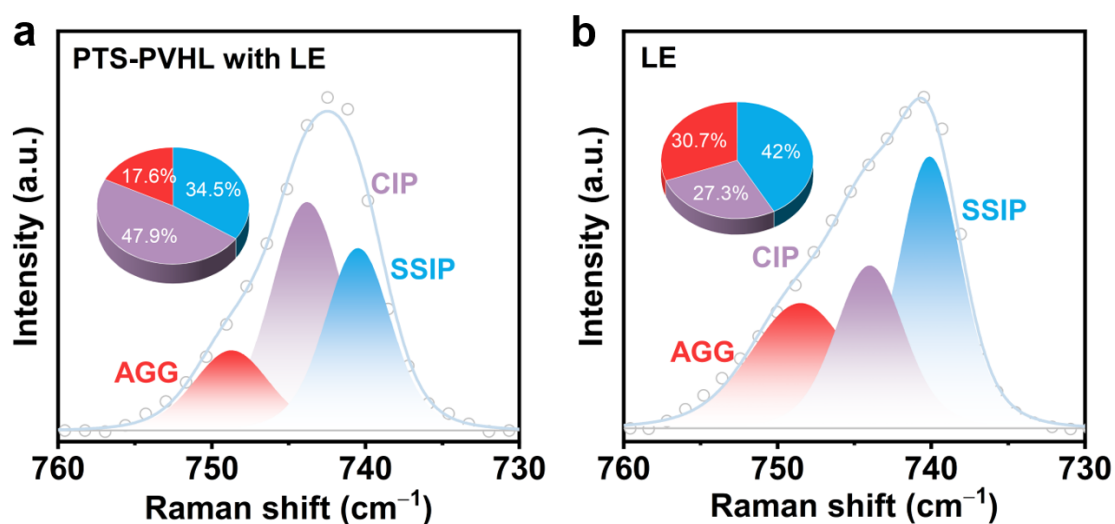


Figure r4. Raman spectra of (a) PTS-PVHL with LE and (b) LE.

Table r2 Recent reports on PVDF-based polymer electrolytes on residual solvents.

| Ref.                                              | Electrolytes    | Residual solvents (wt.%) |
|---------------------------------------------------|-----------------|--------------------------|
| <i>Adv. Mater.</i> 2025, 37, 2513427              | Br-COF@PVDF-HFP | 18                       |
| <i>Angew. Chem. Int. Ed.</i> 2025, 64, e202425221 | PVLN            | 17                       |
| <i>Energy Environ. Sci.</i> 2025, 18, 10318–10327 | PMBN            | 16.3                     |
| <i>Nature</i> 2025, 637, 123–129                  | PALA            | 15.7                     |
| <i>Adv. Energy Mater.</i> 2023, 13, 2203888       | TC SPE          | 12.8                     |
| <i>Energy Environ. Sci.</i> 2024, 17, 8274–8283   | PPM             | 18.3                     |
| <i>Adv. Mater.</i> 2024, 36, 2311195              | PNNO-5          | 13.68                    |
| <i>Nat. Commun.</i> 2026, 17, 1–25                | PVDF-BCTZ       | 13.3                     |

|                                                   |                            |       |
|---------------------------------------------------|----------------------------|-------|
| <i>Nat. Commun.</i> 2025, 16, 3517                | TPISEs                     | 18    |
| <i>Nat. Nanotech.</i> 2023, 18, 602–610           | PVBL                       | 14.4  |
| <i>Energy Environ. Sci.</i> 2024, 17, 3797–3806   | T-BTO <sub>3-x</sub> -PVDF | 15.3  |
| <i>Angew. Chem. Int. Ed.</i> 2026, 1–12           | PLI                        | 9.2   |
| <i>Adv. Funct. Mater.</i> 2025, 35, 2500727       | CIL-MOF/PVDF               | 20    |
| <i>Angew. Chem. Int. Ed.</i> 2024, 63, e202401428 | PV-MS20                    | 17.1  |
| <i>Adv. Funct. Mater.</i> 2026, 36, e14960        | SR-PVDF                    | 12    |
| <i>Nat. Commun.</i> 2023, 14, 6296                | PVMS-15                    | 12.46 |
| <i>eScience.</i> 2026, 6, 100462.                 | SIA-SPE                    | 9.2   |
| <i>Energy Environ. Sci.</i> 2025, 18, 9490–9501.  | PL-FCN                     | 10    |
| <i>Angew. Chem. Int. Ed.</i> 2026, 65, e202519404 | PSI                        | 14.3  |
| <i>J. Am. Chem. Soc.</i> 2026, 148, 11540–11550   | PHM                        | 18    |
| <i>J. Am. Chem. Soc.</i> 2026, 148, 21599–21610   | HFP-ZI                     | 30    |
| <i>J. Am. Chem. Soc.</i> 2026, 148, 25685–25695   | PHL-SL                     | 33    |
| <i>Adv. Mater.</i> 2025, 37, 2504419              | F-PVDF                     | 9.9   |
| <i>Angew. Chem. Int. Ed.</i> 2026, e8139928       | F-CPE                      | 9.5   |
| 10.1038/s41467-026-72527-0                        | PVDF-BCTZ                  | 13.3  |
| <i>Angew. Chem. Int. Ed.</i> 2026, e4082977       | PLI                        | 12.8  |
| <i>Adv. Mater.</i> 2025, e12960                   | PHF-COF-CPE                | 8.5   |
| <i>Angew. Chem. Int. Ed.</i> 2026, 65, e15515     | PHF-MS                     | 9.2   |
| This work                                         | PTS-PVHL                   | 7.3   |