



An ultrathin triazine-anchored hypercrosslinked and nonflammable solid polymer electrolyte for safe Li metal batteries

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ABSTRACT

Solid polymer electrolytes (SPEs) fabricated via in situ polymerization have garnered significant attention due to their excellent interfacial compatibility. Nonetheless, critical challenges, including low ionic conductivity, sluggish Li⁺ transport kinetics, and electrolyte flammability continue to hinder their widespread application. Herein, we introduce a multifunctional tri-arm crosslinker, triallyl isocyanurate (TAIC), to engineer an ultrathin, hypercrosslinked solid polymer electrolyte (TAIC-SPE) through in situ copolymerization with polyethylene glycol diacrylate (PEGDA). TAIC can act as rigid anchoring junctions, effectively avoiding the formation of long polymer chains, thereby enhancing ionic conductivity, and the electron-withdrawing carbonyl and triazine groups promote LiTFSI dissociation via anion coordination, enhancing the Li⁺ transference number. Besides, N-rich, structurally stable triazine ring can endow SPEs with high flame resistance and promote the formation of Li₃N-enriched SEI during electrochemical cycling. The in situ-formed hypercrosslinked network ensures seamless interfacial adhesion and yields an only ~28-μm-thick membrane that provides short ion diffusion pathways. Thus, the optimized TAIC-SPE delivers a remarkable room-temperature ionic conductivity of 1.03 mS cm⁻¹, a high Li⁺ transference number of 0.62, a wide electrochemical window (>4.8 V) and high temperature tolerance. Consequently, the symmetric cells can achieve stable cycling for over 2000 h, and full cells with LiFePO₄ cathode and high-voltage NCM cathode can run stably with a high-capacity retention. This work underscores the viability of hypercrosslinked SPEs toward the practical realization of safe, high-performance solid-state Li metal batteries.

1. Introduction

Lithium metal batteries (LMBs) have garnered significant attention in recent years for next-generation energy storage system due to the high theoretical capacity (3860 mAh g⁻¹), lowest redox potential (−3.04 V vs SHE), and low density (0.534 g cm⁻³) of the Li metal anode. [1–3] However, the path to practical deployment is obstructed by the intrinsic incompatibility between the highly reductive Li anode and organic liquid electrolytes, which induces continuous electrolyte depletion and unstable solid electrolyte interphase (SEI) formation. [4,5] Furthermore, the inherent flammability and volatility of liquid electrolytes pose insurmountable safety hazards that limit large-scale application. [6–8] Consequently, developing intrinsically safe and electrochemically resilient electrolyte systems is an urgent imperative.

In this context, solid-state electrolytes (SSEs) have emerged as a compelling alternative, promising to circumvent the volatility and leakage issues endemic to liquid systems. [9–12] Among the numerous SSEs, SPEs stand out for their unparalleled mechanical flexibility, facile

processability, and superior interfacial compatibility with electrode architectures. [13–15] However, the translational potential of conventional linear SPEs remains severely curtailed by a trio of fundamental limitations: i) intrinsically poor room-temperature ionic conductivity (typically <10⁻⁵ S cm⁻¹), stemming from sluggish segmental dynamics in semi-crystalline domains; ii) inadequate mechanical robustness, which proves insufficient to physically suppress Li dendrite penetration; iii) narrow electrochemical stability windows that preclude pairing with high-voltage cathodes. [16–18] While some prevalent strategies, such as: plasticizer incorporation or inorganic filler blending can partially alleviate ionic conductivity, these approaches often introduce unintended consequences. [19] For instance, small-molecule plasticizers (e. g., DMF, NMP, or acetonitrile) tend to migrate toward the Li metal interface, exacerbating side reactions and accelerating interfacial degradation. [20–22] Simultaneously, despite numerous studies aiming to improve the electrochemical performance and processability of SPEs, most remain flammable, posing safety risks in battery systems. [23–26] Although the introduction of flame-retardant additives (e.g., black

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phosphorus or alkyl phosphates) can mitigate fire risks, this often comes at the expense of reduced ionic conductivity or compromised mechanical integrity. [27–31] Therefore, the simultaneous realization of high ionic conductivity, wide electrochemical stability, robust dendrite suppression, and nonflammability within a single SPEs platform remains a formidable scientific challenge. [32]

In this study, we present a rational molecular engineering strategy to surmount these interconnected obstacles through the construction of a triazine-anchored hypercrosslinked network. Specifically, we employ TAIC, a multifunctional tri-arm crosslinker, to undergo in situ free-radical copolymerization with PEGDA, yielding a hypercrosslinked solid polymer electrolyte, denoted as: TAIC-SPE. The design leverages four synergistic attributes: 1) TAIC serves as rigid anchoring junctions that disrupt PEGDA crystallinity and lower T_g , unlocking segmental motion for enhanced Li^+ conduction; 2) The electron-withdrawing carbonyl and triazine moieties promote LiTFSI dissociation by anion coordination, elevating the Li^+ transference number; 3) N-rich structurally stable triazine rings facilitate the formation of a robust Li_3N -enriched SEI while endow SPEs with high flame resistance; 4) The in situ formed hypercrosslinked architecture ensures seamless interfacial adhesion with a thickness of only $\sim 28\ \mu\text{m}$. Leveraging this design, the optimized TAIC-SPE exhibits outstanding ionic conductivity ($1.03\ \text{mS cm}^{-1}$ at $25\ ^\circ\text{C}$), high Li^+ migration number (0.62), and a broad electrochemical stability window (4.8 V). Symmetric $\text{Li} \parallel \text{Li}$ cells achieve stable cycling over 2000 h, while LiFePO_4 full cells retain 83% capacity after 600 cycles. High-voltage NCM cathodes further demonstrate 89% retention after 100 cycles at 4.3 V. This work establishes hypercrosslinked network engineering as a scalable pathway toward safe, high-performance solid-state LMBs.

2. Result and discussion

2.1. Design principles and preparation of SPEs

To actualize the multifunctional design principles outlined above, we devised a facile in situ thermal crosslinking strategy. The in-situ crosslinking process and double-bond radical polymerization mechanism were illustrated in Fig. 1a. In a typical procedure, the crosslinking agent of TAIC, and the monomer of PEGDA, were uniformly mixed and polymerized via thermal initiation by azobisisobutyronitrile (AIBN), yielding a densely crosslinked, three-dimensional hypercrosslinked network, labeled TAIC-SPE. As shown in Fig. 1b, the initially flowing transparent precursor solution gradually transformed into a dimensionally stable, optically clear SPE membrane upon completion of the polymerization process. [33]

Fourier-transform infrared (FTIR) spectroscopy was employed to examine changes in functional groups before and after polymerization. As shown in Fig. 1c, following polymerization, the characteristic $\text{C}=\text{C}$ stretching vibration peak of PEGDA at $1618\ \text{cm}^{-1}$ disappeared, indicating that both TAIC-SPE and SPE underwent polymerization reactions. [34,35] Furthermore, comparison with the SPE spectrum revealed a signal at $1700\ \text{cm}^{-1}$ for TAIC-SPE, corresponding to the carbonyl ($\text{C}=\text{O}$) vibration of TAIC. Following TAIC incorporation into the polymerization, this $\text{C}=\text{O}$ signal disappeared, confirming the successful chemical grafting and copolymerization of TAIC with the PEGDA matrix. Morphological characterization via scanning electron microscopy (SEM) revealed that the crosslinked polymer networks of TAIC-SPE and SPE uniformly and densely filled the PP separator (Fig. S1). Cross-sectional SEM analysis confirmed a compact morphology with a membrane thickness of $\sim 28\ \mu\text{m}$ (Fig. 1d and Fig. S2–3). This thin architecture ensures short ion diffusion pathways while maintaining robust mechanical integrity, a prerequisite for stable and safe LMBs. Fig. S4

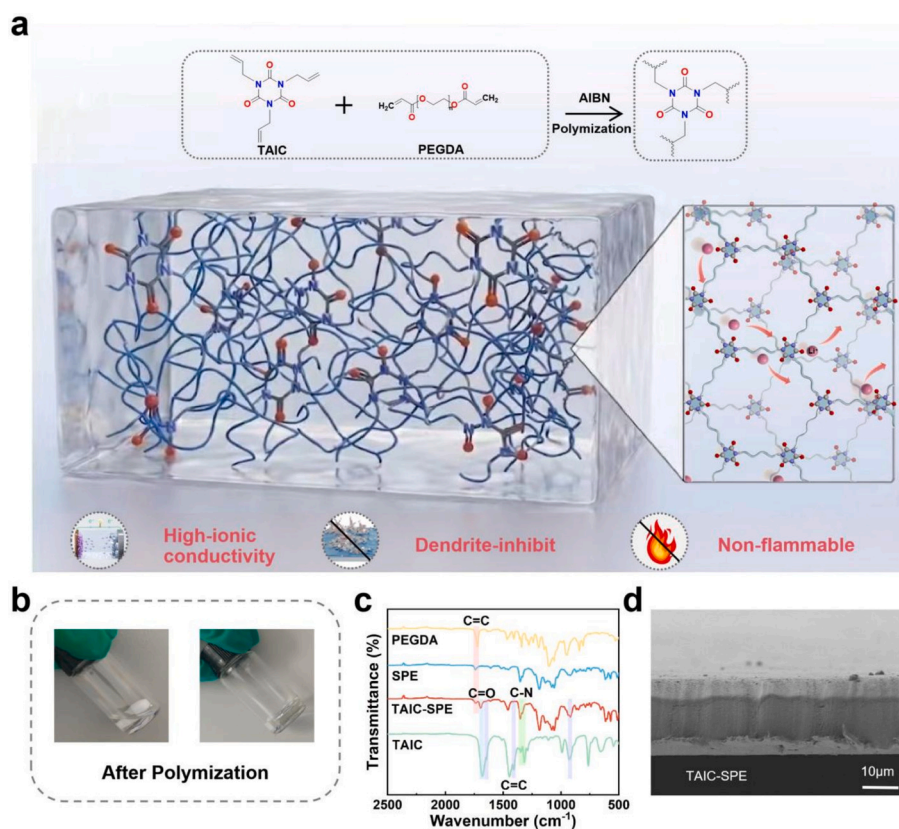


Fig. 1. Structure characterization of the SPEs. (a) Schematic of the copolymerization mechanism of PEGDA and TAIC. (b) Optical photograph of the TAIC-SPE. (c) FTIR spectra, and (d) Cross-section SEM images of TAIC-SPE electrolyte.

showed the results of the tensile test. The elongation at break of TAIC-SPE reached 140%, indicating that the crosslinking centers increased intermolecular interactions, thereby imparting high mechanical elasticity to the polymer.

2.2. Physicochemical properties of the SPEs

Having established the structural and morphological characteristics of the ultrathin TAIC-SPE, we next to analyze its Li^+ transport mechanism and electrochemical stability. To this end, the interactions between the polymer network of TAIC-SPE and LiTFSI were systematically analyzed using Fourier Transform Infrared Spectroscopy (FTIR). As shown in Fig. 2a, the incorporation of TAIC induced a distinct shift of the $\text{C}=\text{O}$ stretching vibration from 1679.8 cm^{-1} to 1695.5 cm^{-1} , signifying a pronounced coordination interaction that perturbed the local electronic environment of the carbonyl moiety. [36] This interaction directly impacted the Li^+ solvation, as revealed by ^7Li nuclear magnetic resonance (NMR) spectroscopy. As shown in Fig. 2b, the Li^+ signal in the

SPE control appeared at -1.120 ppm , indicating a highly bound, slow-exchanging solvation structure. In stark contrast, in the TAIC-SPE, the Li^+ signal was shifted up-field to -1.214 ppm , suggesting that the TAIC-incorporated network facilitated the dissociation of LiTFSI. [22]

Then, to quantify the speciation of the TFSI $^-$ anion, Raman spectroscopy was employed, with the characteristic S–N–S bending region deconvoluted via Gaussian–Lorentzian fitting into three distinct contributions: free anions (SSIP, $\sim 738\text{ cm}^{-1}$), contact ion pairs (CIP, $\sim 742\text{ cm}^{-1}$), and higher-order aggregates (AGG, $\sim 750\text{ cm}^{-1}$). [37,38] As shown in Fig. 2c and f, while both electrolytes exhibited comparable populations of free SSIP species, the ion-association state was markedly redistributed after the incorporation of TAIC: TAIC-SPE exhibited an AGG-rich coordination environment (52.58%), whereas the SPE control was dominated by CIP species (36.08%). This redistribution reflects a pronounced reorganization of the local Li^+ /TFSI $^-$ coordination environment induced by the TAIC-containing network and suggests stronger participation of TFSI $^-$ in the local coordination structure.

Furthermore, density functional theory (DFT) calculations provided

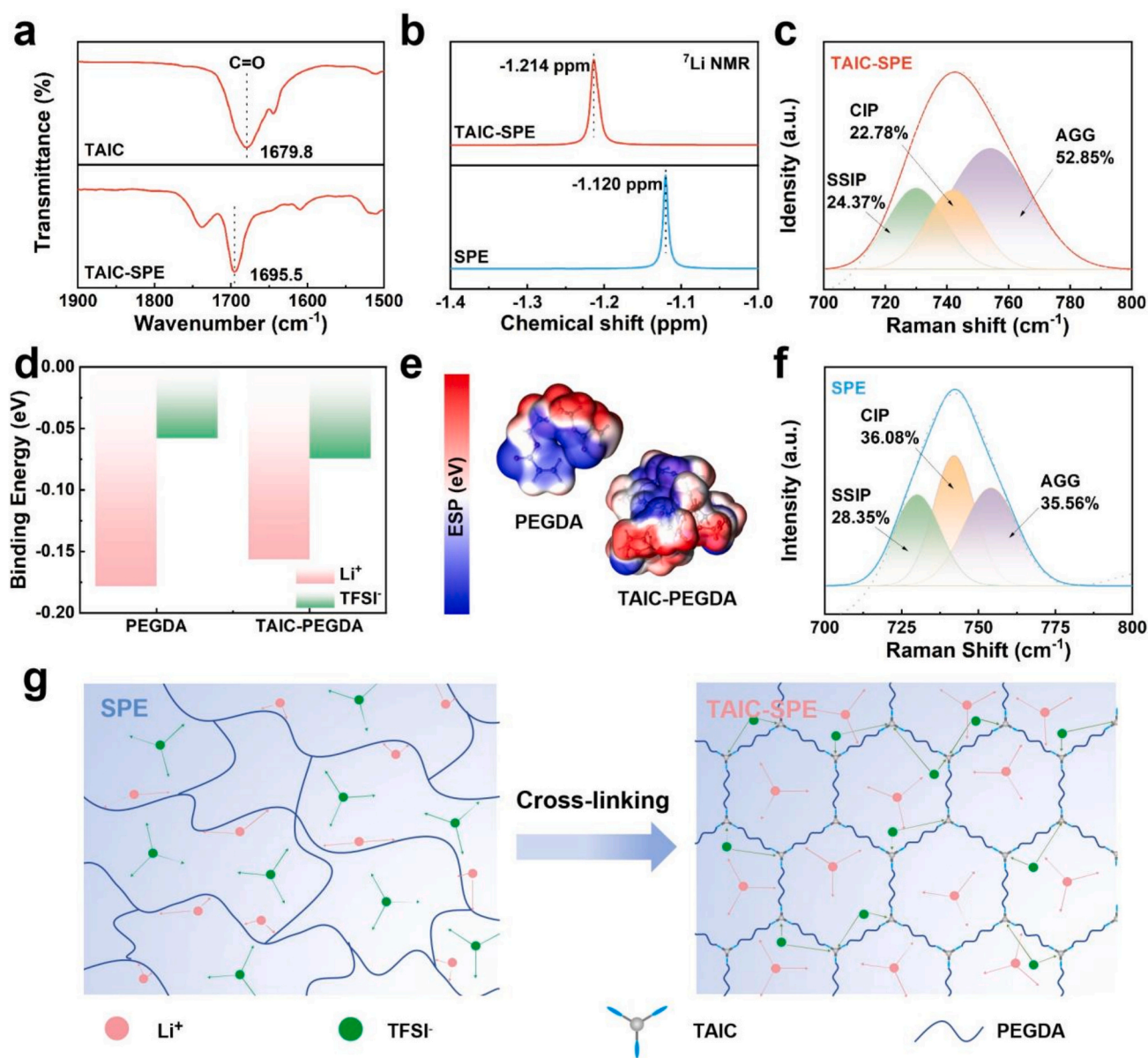


Fig. 2. Ion transport mechanism and electrochemical properties of the SPEs. (a) FTIR spectra of TAIC-SPE and SPE. (b) ^7Li NMR spectra of TAIC-SPE and SPE. Raman spectra of (c) TAIC-SPE and (f) SPE. (d) Binding energy with Li $^+$ or TFSI $^-$ of PEGDA and TAIC-PEGDA. (e) Electrostatic potential of typical clips from PEGDA and TAIC-PEGDA. (g) Ion transport mechanisms of TAIC-SPE and SPE.

complementary theoretical support for this preferential interaction. As shown in Fig. 2d, the TAIC-PEGDA segment exhibited a weaker interaction with Li^+ but a stronger interaction with TFSI^- than the polymer segment, indicating a preferential affinity of the TAIC-containing framework toward TFSI^- , [39] avoiding excessively strong Li^+ binding to the polymer framework, thereby providing a more favorable environment for ion transport.

Electrostatic potential (ESP) maps further illustrated the redistribution of the local electronic environment. [40] As shown in Fig. 2e, the negative electrostatic potential in pristine PEGDA is mainly localized around the ether oxygen atoms. After incorporation of the triazine and carbonyl functionalities in TAIC-PEGDA, the electrostatic potential distribution was substantially redistributed, generating additional polar interaction regions within the polymer framework, [41,42] which provided potential interaction sites for TFSI^- .

Taken together, the Raman-derived coordination-state redistribution, selective binding-energy characteristics, and ESP analysis provide mutually consistent evidence that the TAIC-containing framework preferentially interacts with TFSI^- and modulates the local $\text{Li}^+/\text{TFSI}^-$ coordination environment.

The Li^+ transport mechanism of TAIC-SPE was shown on Fig. 2g. In the conventional SPE, Li^+ transport was constrained by strong coordination to the polymer backbone, resulting in sluggish segmental motion-assisted hopping. However, in the TAIC-SPE, the preferential interaction of TAIC with TFSI^- anions promoted the dissociation of LiTFSI , liberated a higher concentration of free Li^+ , thereby enhancing Li^+ migration efficiency. This mechanism was also directly validated by the measured Li^+ transference number (t_{Li^+}). As shown in Fig. 3a and Fig. S5, the TAIC-SPE achieved a t_{Li^+} of 0.62, more than double that of the SPE (0.29). The parameter values used for migration calculations are summarized in Table S1. Such a high transference number was instrumental in suppressing concentration polarization and fostering uniform Li deposition.

Consistent with this enhanced transport efficiency, temperature-dependent electrochemical impedance spectroscopy and Arrhenius analysis yielded an apparent activation energy (E_a) for ionic transport of 0.11 eV for TAIC-SPE, compared with 0.14 eV for SPE (Fig. 3b and Fig. S6), corresponding to an approximately 21% reduction. The low E_a quantitatively indicated a lower energetic barrier for ion transport in TAIC-SPE, providing direct kinetic evidence for its more favorable ion-transport behavior, which was consistent with the Raman and ^7Li

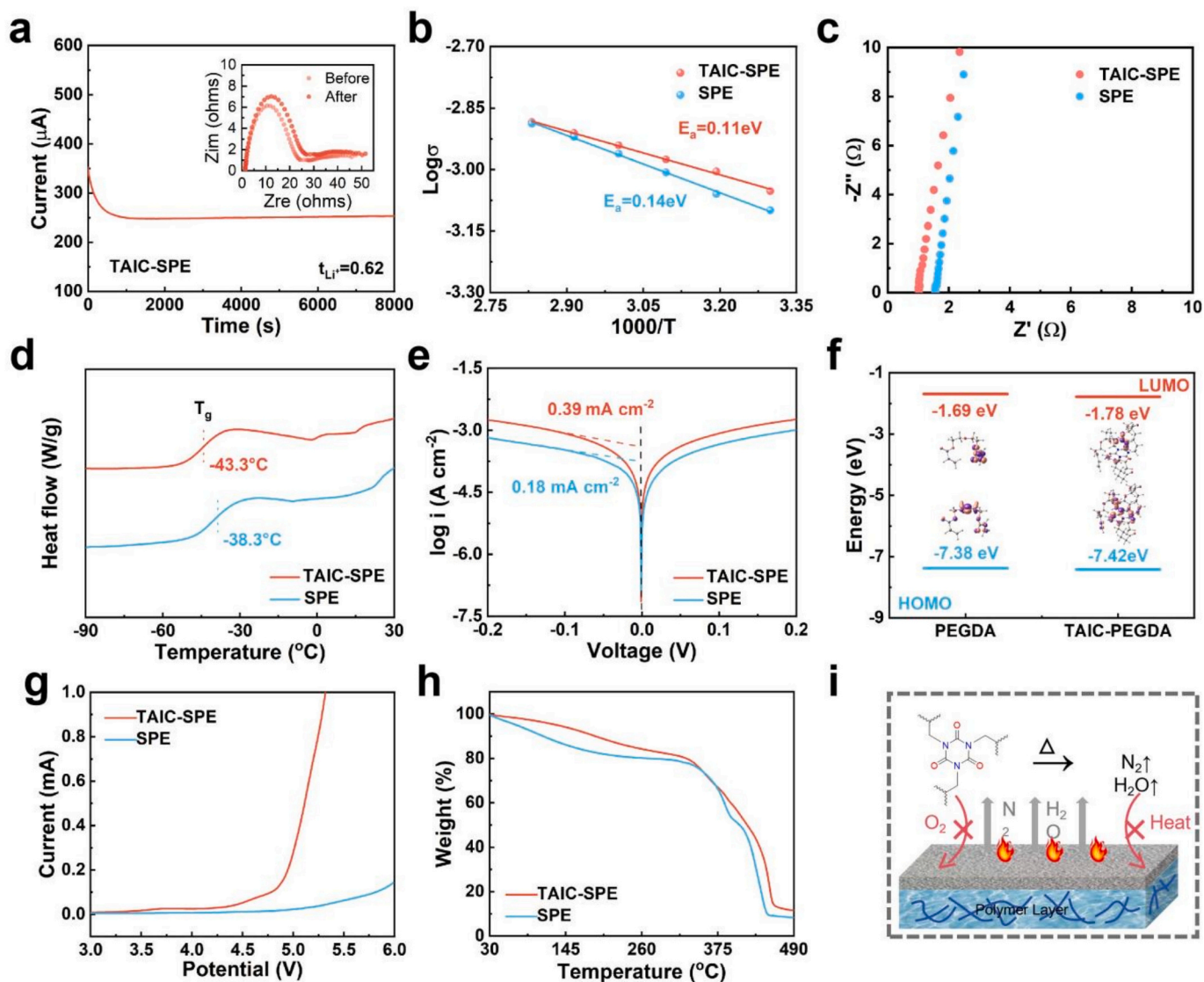


Fig. 3. Physical and chemical properties of SPEs. (a) Current-time curves of Li|TAIC-SPE|Li cells at 10 mV (illustration showed the EIS curves before and after polarization). (b) Arrhenius plots of ionic conductivity for TAIC-SPE and SPE. (c) Impedance diagrams of TAIC-SPE and SPE. (d) DSC curves of the electrolytes. (e) Tafel plots for different electrolytes. (f) Comparison of the HOMO/LUMO orbitals. (g) LSV curves of TAIC-SPE and SPE. (h) TGA curves of TAIC-SPE and SPE at 25–490 °C. (i) Flame retardant mechanism of TAIC-SPE.

NMR analyses, as well as the DFT calculations. Taken together, these complementary spectroscopic, theoretical, and quantitative kinetic results suggest that the preferential regulation of TFSI[−] modified the local Li⁺ coordination environment and reduced the energetic barrier for Li⁺ transport, thereby facilitating ion migration within the polymer matrix. [43] This reduction in the migration energy barrier, coupled with the increased carrier concentration, culminated in a high room-temperature ionic conductivity of 1.03 mS cm^{−1} (Fig. 3c). [44] Meanwhile, differential scanning calorimetry (DSC) traces revealed that the hypercrosslinked TAIC-SPE exhibited a significantly depressed glass transition temperature (T_g) of −43.3 °C, compared to −38.3 °C for the SPE (Fig. 3d). This depression in T_g was a direct consequence of the disrupted crystallinity imparted by the rigid TAIC junctions, which expanded the amorphous fraction and enhanced polymer segmental mobility, a prerequisite for efficient ion transport. [45] Moreover, Tafel analysis also revealed a higher exchange current density for the TAIC-SPE interface, further confirming accelerated Li⁺ transfer kinetics across the electrode/electrolyte interphase (Fig. 3e). Interfacial resistance is a critical parameter that bridges the microscopic structure of the electrolyte and the macroscopic performance of the battery. In polymer solid-state systems, poor interfacial contact or restricted segmental dynamics near the electrode/electrolyte interface can impede Li⁺ transport, aggravate cell polarization, and ultimately compromise rate capability. At the Li-metal interface, nonuniform Li⁺ flux further facilitates dendritic deposition. Therefore, minimizing interfacial resistance while ensuring stable electrode/electrolyte contact is essential for achieving high rate capability, long cycling stability, and enhanced safety in polymer-based solid-state LMBs. [46]

The electrochemical stability of the SPEs was equally critical for compatibility with high-voltage cathodes. As shown in Fig. 3f, the TAIC-PEGDA segment possessed a lowered highest occupied molecular orbital

(HOMO) energy level of −7.42 eV compared to the PEGDA, suggesting enhanced oxidative stability. [47] At the same time, Linear sweep voltammetry (LSV) revealed that TAIC-SPE exhibited a broad electrochemical stability window of 4.8 V, surpassing that of the SPE (4.3 V) and rendering it suitable for high-energy-density cathode chemistries (Fig. 3g). [48] The CV test results of the Li||SS half cells with different electrolyte systems showed the good Li plating/stripping reversibility (Fig. S7).

Thermal and safety characteristics were subsequently evaluated. As shown in Fig. 3h, thermogravimetric analysis (TGA) demonstrated the superior thermal resilience of TAIC-SPE, attributable to the thermal decomposition of isocyanurate groups into non-flammable and inert gaseous species. Concurrently, the formation of a dense, protective char layer during thermal exposure acts as a physical barrier to heat and mass transfer, effectively quenching combustion propagation (Fig. 3i). [49,50] The practical implications of this dual protective mechanism are vividly illustrated by combustion and thermal abuse tests. As shown in Fig. 4a and Videos S1 and S2 (Supporting Information), SPE sustained burning upon exposure to flame, whereas TAIC-SPE exhibited brief combustion followed by rapid self-extinguishment, demonstrating superior flame-retardant properties. Infrared thermal imaging comparisons between TAIC-SPE, SPE, and polypropylene (PP) separators also revealed thermal degradation processes. As shown in Fig. 4b, PP separators exhibited noticeable wrinkling at 100 °C, while SPE separators began wrinkling at 120 °C. In contrast, TAIC-SPE maintained dimensional stability and showed no significant physical changes at 160 °C, indicating superior thermal resistance and structural integrity at elevated temperatures. Collectively, these results establish that the TAIC-SPE not only delivers exceptional ionic transport metrics but also provides an unprecedented margin of safety under extreme thermal duress.

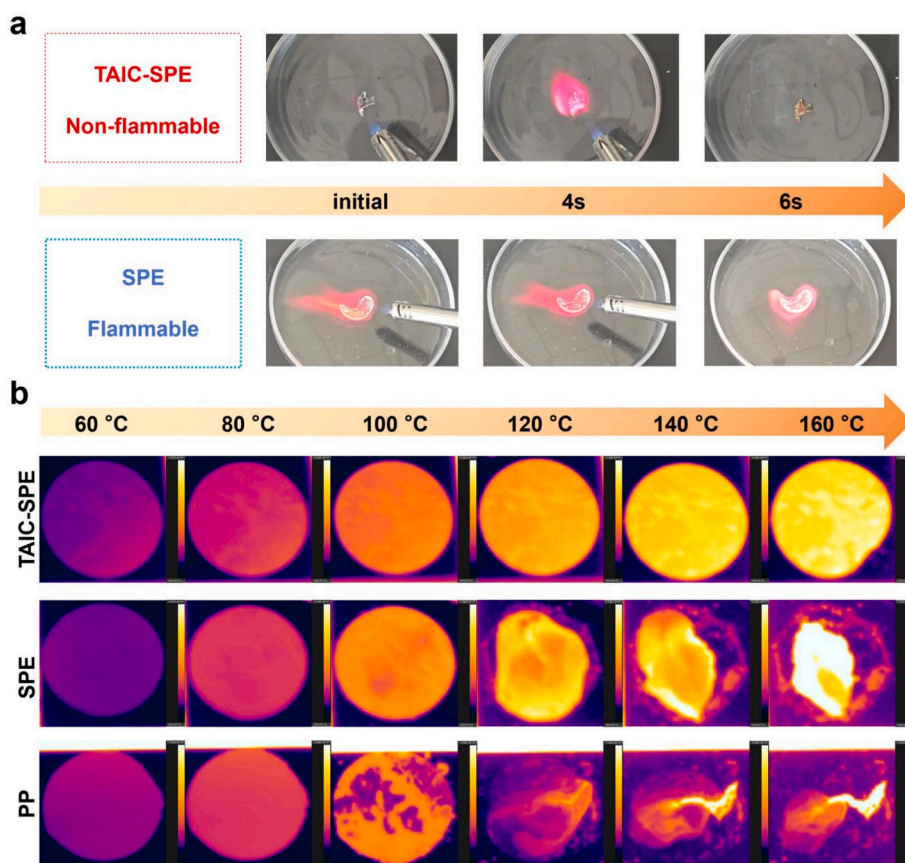


Fig. 4. Thermal stability test of SPEs. (a) Optical images of TAIC-SPE and SPE under the flame test, and (b) Infrared thermography images of TAIC-SPE, SPE, and PP during heating process.

2.3. Interfacial stability and electrochemical performance

Having demonstrated the superior ionic transport properties and intrinsic safety features of the TAIC-SPE, we next assessed its practical viability in LMBs. To this end, galvanostatic cycling of Li||Li symmetric cells were performed at a current density of 0.1 mA cm^{-2} . As shown in Fig. 5a, the cell incorporating TAIC-SPE exhibited remarkably stable voltage profiles over 2000 h, with a consistently low and invariant overpotential. In stark contrast, the overpotential of the Li|SPE|Li symmetric cells sharply declined after 200 h, a signature of incipient soft shorting induced by uncontrolled dendrite growth. Notably, throughout the cycling process, the overpotential of the TAIC-SPE remained consistently lower than that of the SPE without oscillation, underscoring its exceptional capacity to regulate uniform Li plating/stripping behavior (Fig. S8).

After cycling, the Li symmetric cell was disassembled and subjected to SEM examination. As shown in Fig. 5b, the Li metal anode harvested from the TAIC-SPE cells exhibited uniform and smooth deposition without any dendrite formation. In contrast, the Li metal anode from the Li|SPE|Li cells displayed significant non-uniform deposition and

dendrite growth (Fig. S9). The morphology of lithium deposition at different stages of the cycle also demonstrates the inhibitory effect of TAIC-SPE on dendrite formation (Fig. S10). Furthermore, after cycling 200 h, it can be observed that the thickness of the reaction layer on the TAIC-SPE was significantly thinner than that on the SPE, and its structure was denser (Fig. S11). This capacity for dendrite suppression was retained even under more demanding conditions. Furthermore, at an elevated areal capacity of 0.2 mAh cm^{-2} , the TAIC-SPE-based symmetric cell also demonstrated long-term stability (Fig. S12). Through more stringent critical current density (CCD) testing, the maximum current at which Li dendrites could be inhibited was evaluated for both samples. The critical current density for TAIC-SPE reached 2.4 mA cm^{-2} , surpassing the 1.7 mA cm^{-2} achieved by SPE (Fig. 5c). Furthermore, even at a high area capacity of 0.5 mAh cm^{-2} , the Li|TAIC-SPE|Li symmetric cells still exhibited high long-term stability, while the Li|SPE|Li cells exhibited irreversible hard short-circuiting after only 10 cycles (Fig. S13). Electrochemical impedance spectroscopy (EIS) acquired at various cycle intervals further corroborated the superior interfacial stability of TAIC-SPE. As shown in Fig. 5d and e, while the Li|SPE|Li cell exhibited a marked and progressive decrease in interfacial resistance,

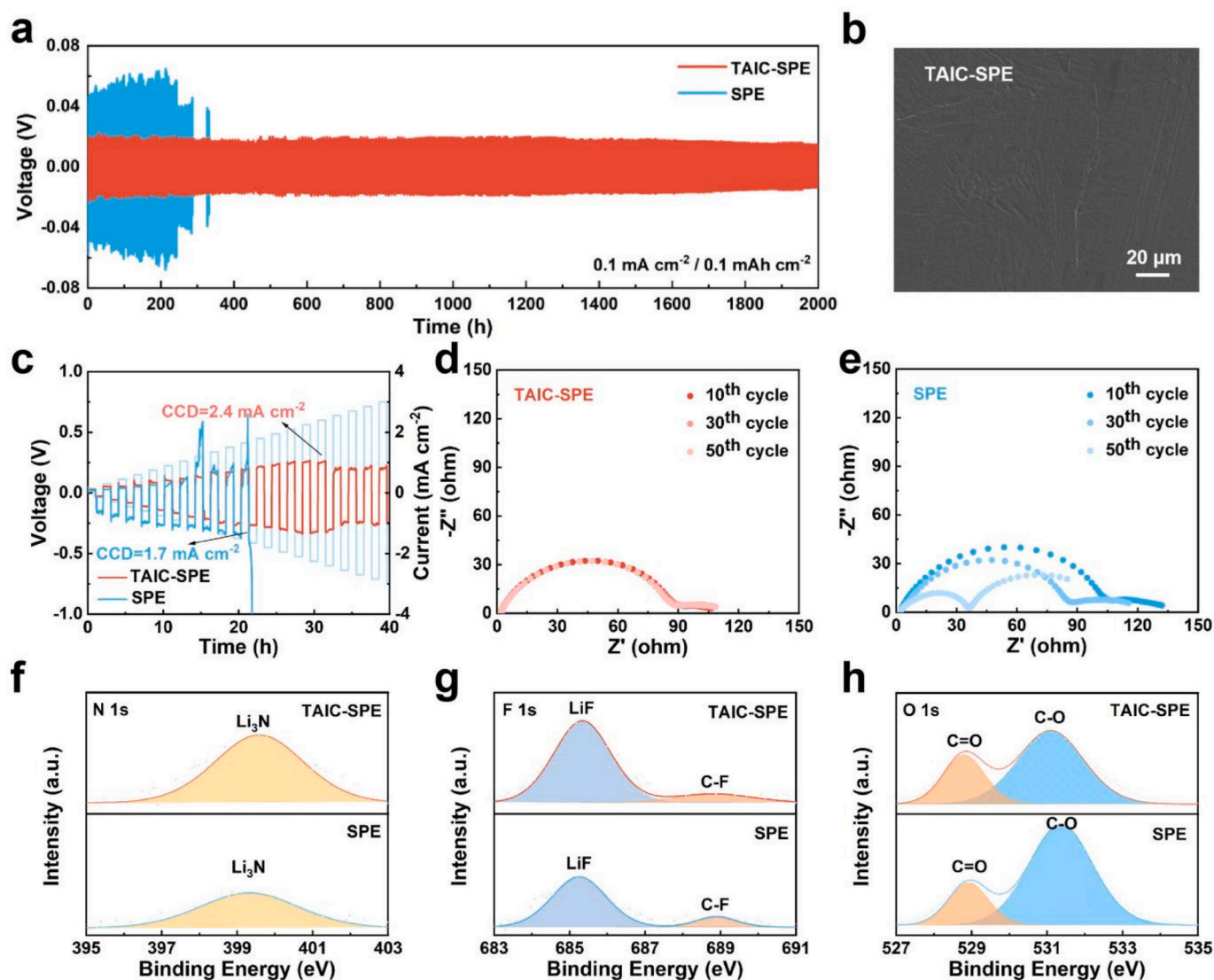


Fig. 5. Li plating/stripping behavior and post analysis. (a) The constant current cycle performance of Li||Li cells assembled by TAIC-SPE and SPE at a current density of 0.1 mA cm^{-2} . (b) SEM images of Li metal anode after cycling with TAIC-SPE. (c) CCD of TAIC-SPE and SPE at the current density of $0.05\text{--}3.5 \text{ mA cm}^{-2}$. Impedance changes after 10, 30 and 50 cycles of the cells with (d) TAIC-SPE and (e) SPE. (f) N 1 s XPS of Li anode after cycling in TAIC-SPE and SPE. (g) F 1 s XPS of Li anode after cycling in TAIC-SPE and SPE. (h) O 1 s XPS of Li anode after cycling in TAIC-SPE and SPE.

the impedance of the Li|TAIC-SPE|Li cell remained essentially invariant, confirming the formation of a stable SEI film. Furthermore, the SEI was probed via X-ray photoelectron spectroscopy (XPS). Li_3N is known to be a beneficial component of the SEI, providing high mechanical strength and ionic conductivity. As shown in Fig. 5f, the TAIC-SPE exhibited a distinct signal (~ 399 eV) for the inorganic component rich in Li_3N , with an intensity significantly higher than that of the SPE, signifying that the nitrogen-rich triazine moieties within TAIC underwent preferential reductive decomposition to generate a Li_3N -rich SEI layer. [21,51] Concomitantly, thanks to the preferential interaction of TAIC with TFSI⁻ anions, a LiF-rich phase can also be observed, which further enhanced the stability of SEI layer (Fig. 5g). Moreover, a significant attenuation of signals associated with organic C-O/C=O species was observed for the TAIC-SPE, indicating suppressed decomposition of organic materials (Fig. 5h). [36] At the same time, as shown in Fig. S14a, compared to the SPE spectrum, the Li_2CO_3 signal was significantly attenuated in the TAIC-SPE spectrum, indicating that the polymer structure remained intact. [52] Furthermore, as observed in the Li 1 s spectrum, the signal intensities of the inorganic phases Li_3N and LiF in TAIC-SPE were higher than those in the SPE (Fig. S14b). This inorganic-rich, hierarchically structured SEI serves as a robust physical and chemical barrier, mitigating parasitic side reactions and enforcing uniform Li^+ flux.

Lastly, the practical impact of this stabilized interface was next evaluated in full cells. The SEM images of the fabricated LFP and NCM cathodes together with the corresponding EDS elemental mapping were shown in Fig. S15. As shown in Fig. 6a, the Li|TAIC-SPE|LFP cells delivered exceptional long-term cyclability, retaining 83.7% of its initial capacity after 600 cycles at 1.0C. In contrast, the Li|SPE|LFP cells suffered from a continuous capacity fade after only 150 cycles, due to uncontrolled side reactions and Li dendrites growth. The corresponding charge-discharge profiles also exhibited well-defined voltage plateaus with minimal polarization growth for the TAIC-SPE system (Fig. 6b and Fig. S16). Rate capability tests further underscored the superior kinetics enabled by the TAIC-SPE. As shown in Fig. 6c, the Li|TAIC-SPE|LFP cells delivered reversible specific capacities of 169.53, 166.67, 155.03, 139.05, and 109.42 mAh g^{-1} at 0.1C, 0.5C, 1C, 2C, and 5C, respectively, systematically outperforming the SPE-based cells. Notably, upon reverting the current density to 0.1C, the capacity recovers fully to 169.8 mAh g^{-1} with negligible degradation, attesting to the excellent electrochemical resilience of the TAIC-SPE. Impressively, even under a high current density of 5C, the Li|TAIC-SPE|LFP cell also maintained a discharge capacity of 101.3 mAh g^{-1} with 89.52% retention after 200 cycles (Fig. 6d). The corresponding charge-discharge curves were shown in Fig. S17. [53]

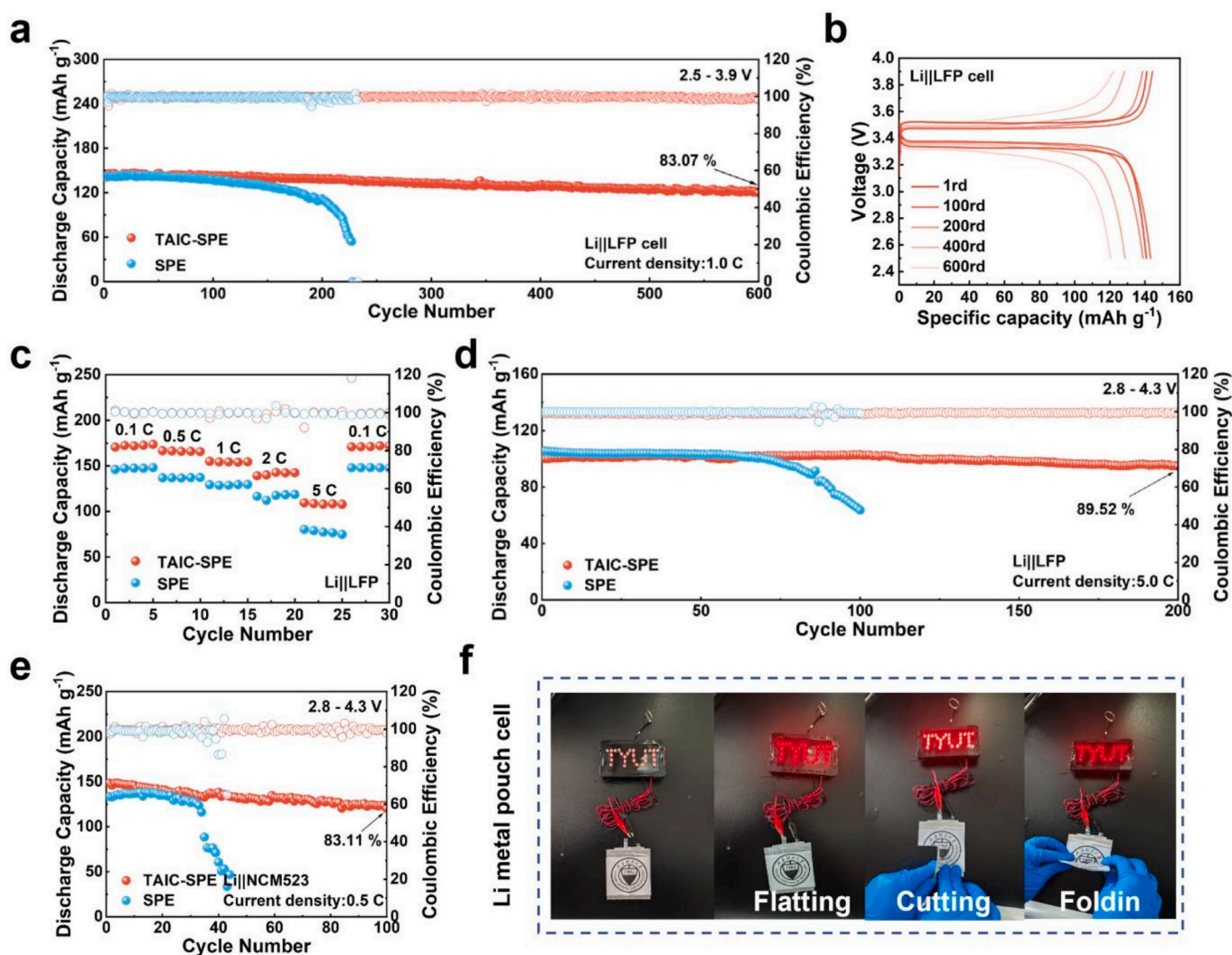


Fig. 6. Electrochemical performance of LMBs. (a) Cycle performance of Li||LFP cells with TAIC-SPE and SPE at the current density of 1.0C. (b) Charging/discharge curve of Li|TAIC-SPE|LFP cells. (c) Rate capability of Li||LFP cells with TAIC-SPE and SPE at the current density of 0.1–5.0C. (d) Cycle performance of Li||LFP cells with TAIC-SPE at the current density of 5.0C. (e) Cycle performance of Li||NCM cells with TAIC-SPE and SPE at the current density of 0.5C. (f) Li|TAIC-SPE|LFP pouch cells in mechanical abuse test.

Leveraging the wide electrochemical stability window of TAIC-SPE (>4.8 V), we further explored its compatibility with high-voltage cathode. As shown in Fig. 6e, when paired with NCM cathode, the full cells also exhibited an initial discharge specific capacity of $148.48 \text{ mAh g}^{-1}$ at 0.5C , retaining 83.11% of this capacity after 100 cycles, demonstrating the feasibility of extending this electrolyte platform to high-energy-density systems. At the same time, when using thick NCM with a higher cathode area loading of approximately 9.2 mg cm^{-2} , the Li|TAIC-SPE|NCM system was still able to maintain stable cycling, whereas the Li|SPE|NCM system lasted only 5 cycles (Fig. S18).

Finally, to demonstrate the practical application potential of TAIC-SPE, we assembled the pouch cells. As shown in Fig. 6f, the TAIC-SPE-based pouch cells continued to power a light-emitting diode (LED) array without interruption or internal short-circuiting, even after being subjected to severe mechanical deformation, including folding and scissor cutting, underscoring the transformative potential of the ultrathin, hypercrosslinked TAIC-SPE design for the realization of safe and durable solid-state LMBs.

3. Conclusion

In summary, we have developed an ultrathin, triazine-anchored hypercrosslinked solid polymer electrolyte (TAIC-SPE) via a facile in situ copolymerization strategy. The strategic incorporation of the multifunctional TAIC crosslinker disrupts polymer crystallinity to unlock segmental dynamics, anchors anions to elevate the Li^+ transference number, and generates a robust Li_3N -rich interphase. These synergistic attributes endow TAIC-SPE with a room-temperature ionic conductivity of 1.03 mS cm^{-1} , a wide electrochemical window (>4.8 V), and intrinsic nonflammability. The resultant SPEs enable dendrite-free Li plating/stripping over 2000 h and stable cycling of both LFP and NCM full cells. Moreover, pouch cells exhibit remarkable resilience to folding and cutting, underscoring the practical viability of this hypercrosslinked design. Performance comparisons with state-of-the-art cross-linked polymer electrolytes are summarized in Table S2 and Fig. S19, underscoring the competitiveness of our strategy for safe, high-performance solid-state LMBs. This work establishes promising molecular engineering for safe, high-performance solid-state LMBs.

CRedit authorship contribution statement

Ran Wang: Writing – original draft, Data curation. **Yongle Yan:** Data curation. **Zelin Lv:** Data curation. **Xiaoxiao Li:** Resources. **Xutao Liang:** Investigation. **Yang Gao:** Data curation. **Mengchao Li:** Software. **Lifeng Hou:** Writing – review & editing, Data curation. **Shi Wang:** Writing – review & editing. **Zhong Jin:** Funding acquisition, Data curation. **Qian Wang:** Writing – review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2026.181270>.

Data availability

Data will be made available on request.

References

- [1] M. Li, J. Yang, Y. Shi, Z. Chen, P. Bai, H. Su, P. Xiong, M. Cheng, J. Zhao, Y. Xu, Soluble organic cathodes enable long cycle life, high rate, and wide-temperature lithium-ion batteries, *Adv. Mater.* 34 (2022) 2107226, <https://doi.org/10.1002/adma.202107226>.
- [2] Q. Sun, S. Wang, Y. Ma, D. Song, H. Zhang, X. Shi, N. Zhang, L. Zhang, Li-ion transfer mechanism of gel polymer electrolyte with sole fluorooethylene carbonate solvent, *Adv. Mater.* 35 (2023) 2300998, <https://doi.org/10.1002/adma.202300998>.
- [3] M. Zhang, H. Wang, A. Shao, Z. Wang, X. Tang, S. Li, J. Liu, Y. Ma, Enabling 4.5 V solid polymer batteries through a $10 \mu\text{m}$, crosslinked polyether electrolyte, *Adv. Energy Mater.* 14 (2024) 2303932, <https://doi.org/10.1002/aenm.202303932>.
- [4] J. Wang, H. Hu, L. Jia, J. Zhang, Q. Zhuang, L. Li, Y. Zhang, D. Wang, Q. Guan, H. Hu, M. Liu, L. Zhan, H. Adenusi, S. Passerini, H. Lin, Fast interfacial electrocatalytic desolvation enabling low-temperature and long-cycle-life aqueous Zn batteries, *InfoMat* 6 (2024) e12558, <https://doi.org/10.1002/inf2.12558>.
- [5] G.-R. Zhu, Q. Zhang, Q.-S. Liu, Q.-Y. Bai, Y.-Z. Quan, Y. Gao, G. Wu, Y.-Z. Wang, Non-flammable solvent-free liquid polymer electrolyte for lithium metal batteries, *Nat. Commun.* 14 (2023) 4617, <https://doi.org/10.1038/s41467-023-40394-8>.
- [6] T. Dong, H. Zhang, L. Huang, J. Ma, P. Mu, X. Du, X. Zhang, X. Wang, C. Lu, S. Dong, Q. Zhou, G. Xu, W. Liu, G. Cui, A smart polymer electrolyte coordinates the trade-off between thermal safety and energy density of lithium batteries, *Energy Storage Mater.* 58 (2023) 123–131, <https://doi.org/10.1016/j.ensm.2023.03.013>.
- [7] J. Mao, J. Iocozzia, J. Huang, K. Meng, Y. Lai, Z. Lin, Graphene aerogels for efficient energy storage and conversion, *Energy Environ. Sci.* 11 (2018) 772–799, <https://doi.org/10.1039/c7ee03031b>.
- [8] B. Tong, Z. Song, W. Feng, J. Zhu, H. Yu, X. Huang, M. Armand, Z. Zhou, H. Zhang, Design of a Teflon-like anion for unprecedentedly enhanced lithium metal polymer batteries, *Adv. Energy Mater.* 13 (2023) 2204085, <https://doi.org/10.1002/aenm.202204085>.
- [9] Z. Jiang, S. Wang, X. Chen, W. Yang, X. Yao, X. Hu, Q. Han, H. Wang, Tape-casting $\text{Li}_{0.34}\text{La}_{0.55}\text{TiO}_3$ ceramic electrolyte films permit high energy density of lithium-metal batteries, *Adv. Mater.* 32 (2019) 1906211, <https://doi.org/10.1002/adma.201906221>.
- [10] K.J. Kim, M. Balaish, M. Wadaguchi, L. Kong, J.L.M. Rupp, Solid-state Li-metal batteries: challenges and horizons of oxide and sulfide solid electrolytes and their interfaces, *Adv. Energy Mater.* 11 (2020) 2002689, <https://doi.org/10.1002/aenm.202002689>.
- [11] D. Zhou, D. Shanmukaraj, A. Tkacheva, M. Armand, G. Wang, Polymer electrolytes for Lithium-based batteries: advances and prospects, *Chem* 5 (2019) 2326–2352, <https://doi.org/10.1016/j.chempr.2019.05.009>.
- [12] L. Zhou, T.-T. Zuo, C.Y. Kwok, S.Y. Kim, A. Assoud, Q. Zhang, J. Janek, L.F. Nazar, High areal capacity, long cycle life 4V ceramic all-solid-state Li-ion batteries enabled by chloride solid electrolytes, *Nat. Energy* 7 (2022) 83–93, <https://doi.org/10.1038/s41560-021-00952-0>.
- [13] Z. Li, J. Fu, X. Zhou, S. Gui, L. Wei, H. Yang, H. Li, X. Guo, Ionic conduction in polymer-based solid electrolytes, *Adv. Sci.* 10 (2022) 2201718, <https://doi.org/10.1002/advs.202201718>.
- [14] Y. Su, F. Xu, X. Zhang, Y. Qiu, H. Wang, Rational design of high-performance PEO/ceramic composite solid electrolytes for lithium metal batteries, *Nano Micro Lett.* 15 (2023) 15:82, <https://doi.org/10.1007/s40820-023-01055-z>.
- [15] G.R. Zhu, Q. Zhang, Y.Y. Zhang, X.L. Wang, G. Wu, Y.Z. Wang, Soft-hard synergistic solid all-polymer electrolyte inspired by musculoskeletal structure for high-temperature lithium metal batteries, *Adv. Funct. Mater.* 35 (2025) 2503481, <https://doi.org/10.1002/adfm.202503481>.
- [16] D. Bao, Y. Tao, Y. Zhong, W. Zhao, M. Peng, H. Zhang, X. Sun, High-performance dual-salt plastic crystal electrolyte enabled by succinonitrile-regulated porous polymer host, *Adv. Funct. Mater.* 33 (2022) 2213211, <https://doi.org/10.1002/adfm.202213211>.
- [17] P. Bonnick, J. Muldoon, The quest for the holy grail of solid-state lithium batteries, *Energy Environ. Sci.* 15 (2022) 1840–1860, <https://doi.org/10.1039/d2ee00842d>.
- [18] S. Han, P. Wen, H. Wang, Y. Zhou, Y. Gu, L. Zhang, Y. Shao-Horn, X. Lin, M. Chen, Sequencing polymers to enable solid-state lithium batteries, *Nat. Mater.* 22 (2023) 1515–1522, <https://doi.org/10.1038/s41563-023-01693-z>.
- [19] Y. Shi, X. Miao, G. Zhao, S. Xiao, Z. Guo, Constructing the non-flammable anion acceptor-containing deep eutectics-based gel polymer electrolyte for high-performance Li-metal batteries, *Adv. Funct. Mater.* 36 (2025) 2524608, <https://doi.org/10.1002/adfm.202524608>.
- [20] J. Han, M.J. Lee, J.H. Min, K.H. Kim, K. Lee, S.H. Kwon, J. Park, K. Ryu, H. Seong, H. Kang, E. Lee, S.W. Lee, B.J. Kim, Fluorine-containing phase-separated polymer electrolytes enabling high-energy solid-state lithium metal batteries, *Adv. Funct. Mater.* 34 (2023) 2310801, <https://doi.org/10.1002/adfm.202310801>.
- [21] M. Liao, Y. Zhou, X. Jiang, R. Wan, In situ construction of 3D Li channels high-temperature-resistant polymer electrolyte and Li_3N -rich interface enabling stable solid-state Li metal battery, *Chem. Eng. J.* 480 (2024) 148020, <https://doi.org/10.1016/j.cej.2023.148020>.
- [22] D. Zhang, Y. Liu, Z. Sun, Z. Liu, X. Xu, L. Xi, S. Ji, M. Zhu, J. Liu, Eutectic-based polymer electrolyte with the enhanced lithium salt dissociation for high-

- performance lithium metal batteries, *Angew. Chem. Int. Ed.* 62 (2023) e202310006, <https://doi.org/10.1002/anie.202310006>.
- [23] Y. Li, W. Yuan, Z. Hu, Y. Shen, G. Wu, F. Cong, X. Fu, F. Lu, Y. Li, P. Liu, Y. Huang, J. Li, Constructing PVDF-based polymer electrolyte for lithium metal batteries by polymer-induced phase structure adjustment strategy, *Adv. Funct. Mater.* 35 (2025) 2424763, <https://doi.org/10.1002/adfm.202424763>.
- [24] P. Shi, J. Ma, M. Liu, S. Guo, Y. Huang, S. Wang, L. Zhang, L. Chen, K. Yang, X. Liu, Y. Li, X. An, D. Zhang, X. Cheng, Q. Li, W. Lv, G. Zhong, Y.-B. He, F. Kang, A dielectric electrolyte composite with high lithium-ion conductivity for high-voltage solid-state lithium metal batteries, *Nat. Nanotechnol.* 18 (2023) 602–610, <https://doi.org/10.1038/s41565-023-01341-2>.
- [25] Q.-K. Zhang, X.-Q. Zhang, J. Wan, N. Yao, T.-L. Song, J. Xie, L.-P. Hou, M.-Y. Zhou, X. Chen, B.-Q. Li, R. Wen, H.-J. Peng, Q. Zhang, J.-Q. Huang, Homogeneous and mechanically stable solid–electrolyte interphase enabled by trioxane-modulated electrolytes for lithium metal batteries, *Nat. Energy* 8 (2023) 725–735, <https://doi.org/10.1038/s41560-023-01275-y>.
- [26] D. Zhou, A. Tkacheva, X. Tang, B. Sun, D. Shanmukaraj, P. Li, F. Zhang, M. Armand, G. Wang, Stable conversion chemistry-based Lithium metal batteries enabled by hierarchical multifunctional polymer electrolytes with near-single ion conduction, *Angew. Chem. Int. Ed.* 58 (2019) 6001–6006, <https://doi.org/10.1002/anie.201901582>.
- [27] L. Han, C. Liao, X. Mu, N. Wu, Z. Xu, J. Wang, L. Song, Y. Kan, Y. Hu, Flame-retardant ADP/PEO solid polymer electrolyte for dendrite-free and Long-life Lithium battery by generating Al, P-rich SEI layer, *Nano Lett.* 21 (2021) 4447–4453, <https://doi.org/10.1021/acs.nanolett.1c01137>.
- [28] G. Jiang, J. Liu, Z. Wang, J. Ma, Stable non-flammable phosphate electrolyte for lithium metal batteries via solvation regulation by the additive, *Adv. Funct. Mater.* 33 (2023) 2300629, <https://doi.org/10.1002/adfm.202300629>.
- [29] X. Liu, C. Zhang, S. Gao, S. Cai, Q. Wang, J. Liu, Z. Liu, A novel polyphosphonate flame-retardant additive towards safety-reinforced all-solid-state polymer electrolyte, *Mater. Chem. Phys.* 239 (2020) 122014, <https://doi.org/10.1016/j.matchemphys.2019.122014>.
- [30] R. Rojaee, S. Cavallo, S. Mogurampelly, B.K. Wheatle, V. Yurkiv, R. Deivanayagam, T. Foroozan, M.G. Rasul, S. Sharifi-Asl, A.H. Phakatkar, M. Cheng, S.B. Son, Y. Pan, F. Mashayek, V. Ganesan, R. Shahbazian-Yassar, Highly-cyclable room-temperature phosphorene polymer electrolyte composites for Li metal batteries, *Adv. Funct. Mater.* 30 (2020) 1910749, <https://doi.org/10.1002/adfm.201910749>.
- [31] Y. Zhu, M. Ge, F. Ma, Q. Wang, P. Huang, C. Lai, Multifunctional electrolyte additives for better metal batteries, *Adv. Funct. Mater.* 34 (2023) 2301964, <https://doi.org/10.1002/adfm.202301964>.
- [32] Y. Meng, D. Zhou, R. Liu, Y. Tian, Y. Gao, Y. Wang, B. Sun, F. Kang, M. Armand, B. Li, G. Wang, D. Aurbach, Designing phosphazene-derivative electrolyte matrices to enable high-voltage lithium metal batteries for extreme working conditions, *Nat. Energy* 8 (2023) 1023–1033, <https://doi.org/10.1038/s41560-023-01339-z>.
- [33] M. Zhou, W. Chen, H. Yang, Y. Hu, T. Lei, D. Chen, S. Wang, Y. Zhang, J. Xiong, Molecular crowding solid polymer electrolytes for lithium metal battery by in situ polymerization, *Adv. Energy Mater.* 15 (2024) 2403082, <https://doi.org/10.1002/aenm.202403082>.
- [34] W. Cao, J. Lu, K. Zhou, G. Sun, J. Zheng, Z. Geng, H. Li, Organic-inorganic composite SEI for a stable Li metal anode by in-situ polymerization, *Nano Energy* 95 (2022) 106983, <https://doi.org/10.1016/j.nanoen.2022.106983>.
- [35] J. Chen, A. Hu, K. Chen, Y. Xia, W. Xu, K. Li, B. Yang, T. Li, R. Xu, Z. Wang, B. Li, F. Li, J. Long, Establishing ion transport channels in plastic crystal electrolytes via multifunctional cross-linked polymer matrices for stable and safe lithium metal batteries, *Nano Energy* 139 (2025) 110959, <https://doi.org/10.1016/j.nanoen.2025.110959>.
- [36] D. Zhang, Z. Luo, H. Xu, Y. Guo, H. Chen, Y. Ye, J. An, J. Hui, Y. Shi, S. Yang, B. Li, Liberating Lithium ions from polymer matrix via harnessing ion-dipole interaction toward stable solid-state Lithium metal batteries, *Adv. Funct. Mater.* 34 (2024) 2409134, <https://doi.org/10.1002/adfm.202409134>.
- [37] C.M. Efav, Q. Wu, N. Gao, Y. Zhang, H. Zhu, K. Gering, M.F. Hurley, H. Xiong, E. Hu, X. Cao, W. Xu, J.-G. Zhang, E.J. Dufek, J. Xiao, X.-Q. Yang, J. Liu, Y. Qi, B. Li, Localized high-concentration electrolytes get more localized through micelle-like structures, *Nat. Mater.* 22 (2023) 1531–1539, <https://doi.org/10.1038/s41563-023-01700-3>.
- [38] G. Yang, C. Chanthad, H. Oh, I.A. Ayhan, Q. Wang, Organic–inorganic hybrid electrolytes from ionic liquid-functionalized octasilsesquioxane for lithium metal batteries, *J. Mater. Chem. A* 5 (2017) 18012–18019, <https://doi.org/10.1039/c7ta04599a>.
- [39] Z. Hu, F. Xian, Z. Guo, C. Lu, X. Du, X. Cheng, S. Zhang, S. Dong, G. Cui, L. Chen, Nonflammable nitrile deep eutectic electrolyte enables high-voltage Lithium metal batteries, *Chem. Mater.* 32 (2020) 3405–3413, <https://doi.org/10.1021/acs.chemmater.9b05003>.
- [40] S. Wang, S. Wang, Z. Wei, Y. Wang, D. Zhang, Z. Chen, C. Zhi, A parts-per-million scale electrolyte additive for durable aqueous zinc batteries, *Nat. Commun.* 16 (2025) 1800, <https://doi.org/10.1038/s41467-025-56607-1>.
- [41] L. Wu, F. Pei, D. Cheng, Y. Zhang, H. Cheng, K. Huang, L. Yuan, Z. Li, H. Xu, Y. Huang, Flame-retardant polyurethane-based solid-state polymer electrolytes enabled by covalent bonding for lithium metal batteries, *Adv. Funct. Mater.* 34 (2023) 2310084, <https://doi.org/10.1002/adfm.202310084>.
- [42] J. Zhang, J. Chou, X.X. Luo, Y.M. Yang, M.Y. Yan, D. Jia, C.H. Zhang, Y.H. Wang, W.P. Wang, S.J. Tan, J.C. Guo, Y. Zhao, F. Wang, S. Xin, L.J. Wan, Y.G. Guo, A fully amorphous, dynamic cross-linked polymer electrolyte for lithium-sulfur batteries operating at subzero-temperatures, *Angew. Chem. Int. Ed.* 63 (2023) e202316087, <https://doi.org/10.1002/anie.202316087>.
- [43] S. Wang, Z. Wei, H. Hong, X. Guo, Y. Wang, Z. Chen, D. Zhang, X. Zhang, X. Yang, C. Zhi, A tellurium iodide perovskite structure enabling eleven-electron transfer in zinc ion batteries, *Nat. Commun.* 16 (2025) 511, <https://doi.org/10.1038/s41467-024-55385-6>.
- [44] H. Peng, T. Long, J. Peng, H. Chen, L. Ji, H. Sun, L. Huang, S.G. Sun, Molecular design for in-situ polymerized solid polymer electrolytes enabling stable cycling of lithium metal batteries, *Adv. Energy Mater.* 14 (2024) 2400428, <https://doi.org/10.1002/aenm.202400428>.
- [45] B. Kim, S.H. Yang, J.H. Seo, Y.C. Kang, Inducing an amorphous phase in polymer plastic crystal electrolyte for effective ion transportation in Lithium metal batteries, *Adv. Funct. Mater.* 34 (2023) 2310957, <https://doi.org/10.1002/adfm.202310957>.
- [46] C. Zhou, D. Chu, W. Zeng, J. Cheng, Z. Fei, Quaternary ammonium-functionalized siloxane semi-IPN for SPEEK membranes: decoupling the conductivity–stability trade-off, *Fuel Cells* 26 (2026) e70115, <https://doi.org/10.1002/face.70115>.
- [47] Q. Zhou, J. Ma, S. Dong, X. Li, G. Cui, Intermolecular chemistry in solid polymer electrolytes for high-energy-density lithium batteries, *Adv. Mater.* 31 (2019) 1902029, <https://doi.org/10.1002/adma.201902029>.
- [48] R. Huang, S. Luo, Q. Sun, L. Qian, S. Yan, New insights into inactive-element substitution in Fe/Mn anionic redox cathodes, *ACS Energy Lett.* 11 (2026) 2301–2315, <https://doi.org/10.1021/acsenenergylett.5c04278>.
- [49] J. Li, C. Li, Y. Yao, Z. Li, J. Yao, L. Luo, W. Liao, X. Ye, W. Dai, F. Li, X. Zhang, Y. Xiang, In situ polymerized flame-retardant crosslinked quasi solid-state electrolytes for high-voltage Lithium metal batteries, *Adv. Energy Mater.* 14 (2024) 2402362, <https://doi.org/10.1002/aenm.202402362>.
- [50] X. Mu, X. Li, C. Liao, H. Yu, Y. Jin, B. Yu, L. Han, L. Chen, Y. Kan, L. Song, Y. Hu, Phosphorus-fixed stable interfacial nonflammable gel polymer electrolyte for safe flexible Lithium-ion batteries, *Adv. Funct. Mater.* 32 (2022) 2203006, <https://doi.org/10.1002/adfm.202203006>.
- [51] M.J. Lee, J. Han, K. Lee, Y.J. Lee, B.G. Kim, K.-N. Jung, B.J. Kim, S.W. Lee, Elastomeric electrolytes for high-energy solid-state lithium batteries, *Nature* 601 (2022) 217–222, <https://doi.org/10.1038/s41586-021-04209-4>.
- [52] Q. Sun, S. Luo, R. Huang, J. Cong, S. Yan, Weakly coordinating co-solvent design of chlorine-free electrolytes: manipulating solvation structure and interfacial chemistry for highly reversible Mg metal anodes, *Energy Storage Mater.* 90 (2026) 105313, <https://doi.org/10.1016/j.ensm.2026.105313>.
- [53] X. Zhang, Z. Wang, T. Zhang, Q. Cai, Q. Li, Z. Xue, H. Sun, Simulation study of charge-discharge characteristics of Li-O₂ batteries with a coupled impedance model, *J. Energy Storage* 165 (2026) 122361, <https://doi.org/10.1016/j.est.2026.122361>.