

RESEARCH ARTICLE

Tailoring Topology of Terpolymers via In Situ Programmed Click Chemistry for Stable Polymer Electrolytes

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ABSTRACT

Polymer electrolytes (PEs), valued for their superior safety and processability in lithium metal batteries (LMBs), often face trade-offs between ionic conductivity and mechanical strength, along with interfacial instability. Herein, we report a molecular programming strategy that encodes desired functionalities directly into the PEs network. This strategy is executed by programming urethane groups as functional units into the network via an in situ programmed click reaction, wherein trace water and Lewis acid salts in the electrolyte mediate the click crosslinking of glycidyl methacrylate with 2-isocyanatoethyl methacrylate. In this programming, each urethane group concurrently serves as a covalent crosslinker for mechanical integrity and a dynamic unit for self-healing, thereby constructing a topological terpolymer framework. Additionally, these units participate in reshaping the ion transport environment, guiding the formation of a mechanochemically stable interphase layer. Consequently, this programmed electrolyte exhibits a surface Young's modulus as high as 3.7 GPa, and excellent ionic conductivity. The 1 Ah pouch cell retains 96.39% capacity after 500 cycles. This work establishes a programming paradigm for PEs, advancing the application of high-performance PEs in LMBs.

1 | Introduction

Polymer electrolytes (PEs) are regarded as one of the most promising candidates for next-generation high-performance lithium metal batteries (LMBs), owing to their intrinsic safety, ease of processing, and good compatibility with electrode interfaces [1–6]. However, the generally low ionic conductivity of PEs has

prompted researchers to incorporate liquid plasticizers into polymer systems to address this issue [7]. Unfortunately, the addition of plasticizers disrupts the original crystalline supporting structure of the polymer, leading to reduced elongation at break and significantly weakened mechanical strength, thereby compromising the mechanical properties of the electrolyte [8, 9]. Previous studies have shown that insufficient mechanical properties make

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it difficult to prevent lithium dendrite growth, increase internal resistance, and elevate thermal runaway risks, which adversely affect the battery's long-term cycling performance and durability [5, 10]. Conversely, to enhance the mechanical properties of polymer electrolytes, current research strategies primarily rely on the introduction of inorganic fillers as a reinforcing phase [11]. However, these fillers are prone to agglomeration, leading to uneven ion transport and additional interfacial resistance [12]. Furthermore, the introduction of rigid monomers such as aromatic rings increases side-chain steric hindrance or promotes chain regularity, thereby enhancing the material's modulus and tensile strength. However, this typically leads to increased brittleness and severely restricts polymer segment motion, drastically reducing ionic conductivity [13]. This dilemma reveals the limitations of traditional designs, where energy dissipation and ion transport mechanisms are either singular or poorly coupled, making it difficult to simultaneously achieve high strength, high toughness, and efficient ion conduction.

Recently, in situ crosslinked polymer electrolytes have garnered significant attention due to their ability to flexibly modulate microstructures. Nevertheless, existing approaches focus on constructing crosslinked networks and achieving fundamental performance, with relatively crude molecular design [14]. On one hand, traditional crosslinking strategies (e.g., rapid UV polymerization based on polyethylene glycol diacrylate, PEGDA) are typically fast and poorly controlled, often resulting in structures with unevenly distributed crosslinking points [15]. This structural defect causes stress to concentrate in weakly crosslinked regions rather than being uniformly distributed, initiating localized failure and rapid crack propagation [16]. Furthermore, reliance on a single crosslinking chemistry limits energy dissipation pathways. While covalent crosslinking significantly enhances strength, it severely restricts the motion of polymer segments, leading to embrittlement and inadequate toughness [17]. Consequently, such materials cannot meet the dual requirements of suppressing lithium dendrite penetration and accommodating electrode volume changes. More critically, the restricted segment dynamics also impede continuous transport pathways for Li^+ , thereby reducing ionic conductivity [18]. On the other hand, functional monomers with diverse properties are often copolymerized to tailor the fundamental properties of the electrolyte. For instance, introducing electron-withdrawing groups (such as $-\text{CF}_3$) can optimize Li^+ solvation and transport [19]. Although these methods yield incremental improvements, the regulation of functional synergistic coupling at the molecular scale remains limited. Therefore, it is necessary to develop new strategies that enable precise control over polymer network architecture to simultaneously achieve excellent macroscopic mechanical properties and efficient, uniform ion transport channels, thereby overcoming the longstanding trade-off between ionic conductivity and mechanical performance.

Herein, we shift from a modular assembly paradigm to molecular programming, proposing a strategy centered on constructing urethane functional units via in situ programmed click chemistry, which enables the topological terpolymer electrolyte (GTI-PE) to enhance mechanical properties without compromising ionic conductivity (Figure 1a). This strategy precisely constructs urethane units as embedded multifunctional coding units within a topological terpolymer network by leveraging an in situ click reac-

tion between the epoxy group on the polymer monomer glycidyl methacrylate and the $\text{N}=\text{C}=\text{O}$ in 2-isocyanatoethyl methacrylate. On one hand, these units enable the polymer chains to construct an ordered topological cross-linked network through covalent bonding. On the other hand, through dynamic hydrogen bond breaking and reorganization, the material exhibits self-healing and energy dissipation behavior, significantly enhancing its toughness and damage resistance. Moreover, these molecular units anchor anions via $-\text{NH}$ sites while coordinating Li^+ ions through $\text{C}=\text{O}$ sites, thereby synergistically regulating the ionic environment to reprogram ion transport and guide interfacial chemical reactions. As a result, this programming strategy endows the electrolyte with a tensile stress of 42.31 MPa and a surface Young's modulus of 3.7 GPa, with an ionic conductivity of $8.35 \times 10^{-4} \text{ S cm}^{-1}$. The $\text{Li}||\text{Li}$ symmetric cells employing GTI-PE exhibited stable cycling performance for 2000 h at a current density of 0.1 mA cm^{-2} , demonstrating its exceptional ability to suppress dendrite growth. Meanwhile, a 1 Ah LiFePO_4 -based pouch cell with the GTI-PE was prepared, and it exhibited a remarkable capacity retention rate of 96.39% after 500 cycles. This study demonstrates that the multifunctional terpolymer topologies achieved through molecular programming offer a novel approach to overcoming performance trade-offs in polymer electrolytes.

2 | Results and Discussion

2.1 | In Situ Programmed Click-Creation of the Urethane Functional Units and Topology of Terpolymer Electrolytes

The terpolymer electrolyte (denoted as GTI-PE, Figure S1) were in situ synthesized from precursors containing glycidyl methacrylate (GMA), trifluoroethyl methacrylate (TFMA), and 2-isocyanatoethyl methacrylate (IEMA) via free radical polymerization of the corresponding monomers. The structures of the terpolymers were characterized by the FT-IR spectra. The FT-IR spectra of GMA, TFMA, IEMA, and GTI-PE are shown in Figure 1b. The disappearance of the characteristic peak at 1637 cm^{-1} , attributed to the $\text{C}=\text{C}$ stretching vibration in the monomer spectrum [20], in the polymer spectrum indicates successful polymerization. In addition, the disappearance of the characteristic $\text{C}=\text{C}$ bond peak in the monomer at 1402 cm^{-1} in the Raman spectrum (Figure S2) could also indicate the successful synthesis of the polymer. It can also be seen from Figure 1b that the characteristic peak of the epoxy group at 907 cm^{-1} in GMA and the characteristic peak of $\text{N}=\text{C}=\text{O}$ at 2260 cm^{-1} in IEMA have both disappeared in the GTI-PE spectrum, while a broad band at $3300\text{--}3600 \text{ cm}^{-1}$ appeared, assigned to $-\text{NH}$ and $-\text{OH}$ stretching vibration [21, 22]. This occurs because the acidic environment formed by lithium salts and trace water in the electrolyte promotes the conversion of epoxy groups in GMA into active intermediates containing hydroxyl ($-\text{OH}$) groups via ring-opening reactions [23, 24]. These intermediates then undergo click addition with isocyanate groups on IEMA, generating the urethane groups ($-\text{NH}-\text{CO}-\text{O}-$, a characteristic $\text{C}=\text{O}$ peak appears at 1701 cm^{-1}), eventually forming a cross-linked polymer structure (Figure 1a) [25, 26]. This demonstrates that the urethane groups have been successfully integrated into the polymer network as core functional units through programmed

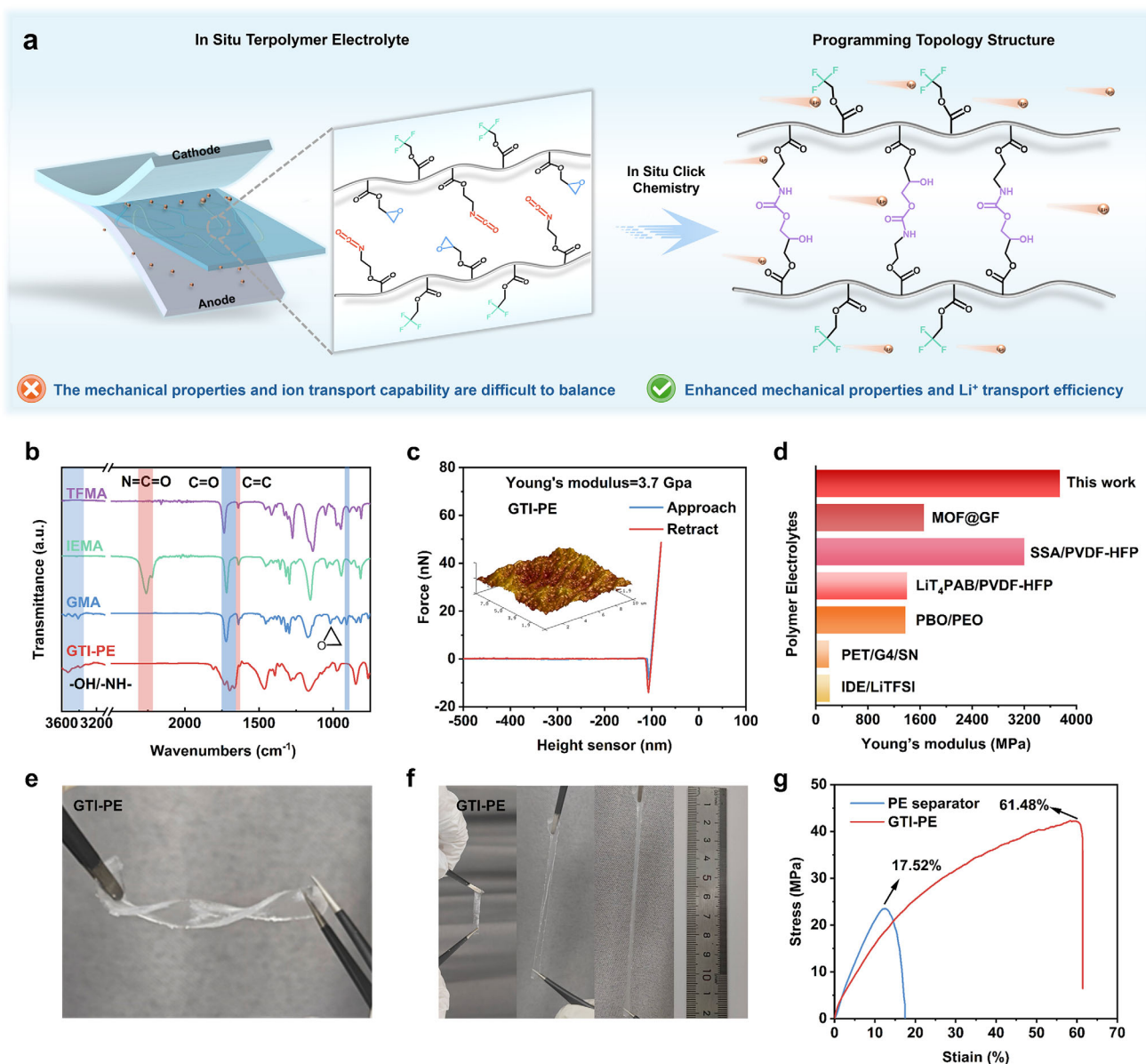


FIGURE 1 | Design, characterizations, and physical properties of the polymer electrolytes. (a) Schematic illustration of the topological network structure enabled by in situ programmed click-created urethane units. (b) FT-IR spectra of GTI-PE, GMA, IEMA, and TFMA. (c) Force-displacement curves for nanoindentation experiments for topological GTI-PE (inset is the 3D image of GTI-PE film surface). (d) Comparison of the mechanical strength of GTI-PE with previous studies. (e) The digital photograph of GTI-PE film in the twisted state. (f) Digital photographs of the tensile test of GTI-PE. (g) Stress-strain curves of GTI-PE polymer membrane and PE blank separator.

click reactions. The formation of crosslinked polymer structures was similarly verified by measuring intermolecular interactions in the polymer electrolyte by ¹H NMR spectra (Figure S3) [27]. To demonstrate the occurrence of cross-linking reaction and the morphology of the product after polymerization, the morphology of the GTI-PE membrane was observed using scanning electron microscopy (SEM) (Figure S4, the digital photos of GTI-PE polymer electrolyte membrane). The results showed that the surface of the polymer electrolyte film after in situ polymerization was uniform and flat, and the thickness of the electrolyte was about 15 μm as shown in the cross-sectional image (Figure S5). And the energy dispersive spectrometer (EDS) images show a uniform distribution of the elements C, O, F, and N (Figure S6).

2.2 | Molecular Programming of Topological Structure for Enhanced Polymer Electrolyte Stability

The molecular programming strategy via in situ click chemistry endows the polymer network with high mechanical robustness and self-healing functionality. Atomic force microscopy (AFM) imaging reveals a smooth and uniform surface morphology of GTI-PE (Figure 1c; Figure S7). Nanoindentation testing demonstrates significantly smaller hysteresis loops in the force-displacement curves of GTI-PE versus GT-PE during loading/unloading cycles (Figure 1c; Figure S8), indicating highly reversible deformation with near-elastic behavior. The

GTI-PE exhibits a Young's modulus of 3.7 GPa with stable mechanical properties, while GT-PE shows plastic deformation with a substantially lower modulus of 1.3 GPa. Compared with recent studies, the GTI-PE exhibits superior mechanical strength (Figure 1d). As demonstrated by the polymer electrolyte in Figure 1e, it exhibits exceptional flexibility while simultaneously achieving strong tensile performance (Figure 1f). When employed as electrolyte membranes, stress-strain tests reveal that GTI-PE demonstrates enhanced stress (42.31 vs. 23.49 MPa) and strain (61.48% vs. 17.52%) compared to pristine PE separators (Figure 1g).

The excellent mechanical properties of the electrolyte are enabled by the topological structure programmed via in situ click chemistry, which cross-links polymer chains into a 3D network. This network structure can effectively dissipate external forces, enhancing the material's rigidity and resistance to deformation, thereby improving mechanical properties such as tensile strength and modulus. Furthermore, the principle behind how the topological design enhances mechanical performance can be further explained by the relationship between entropy and mechanical strength, as described by Equation (1) [28].

$$F = -T \frac{dS(L)}{dL} = -kT \frac{d \ln \Omega(L)}{dL} \quad (1)$$

Here, F denotes the external force, T the chain temperature, S the entropy, and L the average length.

The ingenuity of the topological network structure design of GTI-PE lies in the fact that the material is already in a high conformational entropy (S) state initially, where a covalent cross-linked network provides structural support, while dynamic hydrogen bonds are dispersed throughout as reconfigurable "entropy-buffering units". Upon external loading, these hydrogen bonds preferentially undergo reversible breaking and reconfiguration, allowing part of the energy to be dissipated through the 'entropy buffering' process of dynamic bonds. This process significantly buffers the decrease in the system's conformational entropy, maintaining a relatively low entropy change rate dS/dL . According to Equation (1), a lower entropy change rate implies that the material can retain a high entropic elastic contribution during deformation. Consequently, GTI-PE achieves not only a high modulus but also excellent toughness and energy dissipation capacity due to its gradual entropy dissipation mechanism.

To evaluate the self-healing capability of GTI-PE, as shown in Figure S9, a completely severed membrane can autonomously heal within 24 h at 25°C or rapidly heal within 2 h at 70°C, restoring sufficient mechanical strength to withstand gravity and manual stretching. Complementary high-temperature optical microscopy of scalpel-scratched GTI-PE revealed progressively diminished scratch width with extended heating time, further validating the self-repair behavior (Figure S10). During battery production and operation, the formation of defects such as cracks is virtually inevitable. The self-healing capability inherent to GTI-PE can effectively inhibit lithium dendrite growth, stabilize the interface, and mitigate the mechanical degradation of the electrolyte. Furthermore, studies have shown that during high-rate discharge, the internal temperature of batteries can exceed 70°C, and localized heating may also occur in the tab region, leading to significant temperature increases [29]. Therefore, the

self-healing capability of GTI-PE at 70°C holds practical value under battery assembly or thermal abuse conditions, contributing to enhanced battery safety and extended service life. This self-healing capability originates from the dynamic nature of the hydrogen bonds in the GTI-PE topology, which can reversibly dissociate and recombine to repair damage. It can be seen by variable-temperature FT-IR spectroscopy (Figure S11) that as the temperature increases from room temperature to 75°C, the peak position of the hydrogen bond formed by —NH/—OH shifts to higher wave numbers, proving the presence of dynamic hydrogen bonds [30].

The thermal stability of LE, GT-PE, and GTI-PE was characterized by thermogravimetric analysis (TGA). It is clear that GTI-PE has superior thermal stability, still having about 83% weight retention at 150°C, while GT-PE and the electrolyte have only 76% and 53% of their weight remaining at that temperature (Figure S12). For this reason, the flame-retardant properties of GTI-PE and LE were tested by combustion experiments (Figure S13). Among them, the commercial liquid electrolyte (1 M LiPF_6 in DMC:EC:EMC = 1:1:1 vol%) can be ignited within 2 s and can continue to burn, whereas GTI-PE is difficult to ignite, and even if it continues to be ignited for 8 s, the PE does not produce a flame. This result shows a good flame-retardant ability, which indicates that there is an outstanding flame-retardant ability than the commercial liquid electrolyte. This may be due to the fact that the halogen elements in GTI-PE can inhibit the electrolyte combustion by trapping oxygen radicals during the combustion of organic electrolytes.

2.3 | Electrochemical Properties of Polymer Electrolytes

In addition to constructing mechanically complete topological structures, this molecular programming strategy also participates in regulating the ion transport environment. Different electrochemical testing techniques were employed to evaluate the application potential of GTI-PE in LMBs. The results showed that the ionic conductivity of GTI-PE at room temperature was $8.35 \times 10^{-4} \text{ S cm}^{-1}$ (Figure S14), and the activation energy (E_a) value was 0.11 eV, whereas the room-temperature ionic conductivity of GT-PE was $7.09 \times 10^{-4} \text{ S cm}^{-1}$, with an activation energy of 0.15 eV (Figure 2a; the ionic conductivity at different temperature are shown in Table S1). From the linear sweep voltammetry (LSV) curves, it was observed that the oxidation potential of GTI-PE could reach 5.2 V, whereas GT-PE was gradually decomposed after the voltage exceeded 4 V (Figure 2b), which indicated that GTI-PE had a higher oxidative stability [31]. This can be attributed to the lower lowest unoccupied molecular orbital (LUMO) energy of GTI-PE compared to GT-PE (Figure 2c), which makes it more readily and preferentially reduced. Consequently, GTI-PE participates in forming the solid electrolyte interphase (SEI), thus preventing further redox reactions between the electrolyte and the lithium metal anode [32]. As shown in Figure 2d, the lithium ion transfer number (t_{Li^+}) of GTI-PE reaches 0.56; in contrast, GT-PE exhibits a lower t_{Li^+} (0.49) (Figure S15), indicating that the incorporation of IEMA and the resulting programmed topology are critical for constructing continuous and unobstructed ion transport pathways. To further verify the above results, molecular dynamics (MD) simulations were conducted to

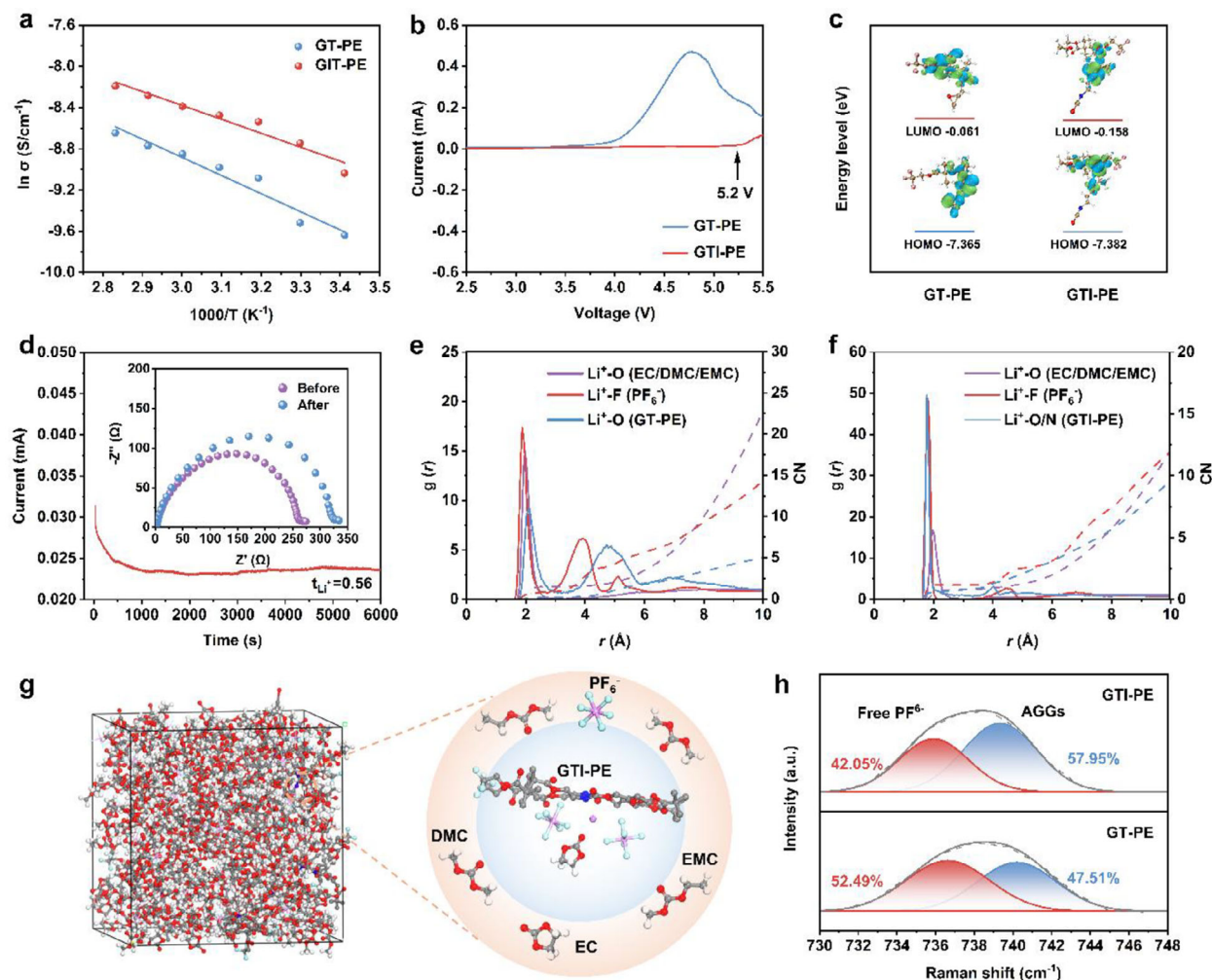


FIGURE 2 | Electrochemical properties and solvation structure of the polymer electrolytes. (a) Temperature-dependent curves of ionic conductivities of PEs. (b) LSV curves of GTI-PE, GT-PE. (c) Molecular orbital energy level calculations for GTI-PE and GT-PE. (d) Polarization curve of $\text{Li}||\text{GTI-PE}||\text{Li}$; insets are Nyquist curves before and after polarization. (e) Calculated RDF curves and coordination numbers in GT-PE. (f) Calculated RDF curves and coordination numbers in GTI-PE. (g) Snapshots of the GTI-PE MD simulation. (h) Raman spectra of GTI-PE and GT-PE.

analyze the solvation structure of Li^+ in the electrolyte. The radial distribution functions (RDFs) and corresponding coordination numbers (CNs) for GT-PE and GTI-PE are shown in Figure 2e,f. In Figure 2e, the primary solvation sheath of Li^+ in GT-PE remains dominated by solvents, with Li^+ exhibiting a CN of 1.79 with O (EC/DMC/EMC), while its CNs with F (PF_6^-) and O (GT-PE) are 1.00 and 0.47, respectively. By contrast, in Figure 2f for GTI-PE, the initial peak positions for $\text{Li}^+-\text{O/N}$ (GTI-PE) and Li^+-F (PF_6^-) appear at 1.78 and 1.83 Å, respectively. These distances are significantly shorter than those for Li^+-O (EC/DMC/EMC) at 1.98 Å. Meanwhile, the Li^+ coordination numbers with F (PF_6^-), O/N (GTI-PE), and O (EC/DMC/EMC) are 1.64, 0.97, and 0.86, respectively. These results indicate that the programmed urethane units guide the GTI polymer segments into the primary solvation sheath of Li^+ and promote the formation of an anion-rich coordination environment [33]. The solvation structures in GT-PE and GTI-PE are shown in the molecular dynamics (MD) simulation snapshots presented in Figure S16 and Figure 2g. Raman spectroscopy further characterized the PF_6^- coordination environment, revealing a significant reduction in free PF_6^- concentration and an increased proportion of coordinated polyanion

clusters (AGGs) in GTI-PE (Figure 2h) [34]. This can be attributed to the strong hydrogen bonding between the -NH groups in the urethane units and PF_6^- anions. This interaction effectively anchors the AGGs onto the polymer backbone, weakens the coordination between Li^+ and solvent molecules, and reduces anion mobility, thereby increasing the lithium-ion transference number. Furthermore, the electron-withdrawing $-\text{CF}_3$ groups further polarize the polymer matrix, promoting ion pair dissociation and facilitating Li^+ transport. The surface electrostatic potentials of the polymer components provide further evidence for the above analysis (Figure S17). The above results indicate that GTI-PE has excellent electrochemical properties and has potential applications in lithium batteries.

2.4 | Evaluation of Interfacial Stability of Polymer Electrolytes

This molecular design strategy achieved an intrinsic balance between mechanical strength and an optimal ion transport environment, not only effectively suppressing lithium dendrite

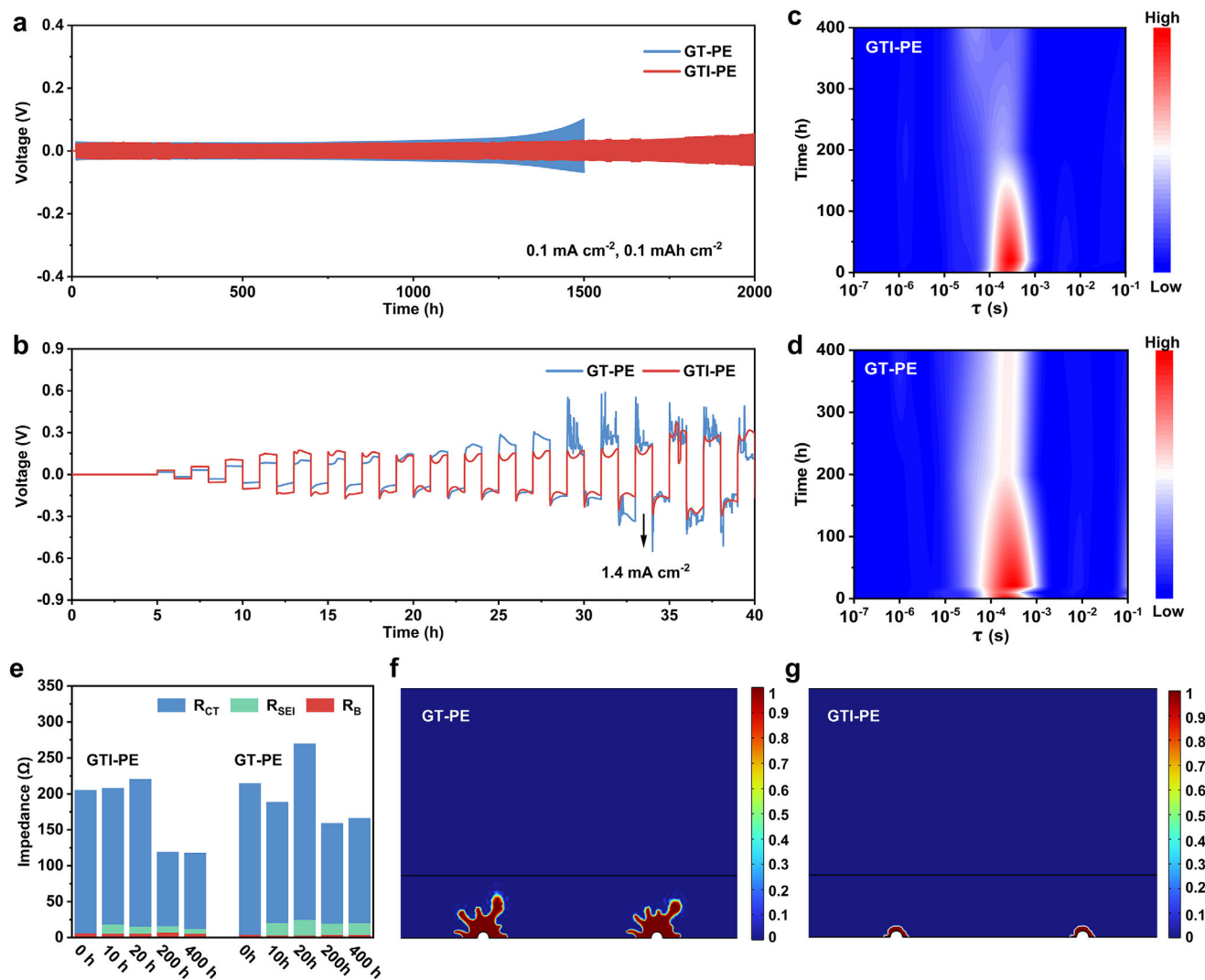


FIGURE 3 | Test of interfacial stability. (a) Constant-current charge/discharge voltage curves of Li||Li cells at a current density of 0.1 mA/cm². (b) Constant-current charge/discharge voltage curves of Li||Li cells at different current densities. (c) Corresponding DRT transformation of the Li||GTI-PE||Li cell. (d) Corresponding DRT transformation of the Li||GT-PE||Li cell. (e) Fitted interfacial impedance results for Li||GTI-PE||Li and Li||GT-PE||Li cells over multiple cycles. (f) COMSOL simplified 2D model of lithium metal dendrite growth with GT-PE. (g) COMSOL simplified 2D model of lithium metal dendrite growth with GTI-PE.

formation but also directly establishing the foundation for its outstanding cycling stability. To this end, Li||Li cells were assembled using GTI-PE and GT-PE and tested by constant-current charging and discharging at a current density of 0.1 mA cm⁻². As shown in Figure 3a, the polarization voltage of the Li||GT-PE||Li cell was high, and the polarization voltage continued to increase after nearly 1200 h of cycling, and eventually short-circuited due to the poor interfacial stability; in contrast, Li||GTI-PE||Li cell with stabilized interfaces formed by the introduction of IEMA was able to cycle stably for 2000 h at the same current density.

More importantly, GTI-PE can provide a critical current density of >1.4 mA cm⁻², in contrast to that of GT-PE (1.1 mA cm⁻²) (Figure 3b). The evolution of the interfacial impedance of Li||Li symmetric cells at different times was analyzed using in situ EIS (Figures S18 and S19). The impedance of the GTI-PE-based cell increased first after 20 h, and then gradually decreased with the increase of the cycling time (The R_{SEI} and R_{ct} were

1.83 and 99.24 Ω at 400 h, Figure 3e), suggesting the formation of highly mechanochemically and chemically stable interfacial layers that are more closely in contact with lithium metal [35]. In contrast, the impedance change of the cell with GT-PE is unstable under different cycle times (The R_{SEI} and R_{ct} were 12.89 and 130.185 Ω at 400 h, Figure 3e). The analysis of EIS data using the relaxation time semiquantitative distribution (DRT) method shows similar results. The relaxation time in the range of 10⁻⁴~10⁻² s corresponds to the evolution of the SEI [36]. In this region, the corresponding peak of GTI-PE decreases and stabilizes during long-term cycling (Figure 3c), whereas the peak in GT-PE remains at a high intensity (Figure 3d). This phenomenon indicates that GTI-PE possesses more stable interfacial chemical properties. In addition, a simplified 2D model was established using COMSOL Multiphysics to simulate the lithium dendrite growth behavior and stress distribution on the lithium metal surface under different electrolyte systems (using the finite element method combined with COMSOL Multiphysics software,

the specific parameters are shown in Table S2 [37]. As shown in Figure 3f, in the GT-PE system, the protruded dendrites grow to form an irregular deposition structure; in contrast, the anode surface in the GTI-PE system is much smoother (Figure 3g). This observation demonstrates that the high mechanical strength of GTI-PE can successfully insert lithium dendrites. From the SEM images of the lithium metal removed from the Li||Li cell after cycling for 50 cycles (Figure S20), it can also be observed that the lithium metal surface with GTI-PE is smooth and flat, with uniform and dense lithium deposition; whereas the anode surface of the GT-PE-based cell exhibits a rough surface after cycling, with large and uneven Li deposition. The above results indicate that GTI-PE demonstrates superior interfacial stability toward lithium metal.

2.5 | Investigation on Electrode/Electrolyte Interface Chemistry Regulated by GTI-PE

To clarify how the programmed topological network of GTI-PE regulates the interfacial chemical stability of lithium metal, the following studies were conducted. The binding energies of GTI-PE and GT-PE on the surface of lithium metal (100) were calculated by density functional theory (DFT) (Figure 4a), and the binding energy of GTI-PE with Li (−1.87 eV) was much lower than that of GT-PE (−0.50 eV), which indicated that lithium metal preferred the adsorption of GTI-PE and the polymer was more prone to the formation of SEIs enriched with the elements of F and N at the negative electrode of lithium metal [38]. By calculating the activation energy of ion diffusion through the SEI layer at different temperatures, the results show that the activation energy of the SEI formed on the basis of GTI-PE is 0.43 eV, while the SEI formed on the basis of GT-PE requires an activation energy of 0.50 eV (Figure 4b; the fitting results of R_{SEI} of the cells are shown in Table S3). The lower activation energy indicates that the unique crosslinked polymer network structure of GTI-PE facilitates Li^+ transport through the electrolyte to the anode and rapid diffusion at the interface, which reduces the lithium nucleation barrier and promotes uniform lithium deposition [39]. Moreover, the incorporation of IEMA makes the Li^+ solvated sheaths rich in PF_6^- anions and polymer fragments containing -NH in the solvated structure of GTI-PE, which facilitates the desolvation process, thus suppressing the side reaction between the solvent molecules and the anode, and at the same time facilitates the formation of mechanochemically stabilized SEI layers enriched with LiF and Li_3N . In this regard, the Tafel curves of Li||Li symmetric cells obtained from LSV tests showed that the exchange current density using GTI-PE (0.077 mA cm^{-2}) was higher than that of GT-PE (0.034 mA cm^{-2}), indicating higher diffusion kinetics of Li^+ in the SEI formed with the participation of GTI-PE (Figure S21). That is, the inorganic-rich interfacial SEI composition is favorable to promote the lithium-ion transfer kinetics. Further, in the ^7Li NMR spectra of Li||Li symmetric cells after 50 cycles, it was found that the chemical shift of Li^+ based on GTI-PE was shifted toward the low-field direction compared to GT-PE (Figure 4c), indicating that the degree of electron shielding around Li^+ was reduced [40]. In addition, FT-IR spectroscopy analysis of the GTI-PE membrane after cycling (Figure S22) revealed that the characteristic -NH/-OH peak at $3300\text{--}3500 \text{ cm}^{-1}$ decreased in intensity compared to the pristine membrane, while the C=O peak at 1701 cm^{-1} also showed a slight reduction. These

changes can be attributed to proton exchange or coordination interactions between -NH and Li^+ (forming -NLi species), and to the participation of C=O groups in interfacial coordination or SEI formation. Meanwhile, the characteristic peaks corresponding to the C=O groups ($1600\text{--}1800 \text{ cm}^{-1}$) remained largely unchanged, and the -NH/-OH peak position remained discernible, indicating that the polymer network maintains its structural integrity. These results further confirm that PF_6^- anions and polymer fragments in the Li^+ solvation sheath of GTI-PE participate in the formation of SEI, contributing to Li^+ rapid migration at the interface [41, 42].

For the above analysis, the lithium metal anode extracted from the Li||Li cell after 50 cycles was analyzed by XPS. In the XPS C 1s spectrum of the SEI layer formed with GTI-PE, compared with that formed with GT-PE, apart from the appearance of a peak corresponding to -C-N (288.6 eV), the peaks associated with the decomposed CO_3^{2-} (290.1 eV) and -C-F (293.2 eV) components were barely detectable (Figure 4d) [43]. This result indicates that GTI-PE constructs a stable interface, which is conducive to the uniform deposition of lithium and reduces the decomposition of the electrolyte. In the XPS N 1s spectra (Figure 4e), the GTI-PE-based SEI layer showed -N-C=O (401 eV), -CONH- (399.7 eV), and -NLi- (398.4 eV) components of the corresponding peaks. Furthermore, the GTI-PE-based SEI is enriched with Li_3N (398.4 eV) in addition to the inorganic phase LiF (685 eV) (Figure 4e,f) [44, 45]. The main components and distribution of SEI in GTI-PE were further investigated by TOF-SIMS (Figure 4g; Figure S23). The SEI was detected with organic components (including C_2HO^- and $\text{C}_2\text{H}_3\text{O}^-$) and inorganic components (e.g. LiF_2^- , LiN^- , and LiO^-) associated with atomic fragments. Among them, LiF_2^- has the highest signal intensity, which proves the LiF rich interface between the electrolyte and the lithium anode. In addition, the inorganic components in SEI include Li_3N , Li_2O , Li_2CO_3 , etc. These inorganic components are primarily distributed within the SEI layer, providing it with high mechanical strength and densification, thereby favorably suppressing lithium dendrite growth [46]. Meanwhile, the coexistence of these inorganic components with high Li^+ conductivity facilitates the formation of a reduced lithium-ion migration barrier, improving ion transport. Besides, the organic constituents in the SEI exhibit moderate surface enrichment to form a flexible interfacial layer while gradually infiltrating toward the intermediate region to composite with the inorganic phase, thereby endowing the SEI layer with rigid-flexible mechanical stability (Figure 4h). The above results indicate that GTI-PE was successfully involved in the formation of a uniform and dense SEI layer. In addition, since the ester group (-C=O) and the amino group (-NH) in the GTI-PE structural unit can form intermolecular hydrogen bonding, the hydrogen-bonded structure within the SEI layer formed by GTI-PE facilitates adaptation to volume changes in electrode materials during cycling, ensuring sustained adaptive contact between the electrolyte and electrodes [47]. According to the FT-IR spectra of GTI-PE, the peak of the C=O groups exhibited splitting, one of which was red-shifted to 1666 cm^{-1} due to the formation of a strong hydrogen bond between the -NH/-OH and C=O groups (Figure S24). According to previous studies, an important reason for the poor cycling stability of lithium metal batteries is due to the fact that an unstable interface enhances the continuous reaction between the lithium metal and the electrolyte, resulting in the continuous thickening of the SEI

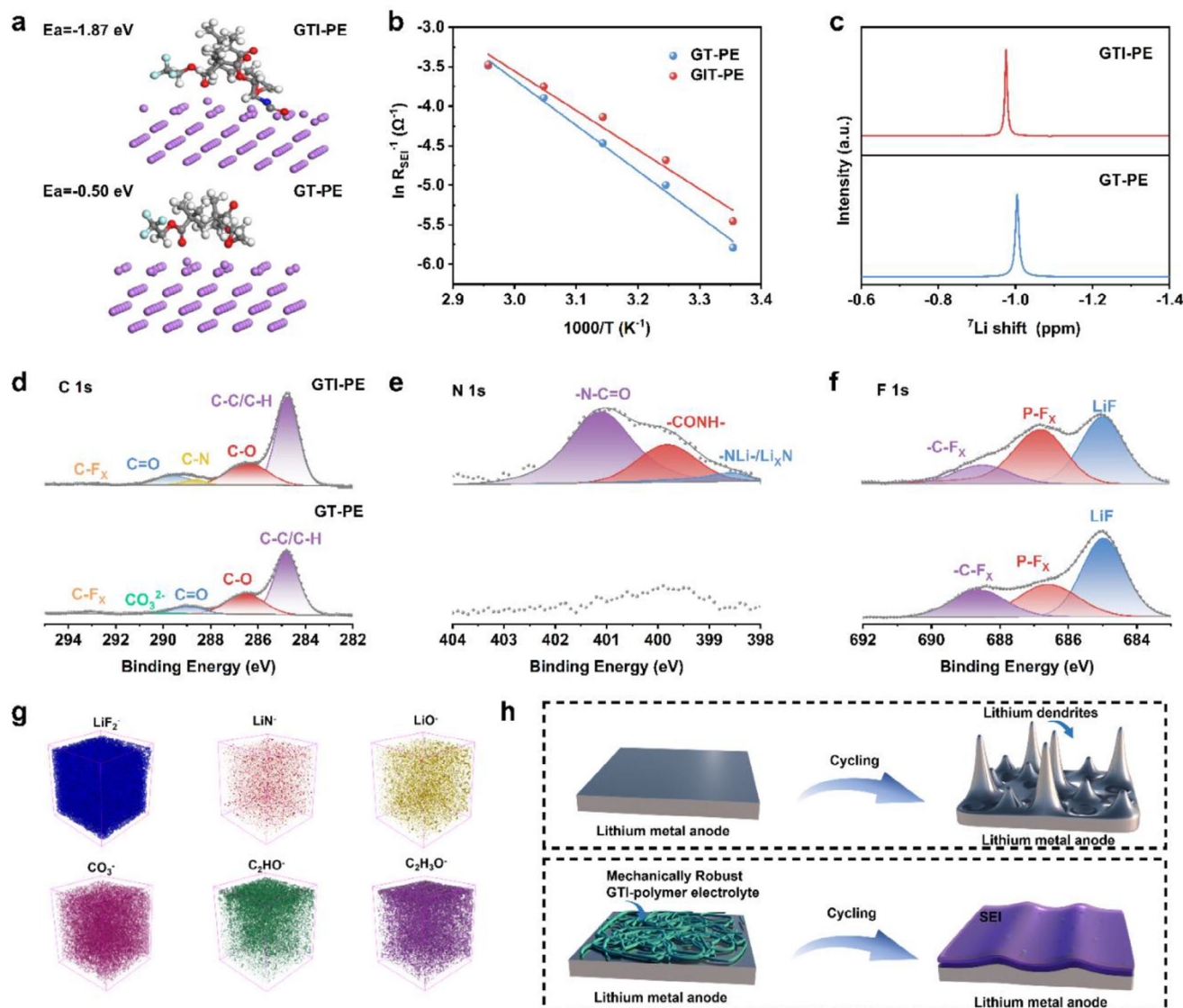


FIGURE 4 | Interfacial chemistry analysis of the polymer electrolytes. (a) Computational structural modeling of GTI-PE and GT-PE and surface binding energies to lithium metal. (b) Arrhenius equation to calculate the activation energy for diffusion through the solid electrolyte interface (SEI) at different temperatures. (c) ⁷Li NMR spectra of the surface SEI of the cycled Li metal anode removed from Li||Li cells with GT-PE and GTI-PE after 50 cycles. X-ray photoelectron spectra (XPS) of (d) C 1s, (e) N 1s, and (f) F 1s. (g) The distribution of inorganic and organic species in the SEI is illustrated by visual maps of 3D TOF-SIMS for the SEI of Li anode obtained from Li||Li cell with GTI-PE. (h) Schematic design of the highly active lithium metal anode and GTI-PE-based high stability solid state electrolyte interface.

and the irreversible loss of lithium, which makes the lithium metal too late to migrate to the surface and be encapsulated by the SEI, thus forming dead lithium with no electrochemical activity, and ultimately leading to the failure of the lithium anode [48–50]. Therefore, the above multi-scale studies demonstrate that the tailored topology of GTI-PE, as the functional output of programmable click chemistry, fundamentally empowers the electrode/electrolyte interface, ensuring its mechanochemical stability for effective anode protection.

2.6 | Performances of Cells with GTI-PE

In order to further verify the role of GTI-PE with a topological network structure in ensuring the long cyclic life of cells,

LiFePO₄||Li and LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂||Li full cells were assembled. As shown in Figure 5a, at room temperature, the initial discharge capacity of the cell was 154.28 mAh g⁻¹ after activation at a current density of 0.1 C, and then exhibited 87.95% capacity retention after 500 stable cycles at 0.5 C. In contrast, the capacity of the cell with GT-PE rapidly decayed after about 120 cycles, with only 37.63% capacity retention after 500 cycles. Figure 5c and Figure S25 demonstrate the rate performance of the LiFePO₄||GTI-PE||Li cell. The discharge capacities of the cell using GTI-PE at different current densities were 153, 152, 149, 144, 135, and 127 mAh g⁻¹, respectively. When restored to 0.1 C, it still has excellent capacity reversibility (154 mAh g⁻¹), while the cell assembled with GT-PE has suffered relatively severe capacity attenuation in the rate cycle of 2 C. To this end, we evaluated the long-term cycling performance of the LiFePO₄||GTI-PE||Li

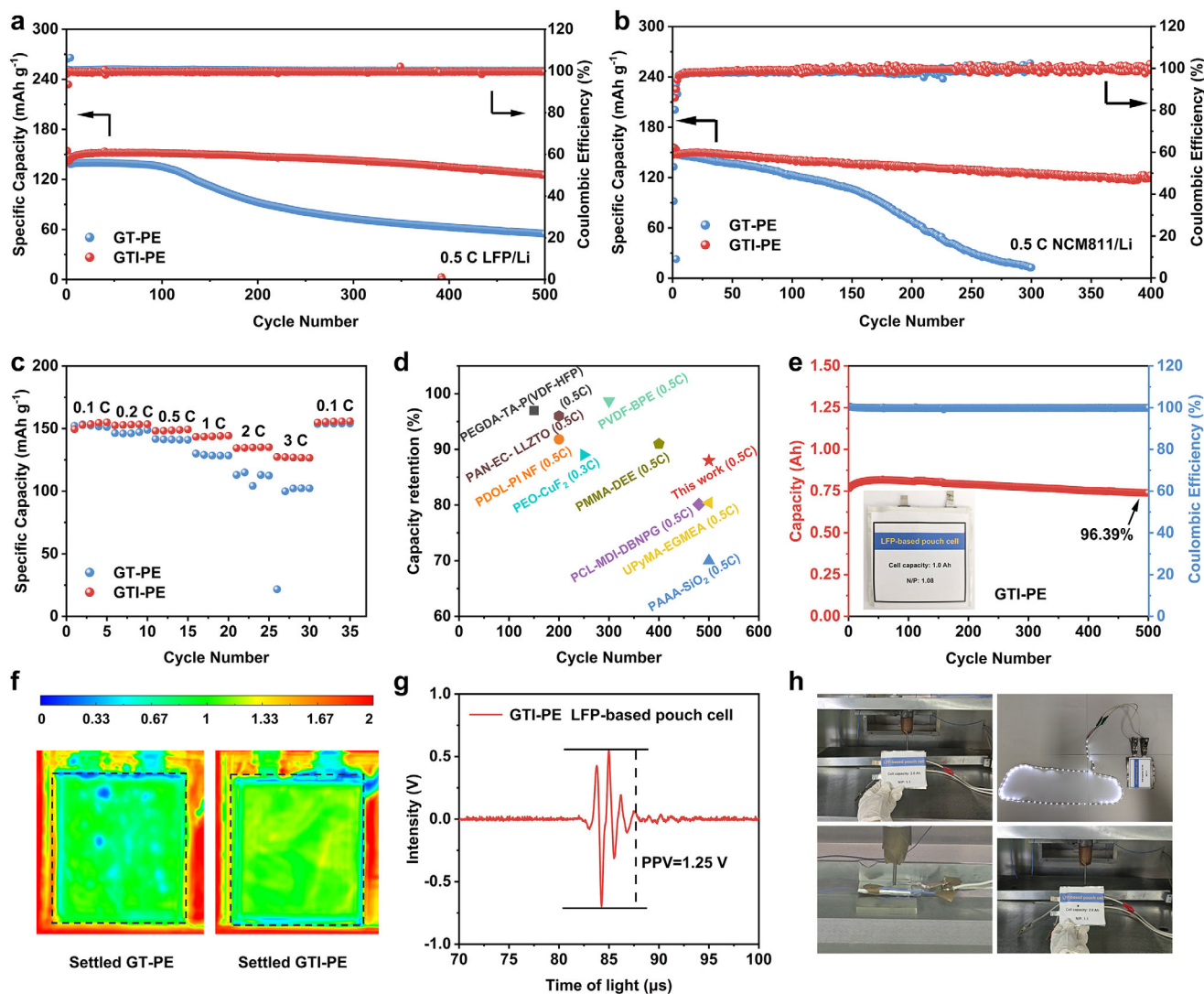


FIGURE 5 | Cycling stability of solid-state cells with GTI-PE or GT-PE. (a) Long-term cycling performance of LFP||Li cells at 0.5 C. (b) Long-term cycling performance of NCM811||Li cells at 0.5 C. (c) Rate capability of LFP||Li cells. (d) Electrochemical performance comparison of LFP||GTI-PE||Li cells with prior studies. (e) Cycling stability of 1Ah GTI-PE LFP-based pouch cell. (inset is the optical photograph of the GTI-PE LFP-based pouch cell). (f) The ultrasonic scanning results of 1 Ah pouch cells of GTI-PE LFP-based pouch cell and GT-PE LFP-based pouch cell. (g) The time-domain waveforms of the ultrasonic transmission signal of the 1 Ah GTI-PE LFP-based pouch cell. (h) Photos of 2 Ah GTI-PE LFP-based pouch cell, lighting up LED lights, and conducting a nail penetration test.

cell at a higher rate of 1 C. As shown in Figure S26, the LiFePO₄||GTI-PE||Li cell maintains a capacity retention of 88.63% after 300 cycles. In contrast, the GT-PE-based cell exhibits unstable coulombic efficiency after 170 cycles and subsequently fails due to short-circuiting. Compared to LiFePO₄||Li cells assembled with previously reported polymer electrolyte systems (Figure 5d), the GTI-PE-based cell maintains superior capacity retention over prolonged cycling. This enhanced stability is attributed to the programmed topological network assembled via click chemistry that reinforces mechanical robustness, while the self-healing functionality effectively mitigates crack formation and deformation during cell operation. The LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂||Li cell assembled with GTI-PE has a capacity retention rate of 77% after 400 cycles at a stable current density of 0.5 C at 4.3 V, while the capacity of the cell with GT-PE starts to decay dramatically after 180 cycles under the same test conditions (Figure 5b). In addition, the discharge capacities of the LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂||GTI-

PE||Li cell at 0.1 C~2 C were 189, 183, 166, 147, and 122 mAh g⁻¹ respectively, which exceeded those of LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂||GT-PE||Li cell (Figure S27). Furthermore, the 1 Ah LiFePO₄-based pouch cell retains 96.39% capacity after 500 cycles within the voltage range of 2.5–4 V (Figure 5e). As shown in Figure 5f, ultrasonic scanning was employed to assess the wettability of the precursor solution on cells prior to thermal curing [51]. The GT-PE LiFePO₄-based pouch cell exhibited a peak-to-peak voltage (PPV) of 0.63 V in time-domain signals (Figure S28), indicating effective wetting across most regions. Partial blue areas likely correspond to trapped air pockets. For the GTI-PE LiFePO₄-based pouch cell, the PPV (Peak Particle Velocity) of the ultrasonic time-domain signal is 1.13 V (Figure 5g), indicating sufficient wetting within the cell when employing the in situ polymerized GTI-PE electrolyte. Simultaneously, the crosslinked network formed via post-curing, possessing high mechanical robustness and self-healing capability, ensures the maintenance and restoration of the

in situ formed favorable interfaces under conditions of long-term cycling, electrode volume changes, and potential damages. Based on this, a 2 Ah GTI-PE LiFePO₄-based pouch cell was further assembled. It initially exhibited a high open-circuit voltage of 3.3 V (Figure S29) and could steadily light up an LED lamp (Figure 5h). To assess the safety performance of GTI-PE LiFePO₄-based pouch cells, the nail penetration test was carried out on the 2 Ah GTI-PE LiFePO₄-based pouch cell. A stainless-steel nail was driven through the center of the cell at a speed of 25 mm/s and kept in place for 400 s. Throughout the entire experiment and the subsequent period, no fire or smoke was observed in the cell. This enhanced safety is attributed to the self-healing capability of GTI-PE, which promptly addresses physical damage induced by penetration, while the mechanically robust crosslinked network provides structural support to resist and confine damage propagation, thereby preventing large-scale cell failure.

3 | Conclusion

In conclusion, we propose a molecular programming paradigm, realized via an in situ programmed click-creation strategy that crafts urethane units as multifunctional code to construct a terpolymer electrolyte with a topological network. This terpolymer electrolyte integrates enhanced mechanical properties, self-healing capability, and excellent electrochemical performance, effectively overcoming the key trade-off between mechanical properties and electrochemical performance in traditional polymer electrolytes. Mechanical tests confirm that the programmed topology endows GTI-PE with a Young's modulus of 3.7 GPa and a tensile stress of 42.31 MPa, demonstrating favorable elastic deformation capacity and mechanical strength. This enables GTI-PE to maintain structural integrity during battery operation and inhibit lithium dendrite penetration, thereby ensuring superior cycling stability. Consequently, the Li||Li symmetric cell based on GTI-PE achieves stable cycling for 2000 h at a current density of 0.1 mA cm⁻², and the 1Ah LiFePO₄-based pouch cell retains 96.39% capacity after 500 cycles. In addition to the specific GTI-PE system presented in this work, the in situ programmed click chemistry strategy is expected to be extended to other polymeric systems. By designing systems with complementary reactive groups (such as amine-epoxy, thiol-ene), it will be possible to rationally design topological polymer electrolytes with tunable mechanical properties, self-healing capabilities, and ionic conductivity. This work provides a novel insight for promoting the practical application of high-energy-density lithium metal batteries.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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