

RESEARCH ARTICLE OPEN ACCESS

Polymer Side-Chain Electronic Effects Regulating Solvation Sheath for Low-Temperature and High-Voltage Lithium Metal Batteries

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Received: 18 June 2026 | **Revised:** 30 August 2026 | **Accepted:** 16 September 2026

Keywords: fluorinated gel polymer electrolytes | LiF-rich interphase | low-temperature lithium metal batteries | side-chain electronic effect | solvation sheath regulation

ABSTRACT

Gel polymer electrolytes (GPEs) rich in ether oxygen side chains have attracted particular interests in high-energy-density lithium metal batteries (LMBs). However, the strong coordination between their polymer framework and lithium ions (Li^+) leads to a high desolvation energy barrier at low temperatures. Herein, by comparing the side-chain electronic effects, this work constructs an ether-oxygen-based gel polymer electrolyte (E-GPE) with electron-donating ether oxygen side chains and a fluorinated GPE (F-GPE) with electron-withdrawing trifluoromethyl side chains, with N,N-dimethyl trifluoroacetamide (FDMA) as a low-temperature additive. Density functional theory (DFT) calculations reveal that the electron-donating side chains in E-GPE enhance the binding energy between the polymer framework and Li^+ , thereby impeding Li^+ desolvation. Conversely, the electron-withdrawing side chains in F-GPE weaken the binding energy between the polymer framework and Li^+ , lowering the Li^+ desolvation barrier and inducing the formation of LiF-rich interphase. Consequently, Li/F-GPE/Li cells stably cycle for over 1000 h at -20°C , and Li/F-GPE/LiCoO₂ coin cells retain 88.7% of their original capacity after 400 cycles at -20°C . Furthermore, pouch cells steadily power a light-emitting diode (LED) after shear damage, demonstrating potential safety. This work provides a new design paradigm for developing GPEs for high-energy-density LMBs in extreme environments.

1 | Introduction

Lithium metal anodes possess an ultrahigh theoretical capacity of 3860 mAh g⁻¹ and an electrode potential as low as -3.04 V (vs. the standard hydrogen electrode), rendering lithium metal batteries (LMBs) a pivotal platform for next-generation high-energy-density energy storage applications [1–3]. However, the intrinsic flammability and leakage risk of liquid organic

electrolytes severely impede their practical application under high oxidation voltage and low temperature conditions [4, 5]. Alternatively, gel polymer electrolytes (GPEs) integrate the safety of solid-state electrolytes with the high Li^+ conductivity of liquid electrolytes, thus attracting considerable attention [6]. The robust mechanical properties of GPEs enable effective suppression of lithium dendrite growth and ensure favorable interfacial contact with the cathodes (e.g., LiCoO₂, NCM811) [7–9]. Furthermore,

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the polymer framework of GPEs features versatile molecular designability, enabling directional optimization of electrolyte properties at the molecular level [10, 11]. However, under the extreme conditions of low temperature and high cutoff voltage, conventional GPEs such as polyether-based GPEs rich in ether oxygen side chains still suffer from interfacial deterioration, inducing sluggish Li^+ migration kinetics with higher barriers [6, 12].

To address the above-mentioned issues, current dominant strategies focus on incorporating low-melting-point solvents into the GPE [6, 13, 14]. For instance, Shan et al. introduced methyl difluoroacetate during in-situ polymerization, which enabled stable cycling of the GPE at -25°C [14]. Furthermore, incorporating fluorine-containing side chains onto the polymer framework can further enhance the high-voltage and low-temperature performance of GPEs [15, 16]. For example, Li et al. confirmed that fluorinated side chains can weaken the dipole interaction between the polymer matrix and Li^+ , thereby significantly improving Li^+ transport and promoting the construction of a LiF-rich interphase [16–18]. The above work confirms the positive role of fluorinated side chains in optimizing Li^+ transport and interfacial stability in GPEs. Compared with GPEs containing fluorinated side chains, GPEs rich in ether oxygen side chains have also been widely used in LMBs due to their excellent interfacial compatibility with lithium metal anodes [19, 20]. However, the electron-donating effect of ether oxygen side chains enhances the coordination between the polymer framework and Li^+ , which leads to interfacial degradation at high voltages and sluggish Li^+ migration kinetics at low temperatures [21, 22]. The influence of these two types of side chains with different electronic effects on the solvation environment and interfacial behavior of Li^+ in GPEs has not yet been systematically compared. Therefore, a direct comparison of the effects of electron-donating and electron-withdrawing side chains on GPE performance is of great value for the rational design of GPEs at the molecular level.

To fill this research gap, this work employed free radical polymerization to construct ether-based GPE (E-GPE) with electron-donating ether oxygen side chains and fluorinated GPE (F-GPE) with electron-withdrawing trifluoromethyl side chains by copolymerizing acrylate monomers bearing different electronic side chain effects with a crosslinker, and introduced N,N-dimethyl trifluoroacetamide (FDMA) as a low-temperature additive to compare the influence of side chain electronic effects on the Li^+ coordination environment and electrochemical performance of the GPEs. Density functional theory (DFT) calculations and experimental characterization reveal that the electron-donating side chains in E-GPE enhance the binding energy between the polymer framework and Li^+ , which enables more FDMA to enter the Li^+ solvation sheath and thereby impedes Li^+ desolvation at low temperatures. In contrast, the electron-withdrawing side chains in F-GPE substantially weaken the binding energy between the polymer framework and Li^+ , facilitating more anions to enter the solvation sheath, lowering the desolvation energy barrier of Li^+ . Moreover, the fluorine-containing side chains also induce the formation of a LiF-rich interphase on the electrodes and endow the GPE with higher oxidative stability in high-voltage LMBs.

Consequently, the F-GPE delivers a Li^+ transference number as high as 0.574 and achieves a Li^+ conductivity of $1.748 \times$

$10^{-4} \text{ S cm}^{-1}$, and the Li/F-GPE/Li cell can stably cycle for over 1000 h at -20°C . Li/F-GPE/LiCoO₂ coin cells retain 97.3% of their initial capacity after 500 cycles at 30°C and 88.7% after 400 cycles at -20°C , respectively. The pouch cells can stably cycle for tens of cycles and still power an LED even after shear damage. This work reveals the influence of polymer side chain electronic effects on the component distribution of the solvation sheath, offering a novel research paradigm for developing GPEs for high-energy-density LMBs operating under extreme conditions.

2 | Results and Discussion

2.1 | Design and Theoretical Calculations of GPE

In GPEs rich in ether oxygen side chains, the electron-donating effect of these side chains strengthens the interaction between the polymer framework and Li^+ , which often leads to sluggish Li^+ migration kinetics and poor interfacial stability at low temperatures [19, 23, 24]. Introducing electron-withdrawing side chains is a potential strategy to weaken this strong coordination [16, 19, 20]. However, the effects of electron-donating and electron-withdrawing side chains on the Li^+ coordination environment and interfacial behavior have not yet been systematically compared. To clarify this issue, this work constructed two types of GPEs with different side chain electronic effects. Specifically, the F-GPE was constructed via the crosslinking polymerization of 2,2,2-trifluoroethyl acrylate (TFEA) and polyethylene glycol diacrylate (PEGDA), with FDMA introduced as a low-temperature additive (Figure 1a and Figure S1). The TFEA monomer contains a strong electron-withdrawing trifluoromethyl group. To clarify the distinct influences of electron-donating and electron-withdrawing side chains on the Li^+ coordination environment, the E-GPE was fabricated as a reference system. This E-GPE was derived from the crosslinking polymerization of 2-ethoxyethyl acrylate (EOEA) and PEGDA, incorporating the same FDMA additive (Figure 1a). In contrast to TFEA, the EOEA monomer features an electron-donating ether oxygen group. The detailed preparation routes for both electrolytes are illustrated in Figures S2 and S3.

The polymerization degree of E-GPE and F-GPE were analyzed by Fourier transform infrared spectroscopy (FTIR) and ^{13}C nuclear magnetic resonance (NMR) spectroscopy. In the FTIR spectra (Figure S4), the $\text{C}=\text{C}$ peak at 1640 cm^{-1} attributed to EOEA and TFEA were no longer observed in both electrolytes, while new peaks corresponding to $\text{C}=\text{O}$ at 1730 cm^{-1} and $\text{C}-\text{O}-\text{C}$ at 1100 cm^{-1} appeared [25, 26]. In the ^{13}C NMR spectra (Figure S5), the characteristic signals of the $\text{C}=\text{C}$ bond carbons in the 128–132 ppm region, which are present in the solution-state ^{13}C NMR spectra of the EOEA and TFEA monomers (Figure S5a,b), completely disappear in the solid-state ^{13}C NMR spectra of p(EOA-PEGA) and p(TFA-PEGA) (Figure S5c,d). The signal at 124.3 ppm in p(TFA-PEGA) is assigned to the side-chain $-\text{CF}_3$ carbon rather than to the $\text{C}=\text{C}$ bond carbons. Additionally, both polymers exhibit signals of saturated carbon skeletons in the 20–70 ppm region, and ester carbonyl carbon signals are observed around 175 ppm. These results indicate that the $\text{C}=\text{C}$ bonds in EOEA and TFEA have been fully converted, confirming that the polymerization is complete (Figure S5).

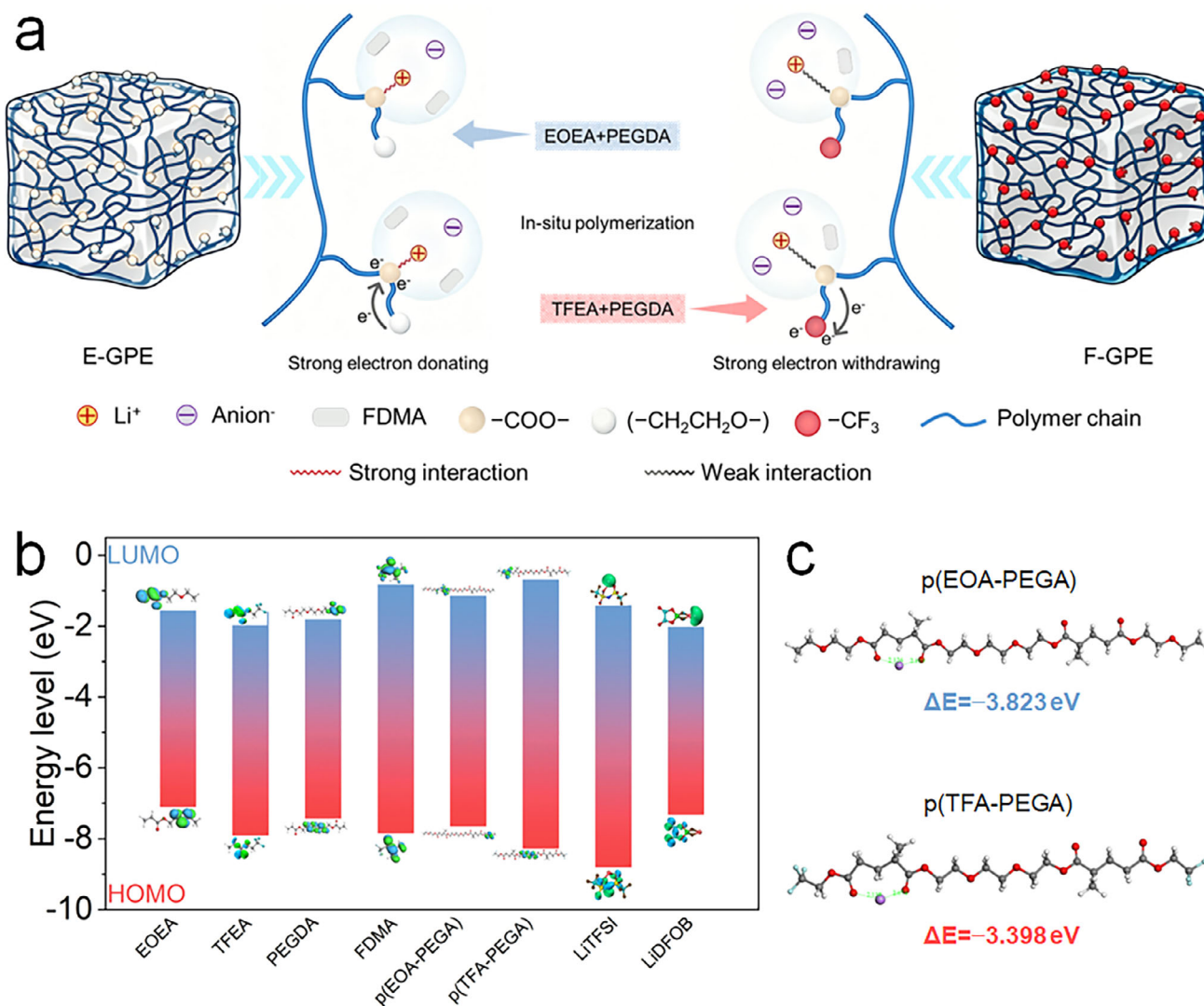


FIGURE 1 | (a) Schematic illustration of the Li^+ solvation structures in E-GPE and F-GPE. (b) HOMO and LUMO orbital energy levels of monomers, lithium salt, and polymers. (c) Optimized geometric configurations and binding energies of p(EOA-PEGA) and p(TFA-PEGA) with Li^+ .

The segmental dynamics of the polymer directly affect the transport properties of Li^+ , especially at low temperatures. Differential scanning calorimetry (DSC) measurements reveal that the glass transition temperature (T_g) of F-GPE is -46.3°C , which is significantly lower than that of E-GPE (-39.6°C) (Figure S6). This can be attributed to the larger free volume arising from the $-\text{CF}_3$ side chains and the weakening of dipole-dipole interactions between polymer chains, which enhance segmental flexibility and facilitate segmental motion at low temperatures [27]. Thermogravimetric analysis (TGA) reveals a higher initial decomposition temperature for F-GPE compared with E-GPE (Figure S7), which originates from the high bond energy of the C-F bonds that suppresses thermal degradation of the polymer framework at elevated temperatures [20]. X-ray diffraction (XRD) patterns reveal that E-GPE and F-GPE exhibit broad diffuse peaks without any sharp crystalline diffraction peaks. This confirms their fully amorphous structure (Figure S8), which facilitates Li^+ transport [28].

To verify the influence of side chain electronic effects on high voltage stability, DFT calculations were conducted to determine the

molecular orbital energy levels of the polymer framework. The p(TFA-PEGA) framework of F-GPE exhibits a lower highest occupied molecular orbital (HOMO) energy level than the p(EOA-PEGA) framework of E-GPE due to the electron-withdrawing $-\text{CF}_3$ group (Figure 1b), indicating stronger oxidation resistance of F-GPE [19, 29]. Linear sweep voltammetry (LSV) verified this result. The E-GPE showed an oxidation current rise at 4.9 V, while the oxidation onset potential for F-GPE was 5.2 V (Figure S9a). Potentiostatic floating tests further revealed that E-GPE decomposed at 4.6 V, whereas F-GPE exhibited an increase in leakage current at 4.7 V (Figure S9b). These findings demonstrate that fluorine-containing side chains lower the HOMO energy level and enhance the high-voltage oxidation resistance of GPEs.

Side chain electronic effects also influence the Li^+ coordination environment. DFT calculations show that the binding energy of Li^+ with p(EOA-PEGA) is -3.823 eV, while that with p(TFA-PEGA) is -3.398 eV (Figure 1c). Compared with the electron-donating side chains in E-GPE, the electron-withdrawing side chains in F-GPE weaken the coordination between the polymer framework and Li^+ , enabling more anions to enter the solvation

sheath and optimizing the low-temperature desolvation kinetics of Li^+ . Electrostatic potential calculations show that the carbonyl oxygen atoms on the p(EOA-PEGA) framework exhibit pronounced negative potential regions, reflecting high electron cloud density, which originates from the electron-donating effect of the ether oxygen side chains. In contrast, the negative potential regions around the carbonyl oxygen in the p(TFA-PEGA) framework are significantly weakened by the electron-withdrawing inductive effect of the $-\text{CF}_3$ groups (Figure S10). This difference is consistent with the DFT calculation results of HOMO energy levels and Li^+ binding energies (Figure 1b,c), indicating that the side chain electronic effect significantly influences the electron cloud density of the coordination sites.

2.2 | Characterization of the Li^+ Solvation Structure

To understand the Li^+ coordination environment in F-GPE and E-GPE, this work employs molecular dynamics (MD) simulations, Raman spectroscopy, FTIR spectroscopy, solution-state ^{19}F NMR spectroscopy and ^7Li NMR spectroscopy to investigate the Li^+ solvation structures and diffusion behaviors of the two electrolytes.

MD simulations reveal the differences in solvation structures at the microscopic level (Figure 2a,b). The simulation snapshots show that Li^+ , TFSI^- , DFOB^- , FDMA, and the polymer framework are located in the same solvation sheath. In E-GPE, the coordination numbers of Li^+ with DFOB^- , TFSI^- , and FDMA are 0.068, 1.779, and 1.874, respectively. In F-GPE, the corresponding values are 0.074, 2.066, and 1.489 (Figure 2d,e). This indicates that the electron-withdrawing trifluoromethyl side chains shift the coordination preference of Li^+ from FDMA toward anions, promoting more anions to participate in the construction of the SEI and CEI [30, 31]. Radial distribution function analysis confirms that the coordination number of carbonyl oxygen in the polymer framework with Li^+ is higher in E-GPE than in F-GPE, further demonstrating that the side-chain electronic effect regulates the solvation structure of GPEs (Figure 2f). Mean square displacement (MSD) calculations show that the Li^+ diffusion coefficient of F-GPE at 30°C is $2.35 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, higher than that of E-GPE ($1.86 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) (Figure 2c), indicating lower Li^+ migration resistance in F-GPE [32, 33].

Spectroscopic characterization was conducted to verify these findings. Raman spectroscopy shows that the characteristic peak of TFSI^- in F-GPE exhibits a blueshift relative to that in E-GPE, confirming enhanced coordination between anions and Li^+ (Figure 2g) [26, 34]. In the FTIR spectra, the carbonyl stretching vibration peak of F-GPE exhibits a blueshift relative to that of E-GPE (Figure S11), which is mainly attributed to the electron-withdrawing inductive effect of the $-\text{CF}_3$ side chains. To distinguish the contribution of the side-chain electronic effect from that of Li^+ coordination, control samples without lithium salts (F-control and E-control) were introduced. The results show that the redshift of the carbonyl peak in F-GPE is approximately 5 cm^{-1} , which is smaller than that of E-GPE (approximately 8 cm^{-1}). The larger redshift of the carbonyl peak in E-GPE due to Li^+ coordination indicates stronger coordination between its polymer framework and Li^+ , which is consistent with the higher coordina-

tion number of carbonyl oxygen with Li^+ in E-GPE, as obtained from MD simulations (0.662 vs. 0.436). These control experiments confirm that the $-\text{CF}_3$ side chains in F-GPE weaken the coordination between Li^+ and the polymer framework [16, 35, 36].

Solution-state ^7Li and ^{19}F NMR spectra show that the ^7Li signal in F-GPE shifts downfield by 0.03 ppm relative to that in E-GPE, while the ^{19}F peak of TFSI^- shifted downfield by 0.08 ppm (Figure 2h,i). The downfield shift of ^7Li indicates a decrease in electron density around the Li^+ , associated with the entry of more electron-withdrawing anions into the solvation sheath. The downfield shift of ^{19}F reflects a reduction in electron density around the fluorine atoms, consistent with enhanced anion and Li^+ coordination in F-GPE [16, 37].

MD simulations and spectroscopic characterization reveal the mechanism by which side-chain electronic effects influence the Li^+ solvation structure. Compared with the electron-donating ether oxygen side chains, the electron-withdrawing trifluoromethyl side chains weaken the coordination between the polymer framework and Li^+ , enabling more anions (TFSI^- and DFOB^-) to enter the Li^+ solvation sheath. This lowers the desolvation energy barrier of Li^+ and enhances Li^+ transport efficiency.

2.3 | Analysis of Li^+ Transport Kinetics and Electrochemical Performance

To elucidate the influence of side-chain electronic effects on Li^+ transport, the Li^+ conductivity of E-GPE and F-GPE was evaluated at different temperatures. At -20°C , the Li^+ conductivity of F-GPE is $1.748 \times 10^{-4} \text{ S cm}^{-1}$, higher than that of E-GPE ($1.602 \times 10^{-4} \text{ S cm}^{-1}$) (Figure 3a and Figure S12a), indicating good low-temperature Li^+ transport performance of F-GPE. Upon further decreasing the temperature to -30°C , the Li^+ conductivity of F-GPE is $1.156 \times 10^{-4} \text{ S cm}^{-1}$, which remained higher than that of E-GPE ($9.803 \times 10^{-5} \text{ S cm}^{-1}$) (Figure S12b), indicating that its good Li^+ transport capability is preserved at even lower temperatures. At 30°C , the Li^+ conductivity of E-GPE is $9.445 \times 10^{-4} \text{ S cm}^{-1}$, slightly higher than that of F-GPE ($6.954 \times 10^{-4} \text{ S cm}^{-1}$), which is ascribed to the stronger dissociation capability of the ether oxygen side chains for lithium salts (Figure S13) [19, 36]. The Li^+ migration activation energy of F-GPE obtained from Arrhenius fitting is 0.102 eV, lower than that of E-GPE (0.114 eV) (Figures S14), demonstrating that the electron-withdrawing trifluoromethyl side chains reduce the Li^+ migration energy barrier. Tafel polarization tests show that the exchange current density of F-GPE at -20°C is higher than that of E-GPE, indicating lower interfacial charge transfer resistance with the lithium metal (Figure 3a and Figure S15) [38]. Critical current density (CCD) measurements reveal that the CCD values of E-GPE and F-GPE are 1.1 and 1.8 mA cm^{-2} , respectively (Figure 3b and Figure S16). The higher CCD and exchange current density of F-GPE are attributed to its fast Li^+ desolvation kinetics, which suppresses concentration polarization and lithium dendrite growth [38, 39]. The Bruce-Vincent method reveals a high Li^+ transference number (t_{Li^+}) of 0.574 for F-GPE, markedly superior to that of E-GPE, indicating that F-GPE alleviates concentration polarization and promotes uniform Li^+ deposition on the lithium metal anode (Figure S17) [39].

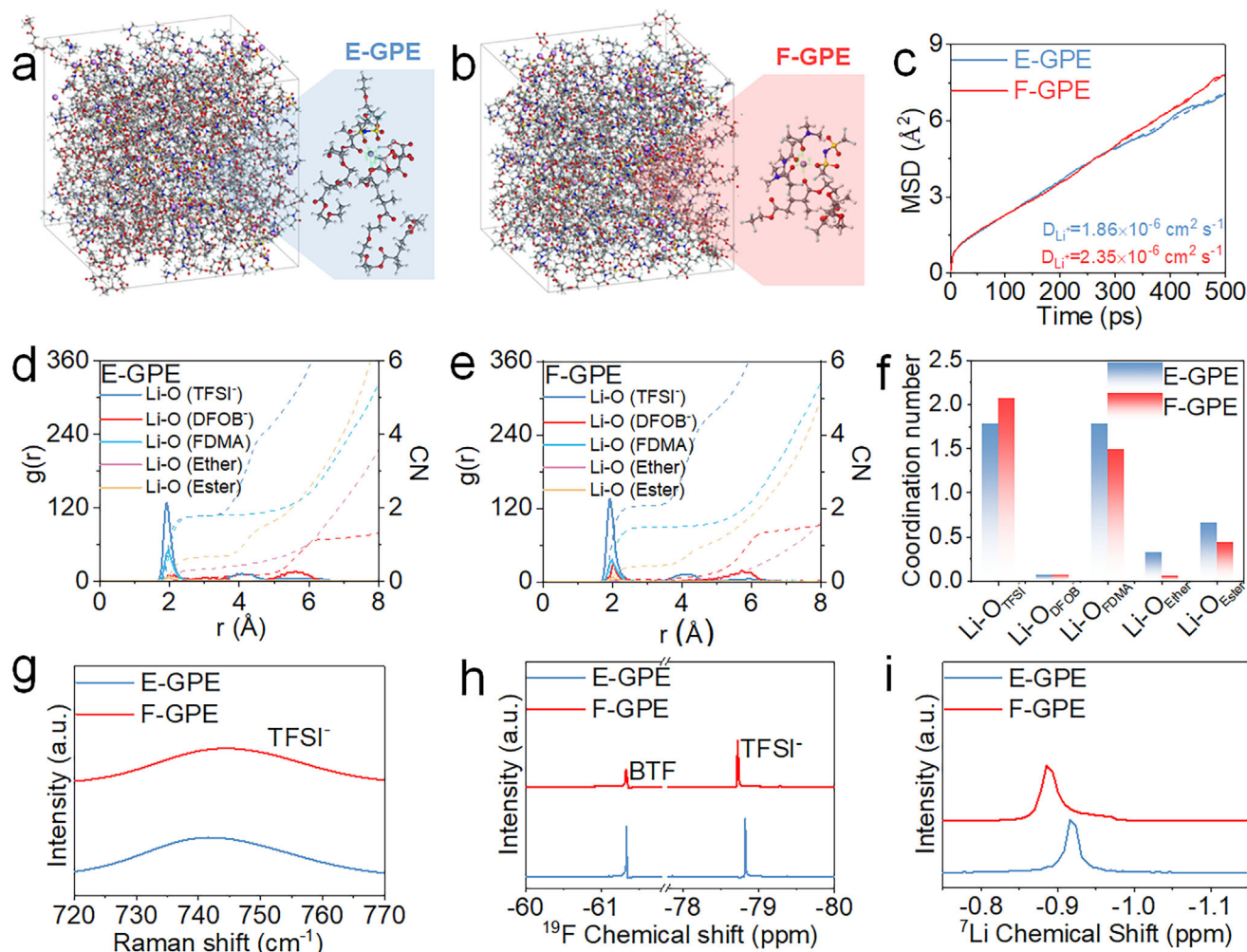


FIGURE 2 | (a,b) Snapshots and Li⁺ solvation structures of E-GPE and F-GPE during MD simulations. (c) Mean square displacements of Li⁺ for E-GPE and F-GPE over the simulation time at 30°C. (d,e) Radial distribution functions and coordination numbers for E-GPE and F-GPE. (f) Coordination numbers of Li⁺ with anions, solvents and polymer frameworks in E-GPE and F-GPE. (g) Comparison of the characteristic peaks of TFSI⁻ in Raman spectra. (h) Solution ¹⁹F NMR spectra of E-GPE and F-GPE. (i) Solution ⁷Li NMR spectra of E-GPE and F-GPE.

The cycling performance of lithium symmetric cells verifies the interfacial stability of F-GPE. At -20°C, the Li/F-GPE/Li symmetric cell exhibited stable cycling for 1000 h at 0.2 mA cm⁻² and 0.2 mAh cm⁻² with an overpotential of 150 mV, whereas the Li/E-GPE/Li symmetric cell short-circuited after only 600 h (Figure 3c). After 600 h of cycling at -20°C, scanning electron microscopy (SEM) characterization displayed that the lithium metal surface in the E-GPE system exhibited distinct mossy lithium dendrites, whereas that in the F-GPE system was relatively smooth and dense (Figure S18). At 30°C, the Li/F-GPE/Li coin cell stably cycled for over 2000 h with a polarization overpotential of approximately 50 mV, while the Li/E-GPE/Li symmetric cell failed after 1000 h (Figure S19). These results indicate that the weak Li⁺ coordination environment of F-GPE improves the reversibility of Li⁺ plating and stripping at different temperatures [33, 37].

At -20°C, the Li/F-GPE/LiCoO₂ coin cell retained 88.7% of its initial capacity after 400 cycles, whereas the Li/E-GPE/LiCoO₂ coin cell decayed to 50.7% after 200 cycles (Figure 3d). The F-GPE system exhibited a more stable voltage profile during cycling than

the E-GPE system (Figure S20). At -20°C, rate capability tests showed that the F-GPE system delivered higher specific discharge capacity and lower polarization voltage at various rates (Figure 3e and Figure S21). The superior low-temperature performance of F-GPE is attributed to the reduced desolvation energy barrier resulting from its weak Li⁺ coordination environment [16]. Compared with other recently reported GPEs [16, 29, 40–43], a radar chart demonstrates that F-GPE exhibits distinct advantages in high-voltage stability, low-temperature rate capability, and low-temperature cycling performance (Figure 3f).

The cycling and rate performance of Li/F-GPE/LiCoO₂ coin cells at 30°C were further characterized to evaluate the universality of this strategy under conventional operating conditions. After 500 cycles at 30°C, the Li/F-GPE/LiCoO₂ coin cell retained 97.3% of its initial capacity, whereas the Li/E-GPE/LiCoO₂ coin cell retained only 74.9% (Figure S22a). The F-GPE system exhibited a lower polarization voltage during cycling than the E-GPE system (Figure S22b,c). This difference is attributed to the higher oxidative stability of F-GPE, which suppresses continuous parasitic reactions at the cathode interface under high voltage. Cyclic

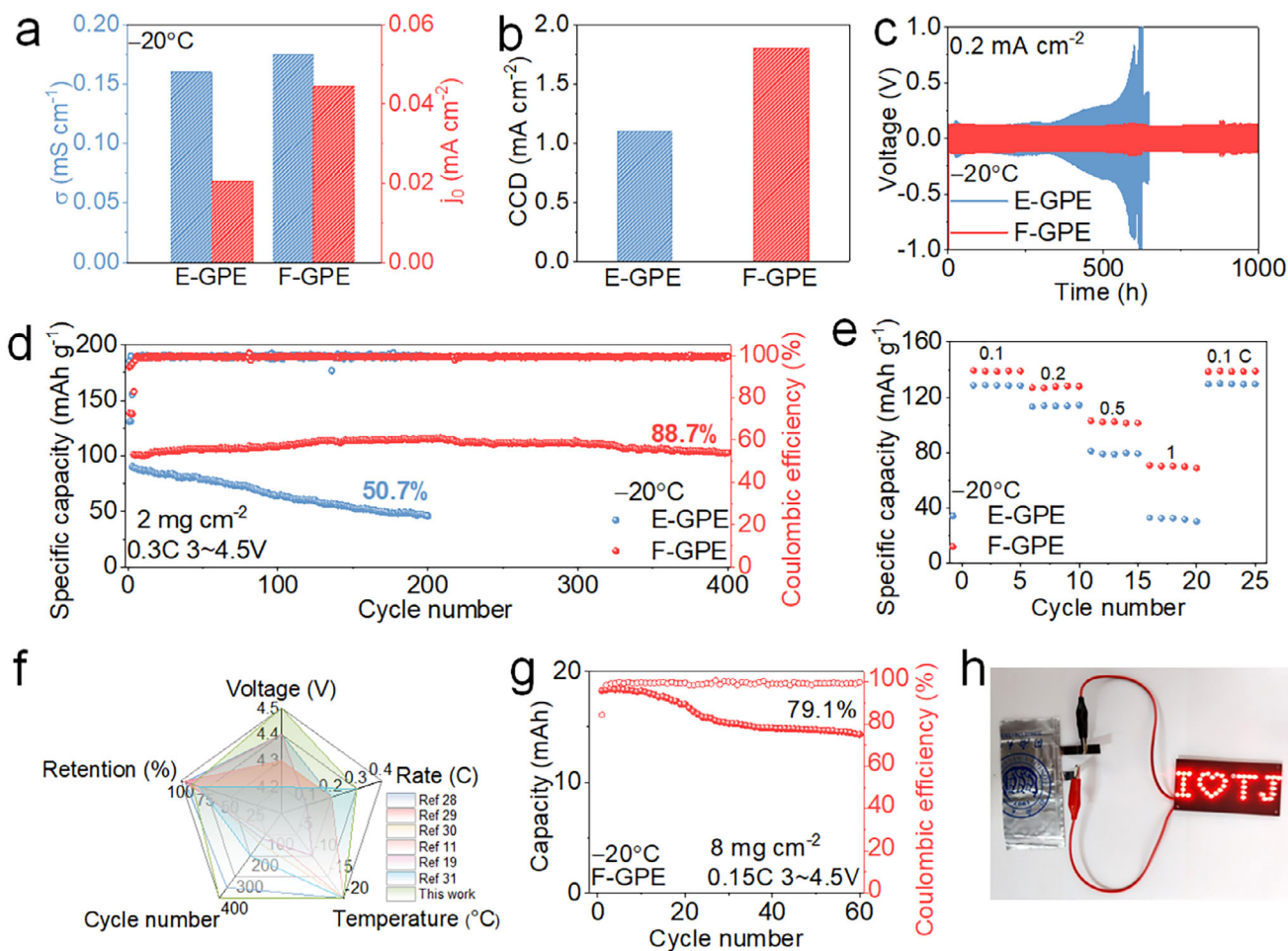


FIGURE 3 | (a) Li⁺ conductivity and exchange current density of E-GPE and F-GPE at -20°C. (b) CCD of E-GPE and F-GPE. (c) Galvanostatic cycling performance of Li/Li coin cells at -20°C under 0.2 mA cm⁻² and 0.2 mAh cm⁻². (d) Cycling performance of Li/LiCoO₂ coin cells at -20°C. (e) Rate capability of Li/LiCoO₂ coin cells at -20°C. (f) Radar chart comparing the electrochemical performance of Li/LiCoO₂ cells based on different GPEs from this work and the literature at low temperatures. (g) Cycling performance of Li/F-GPE/LiCoO₂ pouch cells at -20°C. (h) Shear damage test of the Li/F-GPE/LiCoO₂ pouch cell.

voltammetry (CV) curves showed that the Li/F-GPE/LiCoO₂ coin cell exhibited a high degree of overlap during cycling, whereas the CV curves of the Li/E-GPE/LiCoO₂ coin cell shifted distinctly (Figure S23), agreeing with the cycling performance results and confirming the advantage of F-GPE in stabilizing the electrode/electrolyte interface. At 30°C, the Li/F-GPE/LiCoO₂ and Li/E-GPE/LiCoO₂ coin cells delivered specific discharge capacities of 130 and 115 mAh g⁻¹ at 4C, respectively, with the former exhibiting a lower polarization voltage (Figures S24 and S25), confirming the advantage of F-GPE in improving Li⁺ transport kinetics.

To verify the feasibility of F-GPE in practical applications, Li/F-GPE/LiCoO₂ pouch cells were assembled and evaluated. At 0.15C, the pouch cell delivered a discharge capacity of approximately 25 mAh at 30°C and 18 mAh at -20°C. After 60 cycles, the pouch cell achieved capacity retentions of 80.6% at 30°C and 79.1% at -20°C, with negligible fluctuation in polarization voltage during cycling, demonstrating excellent wide-temperature adaptability (Figure 3g, Figures S26 and S27). In safety tests, the pouch cell was able to continuously power an LED after shear damage (Figure 3h), confirming its safety performance.

2.4 | Interfacial Lithium Deposition Behavior and SEI Characterization

To reveal the mechanism by which F-GPE suppresses lithium dendrite growth, finite element simulations were employed to model the Li⁺ concentration distribution at the lithium anode interface and the morphological evolution of lithium deposition in the two electrolyte systems. At 30°C, the E-GPE system exhibited a pronounced Li⁺ concentration gradient at the interface (Figure 4a), whereas the F-GPE system showed a relatively uniform Li⁺ concentration distribution (Figure 4b). At -20°C, the Li⁺ concentration inhomogeneity intensified with increasing deposition time in the E-GPE system (Figure S29a), while the F-GPE system maintained a relatively uniform concentration distribution (Figure S29b). In the E-GPE system, small protrusions on the lithium anode surface triggered a tip effect at -20°C, inducing rapid dendrite growth (Figure S29c). At 30°C, although the growth rate of lithium dendrites slowed down, the lithium deposition interface remained uneven (Figure S28a). In contrast, owing to the uniform Li⁺ concentration distribution at the interface, the F-GPE system enabled uniform Li⁺ deposition over a wide temperature range without obvious dendrite

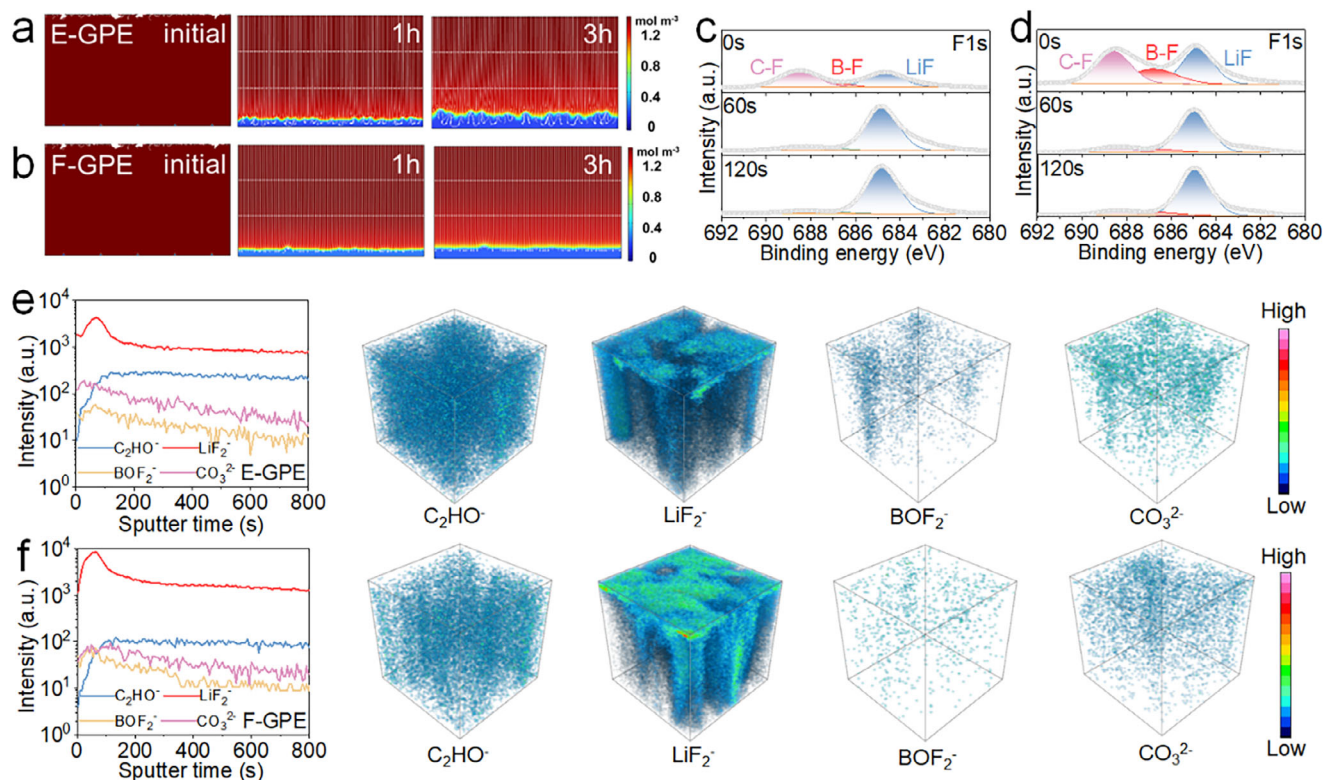


FIGURE 4 | (a,b) Finite element simulation results of Li^+ concentration distribution at the lithium metal interface in E-GPE and F-GPE systems at 30°C . (c,d) F 1s spectra of the SEI formed on lithium metal anodes after 200 cycles in E-GPE and F-GPE systems, respectively. (e,f) Depth sputtering profiles and 3D views of secondary ions in the SEI formed on the lithium metal anode in the E-GPE and F-GPE system after 200 cycles, respectively.

formation (Figures S28b and S29d). The above difference originates from the electronic effects of the two polymer side chains. In E-GPE, the electron-donating ether oxygen side chains slow down the Li^+ desolvation kinetics, and low temperatures further aggravate the Li^+ transport resistance [5, 44]. In F-GPE, the electron-withdrawing $-\text{CF}_3$ side chains increase the Li^+ transference number and improve the desolvation kinetics, thereby alleviating concentration polarization and consequently suppressing dendrite growth [15, 16].

The chemical composition and spatial distribution of the SEI directly affect the interfacial transport behavior of Li^+ and the cycling stability of LMBs. To elucidate the mechanism by which side-chain electronic effects influence the interfacial chemistry, the lithium anodes in Li/E-GPE/Li and Li/F-GPE/Li cells after 200 cycles at 30°C were characterized by x-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS). XPS depth profiling showed that the peak intensities of C—O (286.5 eV), C=O (288.0 eV), and Li_2CO_3 (290.0 eV) in the C 1s spectrum of the E-GPE system were higher than those in the F-GPE system (Figure S30), indicating severe oxidative decomposition of the polymer framework in the E-GPE system [39, 45]. The reduced intensities of these oxygen-containing component peaks in the F-GPE system demonstrated its superior interfacial chemical stability. In the F 1s spectra (Figure 4c,d), the LiF peak (685.0 eV) in the F-GPE system gradually intensified with increasing etching depth, indicating the formation of uniformly distributed LiF within the SEI, which is attributed to the weak Li^+ coordination environment that promotes preferential decomposition of anions [18]. A distinct

C—F signal (688.0 eV) was also detected on the surface of the SEI in the F-GPE system at the initial etching stage, suggesting the presence of residual fluorinated polymer fragments on the lithium metal surface (Figure 4d) [26]. The B 1s spectra showed that the Li—B—O peak intensity (~ 192.0 eV) changed little during etching in both systems, indicating that the spatial distribution of the $\text{Li}_x\text{BO}_y\text{F}_z$ component in the SEI was relatively uniform (Figure S31) [39, 45]. This is attributed to the low LUMO energy level of LiDFOB, which promotes its reductive decomposition on the lithium metal surface (Figure 1b) [26]. Quantitative analysis of the elemental content in the SEI during sputtering further verifies the aforementioned compositional differences (Figure S32). Compared with the E-GPE system, the SEI induced by the F-GPE system exhibits a higher relative content of fluorine and a lower relative content of oxygen, demonstrating that the F-GPE system promotes the formation of an SEI with a higher proportion of LiF and a lower proportion of oxygen-containing organic species.

TOF-SIMS analysis revealed that the signals of C_2HO^- and LiF_2^- fragments initially increased and then stabilized with sputtering time, whereas the BOF_2^- and CO_3^{2-} signals showed minor fluctuations, consistent with the XPS results (Figure 4e,f). In the F-GPE system, the LiF_2^- and BOF_2^- signals were higher than those in the E-GPE system, while the C_2HO^- and CO_3^{2-} signals were weaker, indicating that the F-GPE-induced SEI was enriched in LiF and $\text{Li}_x\text{BO}_y\text{F}_z$ with fewer organic decomposition products. The SEI induced by F-GPE exhibited a gradient distribution with a LiF-rich inner layer. This LiF-rich layer possesses a high Young's modulus and excellent electronic insulation [46–48].

These properties suppress lithium dendrite growth, homogenize interfacial Li^+ flux, and inhibit side reactions. These interfacial chemical characteristics originate from the weak Li^+ coordination environment, which promotes preferential anion decomposition to form LiF while suppressing oxidative decomposition of the polymer framework.

2.5 | Characterization of the CEI and Lithiation Kinetics of LiCoO_2

The chemical composition and microstructure of the CEI directly affect the intercalation and deintercalation behavior of Li^+ within cathode particles and the structural stability of the cathode, which are critical for determining the cycling life and low-temperature adaptability of high-voltage LMBs [49–51]. To reveal the mechanism by which side-chain electronic effects influence the cathode interface, the morphology and interfacial composition of LiCoO_2 cathodes in the F-GPE system were characterized and compared with those in the E-GPE system.

Morphological characterization after cycling revealed a pronounced difference between the two systems in preserving cathode structural integrity. After cycling at 30°C , the LiCoO_2 particles in the E-GPE system exhibited a few microcracks, whereas those in the F-GPE system remained intact with smooth surfaces and no obvious cracks (Figure 5a,b). At -20°C , this difference became more prominent, with clear cracks in the E-GPE system while the particles in the F-GPE system remained structurally intact (Figure S33), indicating that F-GPE effectively protects the cathode and suppresses mechanical degradation under room-temperature and low-temperature conditions. Transmission electron microscopy (TEM) further elucidated the microstructural characteristics of the CEI layer. After 500 cycles at 30°C , the CEI layer in the E-GPE system was rough and uneven, ranging from 1.1 to 11.4 nm, with a significantly larger standard deviation compared with that of the F-GPE system. In contrast, the CEI formed in the F-GPE system was uniform and dense with a thickness of 3.8 nm (Figure 5c,d). After 200 cycles at -20°C , the CEI formed in the E-GPE system exhibited an uneven thickness distribution, with the thickness varying from 2.8 to 13.5 nm, indicating aggravated interfacial degradation under low temperature. Meanwhile, the CEI in the F-GPE system remained uniform with a thickness of approximately 4.5 nm (Figure S34). This thin and uniform CEI layer facilitates rapid Li^+ transport, isolates the cathode from direct electrolyte contact, and alleviates mechanical stress during cycling, thereby suppressing cracking of the LiCoO_2 particles [52–54].

To elucidate the mechanism underlying the good Li^+ intercalation and deintercalation kinetics of the LiCoO_2 cathode in the F-GPE system, finite element analysis (FEA) was employed to simulate Li^+ diffusion within the cathode particles and the influence of the CEI layer on Li^+ transport kinetics. Simulations of Li^+ concentration distribution show that in the E-GPE system, the Li^+ concentration decreased from the surface to the interior with increasing lithiation depth, indicating sluggish Li^+ transport kinetics (Figure 5e) [8, 55]. In contrast, the F-GPE system displayed a more uniform Li^+ concentration distribution with a reduced concentration gradient, indicating improved Li^+ diffusion kinetics (Figure 5f) [8, 55, 56]. The lithiation state curves

of the E-GPE system exhibited substantial fluctuations, indicating that the inhomogeneous CEI induced local high current densities and large variations in lithiation degree. The F-GPE system showed smoother curves with smaller differences in lithiation degree among different regions, demonstrating that the uniform CEI layer enabled a homogeneous Li^+ flux distribution on the cathode surface (Figure S35).

XPS analysis was performed to characterize the chemical composition of the CEI on the cathode after 100 cycles at 30°C . In the C 1s spectra, the peak intensities of C–O (286.5 eV), C=O (288.8 eV), and Li_2CO_3 (289.8 eV) in the E-GPE system were higher than those in the F-GPE system (Figure 5g,h), indicating that the polymer framework in E-GPE underwent oxidative decomposition under high voltage, generating oxygen-containing organic species and Li_2CO_3 [39, 45]. The F-GPE system reduced the content of organic decomposition byproducts within the CEI, which is ascribed to the electron-withdrawing effect of the trifluoromethyl side chains that suppresses decomposition of the polymer framework. In the F 1s spectra (Figure 5i,j), the LiF peak (685.0 eV) intensity in F-GPE was higher than that in E-GPE and increased with etching depth, indicating that the weak Li^+ coordination environment promotes preferential decomposition of anions and generates a LiF -rich CEI [18]. The B 1s spectra showed that the spatial distribution of $\text{Li}_x\text{BO}_y\text{F}_z$ (192.0 eV) was relatively uniform in both systems (Figure S36), which is attributed to the high HOMO energy level (-7.325 eV) of LiDFOB that facilitates its oxidative decomposition on the LiCoO_2 cathode surface [26]. Quantitative analysis of the elemental content in the CEI further confirms the compositional differences (Figure S37). Compared with the E-GPE system, the F-GPE system exhibits a higher proportion of fluorine and a lower proportion of oxygen, indicating the formation of a CEI enriched in LiF with reduced amounts of oxygen-containing organic species. Such a LiF -rich CEI layer possesses higher mechanical strength and electrochemical stability, which serves to preserve the structural integrity of cathode materials and mitigate performance degradation during high-voltage cycling.

In summary, the F-GPE and E-GPE systems exhibit distinct interfacial chemical characteristics at the cathode and anode. At the cathode, the CEI formed in the E-GPE system is rich in organic species and unevenly distributed, indicating poor high-voltage stability. In contrast, the F-GPE system constructs a thin, uniform, and LiF -rich CEI with higher mechanical strength and oxidative stability, thereby preserving cathode structural integrity and suppressing side reactions and performance degradation (Figure 5k). At the lithium metal anode, the E-GPE system exhibits non-uniform lithium deposition with dendrite formation and an unstable SEI rich in organic components. The F-GPE system constructs a dense LiF -rich SEI, which facilitates uniform Li^+ deposition. These differences originate from the distinct Li^+ solvation sheaths in the two systems. In E-GPE, the ether oxygen side chains strengthen the coordination between the polymer framework and Li^+ , promoting more FDMA to enter the solvation sheath. This induces a higher Li^+ desolvation energy barrier, uneven interfacial ion distribution, and dendrite growth. In F-GPE, the trifluoromethyl side chains weaken the coordination between the polymer framework and Li^+ , facilitating more anions to enter the solvation sheath [33, 37]. This effectively reduces the Li^+ desolvation energy barrier and achieves fast Li^+ desolvation.

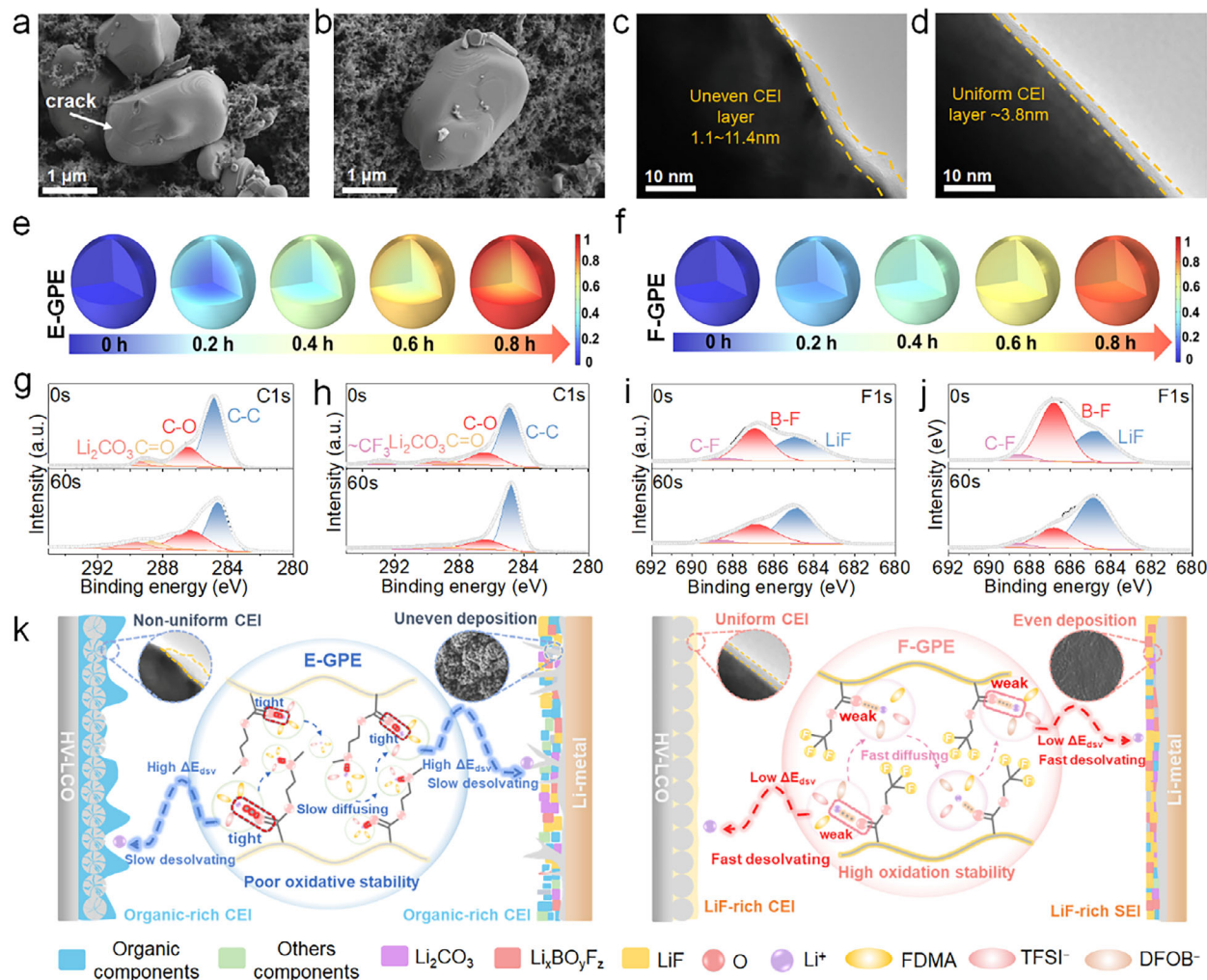


FIGURE 5 | (a,b) SEM images of LiCoO₂ cathode particles after 500 cycles in the E-GPE and F-GPE systems at 30°C, respectively. (c,d) TEM images of LiCoO₂ cathode particles after 500 cycles in the E-GPE and F-GPE systems at 30°C, respectively. (e,f) Finite element analysis simulations of Li⁺ concentration distribution within LiCoO₂ cathode particles during charging in the E-GPE and F-GPE systems, respectively. (g,h) C1s and F1s spectra of the CEI formed on LiCoO₂ cathode after 100 cycles in the E-GPE system. (i,j) C1s and F1s spectra of the CEI formed on LiCoO₂ cathode after 100 cycles in the F-GPE system. (k) Schematic diagrams of the cathode and anode interface structures and the Li⁺ solvation structures in the E-GPE and F-GPE systems.

3 | Conclusions

In summary, this work constructs E-GPE and F-GPE by comparing the electronic effects of polymer side-chains and incorporating FDMA as a low-temperature additive. Compared with the strong electron-donating ether oxygen side chains in E-GPE, the strong electron-withdrawing trifluoromethyl side chains in F-GPE reduce the electronic density of the polymer framework, creating a weak Li⁺ coordination environment that weakens the polymer-Li⁺ interaction and accelerates Li⁺ desolvation kinetics. This weak coordination environment promotes more anions to enter the solvation sheath and facilitates their decomposition on the electrode surface, forming LiF-rich SEI and CEI layers on the Li metal anode and LiCoO₂ cathode, which effectively suppress interfacial side reactions and lithium dendrite growth. Consequently, the Li/F-GPE/Li symmetric cell stably cycles for over 2000 h at 30°C and over 1000 h at -20°C. The Li/F-GPE/LiCoO₂ coin cell achieves a capacity retention of 97.3% after 500 cycles at 30°C and retains 88.7% after 400 cycles at -20°C,

respectively, demonstrating favorable cycling performance across a wide temperature range. Furthermore, the Li/F-GPE/LiCoO₂ pouch cell stably powers an LED after shearing, confirming its safety. This work not only provides a high-performance GPE for LMBs operating under extreme conditions, but also systematically compares the electronic effects of electron-donating and electron-withdrawing side chains, thereby establishing structure-performance relationships that span from molecular structure to solvation structure, interfacial chemistry, and macroscopic performance, and thus pioneering a new pathway for developing GPEs with wide-temperature adaptability and high safety.

Author Contributions

Xianbin Wu: data curation, investigation, validation, Writing – original draft, formal analysis. **Zhenxiang Zhu:** writing – review and editing, methodology, investigation, writing – original draft, data curation,

formal analysis, software. **Haotian Yang**: investigation, validation, data curation. **Dayao Zhang**: investigation, validation. **Zhen Geng**: conceptualization, writing – original draft, writing – review and editing, project administration, supervision. **Cunman Zhang**: writing – review and editing, project administration, supervision. **Mingzhe Xue**: writing – review and editing, project administration, supervision, funding acquisition, conceptualization. **Jian Wang**: conceptualization, investigation, writing – original draft, writing – review and editing, supervision.

Acknowledgments

This work is supported by National Natural Science Foundation of China (Grant No. 22479114), Open Project of Inner Mongolia Engineering Research Center of Lithium-Sulfur Battery Energy Storage (No. MDK2025071), Opening funding from Key Laboratory of Engineering Dielectrics and Its Application (No. KFM202507). Dr. Jian Wang also thanks the funding support by Alexander von Humboldt Foundation.

Open access funding enabled and organized by Projekt DEAL.

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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