

Siloxy-Functionalized Gel Polymer Electrolyte for High-Temperature Stable Lithium-Ion Batteries

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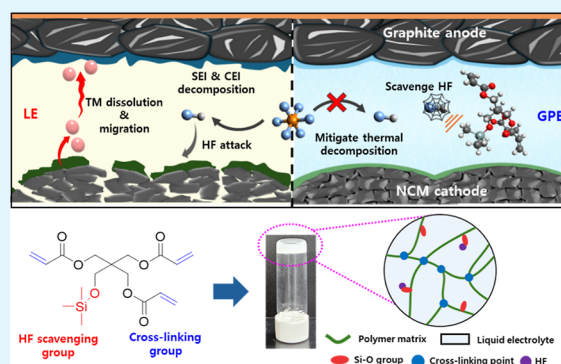
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ABSTRACT: The rapid transition toward electric vehicles and large-scale energy storage systems has intensified the demand for lithium-ion batteries (LIBs) capable of reliable operation under harsh temperature conditions. However, conventional liquid electrolytes suffer from severe degradation at elevated temperatures. Herein, we report a multifunctional gel polymer electrolyte (GPE) employing a siloxy-functionalized cross-linker, siloxy-pentaerythritol triacrylate (SiO-PETA), to enhance the high-temperature cycling stability and safety of LIBs. The trimethylsilane groups in SiO-PETA effectively scavenge corrosive HF, thereby mitigating cell degradation associated with transition metal dissolution. In addition, the chemically cross-linked polymer matrix encapsulates the liquid components in the GPE, suppressing parasitic side reactions and reducing electrolyte vaporization at elevated temperatures. A graphite/Li-Ni_{0.6}Co_{0.2}Mn_{0.2}O₂ pouch-type cell employing the GPE exhibits superior capacity retention at 70 °C, markedly outperforming a conventional liquid-electrolyte cell. Furthermore, the GPE provides enhanced safety, as evidenced by stable open-circuit voltage at 150 °C and reduced flammability. These results demonstrate that the SiO-PETA-based GPE effectively suppresses electrolyte and electrode degradation, enabling stable LIB operation at high temperatures.

KEYWORDS: gel polymer electrolyte, high temperature operation, lithium-ion batteries, siloxy-functionalized cross-linker, HF scavenging, thermal safety and stability



INTRODUCTION

The rapid expansion of the lithium-ion battery (LIB) market has shifted its primary applications from portable electronics to large-scale systems, including electric vehicles and grid-level energy storage.^{1,2} These applications require not only high energy density but also long-term reliability and safety under a wide range of operating conditions.^{3,4} Among these, stable operation at elevated temperatures has become a critical requirement, since large-format battery packs are frequently exposed to harsh thermal environments, such as hot climates, fast-charging conditions, and high-rate discharging, all of which generate significant internal heat and can accelerate cell degradation.^{5,6} Although active thermal management systems are commonly employed to control cell temperature, they increase system complexity, consume additional energy, and reduce overall efficiency. Therefore, minimizing reliance on external cooling is essential for next-generation battery systems. This challenge highlights the urgent need for advanced electrolytes that can maintain electrochemical and thermal stability, suppress degradation reactions, and ensure safe operation under elevated-temperature conditions.⁷

However, conventional LIBs employing liquid electrolytes suffer from severe chemical and physical degradation at elevated temperatures. The thermal instability of LiPF₆-based

electrolytes leads to the formation of hydrofluoric acid (HF), which triggers a series of parasitic reactions within the cell.^{8,9} In high energy density batteries using LiNi_xCo_yMn_zO₂ (NCM) cathodes, HF accelerates transition metal dissolution and promotes structural degradation of the cathode active materials, resulting in rapid capacity fading.^{10,11} In addition, the high vapor pressure of organic carbonate solvents at elevated temperatures causes electrolyte volatilization and gas generation, leading to pouch swelling. This swelling deteriorates interfacial contact between cell components, increases internal resistance, and ultimately results in premature cell failure.^{12,13}

To address these challenges, various strategies have been explored. Solid electrolytes have attracted considerable attention because they can enhance battery safety and improve high-temperature tolerance. However, their practical application is still hindered by high interfacial resistance and

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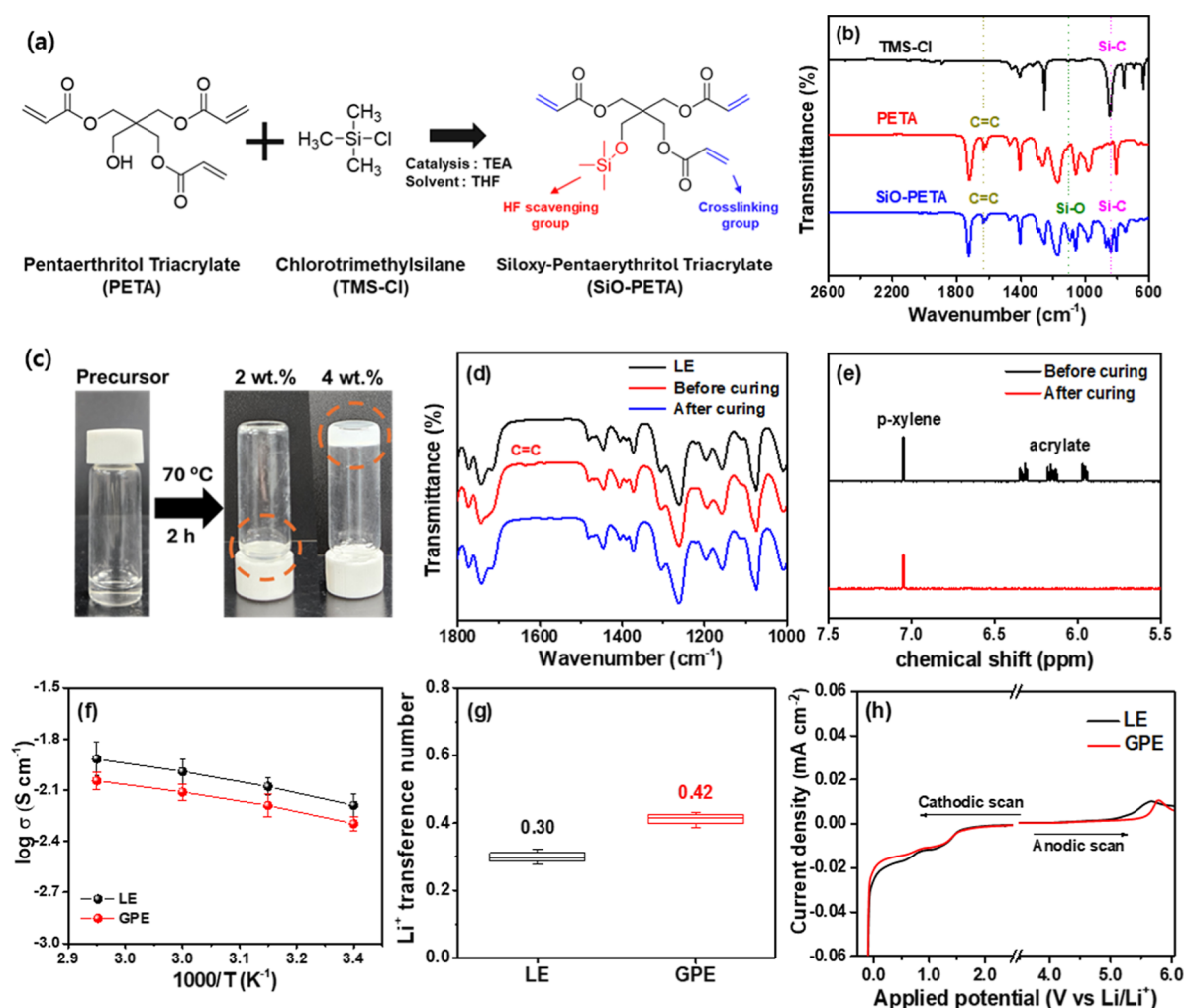


Figure 1. (a) Schematic illustration of the synthesis of SiO-PETA. (b) FT-IR spectra of the reactants (TMS-Cl and PETA) and the product (SiO-PETA). (c) Photographs of the GPE precursor and the resulting GPEs after thermal curing at 70 °C. (d) FT-IR and (e) ^1H NMR spectra of the GPE before and after thermal curing. (f) Ionic conductivities of the LE and GPE measured at different temperatures. (g) Li^+ transference numbers and (h) linear sweep voltammetry curves of the LE and GPE.

insufficient ionic conductivity at ambient temperature.^{14–16} Another approach involves the use of functional additives, such as trimethylsilyl phosphate (TMSP), which act as HF scavengers.^{17–20} Although these additives can mitigate acid-induced side reactions, they do not possess the physical capability to suppress solvent vaporization at elevated temperatures. Moreover, some silyl-based additives have been reported to generate gaseous Si–F byproducts under extreme thermal conditions, which can aggravate cell swelling.^{21,22} Gel polymer electrolytes (GPEs) have also been investigated as a safer alternative to conventional liquid electrolytes because they reduce electrolyte reactivity and improve mechanical stability. However, they still rely on liquid components and therefore cannot provide fundamental protection against chemical degradation processes, such as HF-induced corrosion and degradation.^{23–25}

In this work, we developed a multifunctional gel polymer electrolyte (GPE) based on a newly synthesized cross-linker, siloxy-pentaerythritol triacrylate (SiO-PETA). The SiO-PETA-based GPE is designed to provide dual protection: chemical stabilization through HF-scavenging trimethylsilane groups and physical stabilization by encapsulating liquid components within a chemically cross-linked polymer network.^{26,27} We

systematically investigated the interfacial chemistry and structural integrity of the electrodes using surface characterization techniques. Electrochemical evaluations revealed that the SiO-PETA-based GPE significantly enhances the cycling stability of graphite/ $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NCM) cells at both 55 and 70 °C compared with cells employing a conventional liquid electrolyte containing the TMSP additive. Notably, practical pouch-type cells incorporating the GPE exhibited stable operation at 70 °C even without external mechanical pressure, a condition under which liquid electrolyte-based cells typically fail due to electrolyte vaporization and loss of interfacial contact. Combined with improved thermal and mechanical stability, these results demonstrate that the SiO-PETA-based GPE provides a robust and practical platform for next-generation LIBs requiring reliable performance and enhanced safety under extreme thermal conditions.

EXPERIMENTAL SECTION

Materials

Pentaerythritol triacrylate (PETA) was purchased from Alfa Aesar and purified by column chromatography prior to use. Chlorotrimethylsilane (TMS-Cl), trimethylsilyl phosphate (TMSP), triethylamine (TEA), and tetrahydrofuran (THF) were purchased from TCI and

used as received. Azobis(isobutyronitrile) (AIBN, Junsei Chemical Co.) was employed as a thermal initiator. The liquid electrolyte (LE) consisted of 1.15 M lithium hexafluorophosphate (LiPF₆) dissolved in a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) (EC/EMC/DEC = 3:5:2 by volume), containing 5 wt-% fluoroethylene carbonate (FEC), and was supplied from Donghwa Electrolyte Co., Ltd.

Synthesis of SiO-PETA

SiO-PETA was synthesized via a silylation reaction between the hydroxyl groups of PETA and the chlorine atom of TMS-Cl, as illustrated in Figure 1a. PETA (4.2 mmol) and TMS-Cl (6.5 mmol) were reacted with TEA (1.0 g) in THF (15 mL) under an Ar atmosphere. The reaction was carried out at 25 °C for 24 h. After completion, the mixture was filtered to remove the TEA·HCl salt. The product was purified by repeated washing with deionized water and extraction with dichloromethane, followed by drying with a rotary evaporator and further dehydrated using a 4 Å molecular sieve. The yield of SiO-PETA was approximately 71%.

Cell Assembly

The cathode was prepared by casting a slurry composed of LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ (Umicore), poly(vinylidene fluoride) (PVdF, Solvay) binder, and Super P carbon (95:3:2 by weight) onto an Al current collector. The anode was fabricated by casting a slurry composed of artificial graphite (BTR), PVdF, and Super P (91:8:1 by weight) onto a Cu current collector. The active mass loadings of the cathode and anode were 16.8 and 9.3 mg·cm⁻², respectively, corresponding to a calculated N/P ratio of approximately 1.1. The GPE precursor was prepared by mixing SiO-PETA with the liquid electrolyte, along with a trace amount of AIBN as a thermal initiator. Coin cells were assembled using the graphite anode, NCM cathode, and polyethylene separator (ND420, Asahi) with a thickness of 20 μm. A pouch-type cell was assembled using a double-coated cathode and two single-coated anodes, with a cathode size of 2 × 3 cm². The active materials and mass loading of the electrodes were kept consistent with those used in the coin-cell configuration to ensure a fair comparison. Based on the electrode area and mass loading, the nominal capacity of the pouch cell was approximately 35 mAh. LE or GPE precursor was injected into the cell. The cell assembled with GPE precursor underwent thermal curing at 70 °C for 2 h, resulting in chemical cross-linking and formation of the GPE.

Electrochemical Measurements

The ionic conductivities of the electrolytes were measured using an AC impedance analyzer (CHI 660d, CH Instruments). Linear sweep voltammetry was performed to evaluate the electrochemical stability of the electrolytes. The cycling performance of the cells was evaluated using a battery tester (WBCS3000, WonATech) within a voltage range of 2.5–4.2 V at 25, 55, and 70 °C. All cells were recycled at 0.1 C for two cycles at 25 °C, followed by cycling at 1.0 C at the designated temperatures. Electrochemical impedance spectroscopy (EIS) of the cells during cycling at 70 °C was conducted at the charged state over a frequency range of 0.001 Hz to 1 MHz with an amplitude of 5 mV.

Characterization

Density functional theory (DFT) calculations were conducted to determine the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the electrolyte components. Calculations were carried out using the Gaussian 16 package, employing the Becke three-parameter hybrid functional combined with the Lee–Yang–Parr correlation functional (B3LYP). Geometry optimizations and vibrational frequency analyses were performed at the 6–311++G(d,p) level. FT-IR spectra were recorded in the range of 400–4000 cm⁻¹ using a Nicolet iS50 spectrometer. ¹H and ¹³C NMR spectra were obtained using a VNMRs 600 MHz NMR spectrometer (Varian) with chloroform-d as the solvent to confirm the chemical structure of SiO-PETA. ¹⁹F NMR spectra were recorded in tetrahydrofuran-d₈ using a coaxial NMR tube to examine HF generation in the electrolytes. Liquid chromatography–mass

spectrometry (LC–MS) was performed using an Agilent 6545XT AdvanceBio system (Agilent Technologies). Transition metal dissolution was analyzed by inductively coupled plasma mass spectrometry (ICP–MS; iCAP RQ, Thermo Fisher Scientific). Field-emission scanning electron microscopy (FE-SEM; Verios C4UC, FEI) and high-resolution transmission electron microscopy (HR-TEM; JEOL 2100F) were used to examine the micro-morphology of the cathodes and anodes. The surface chemical compositions of the electrodes were characterized using X-ray photoelectron spectroscopy (XPS; Thermo Fisher) and time-of-flight secondary-ion mass spectrometry (TOF-SIMS; ION-TOF).

RESULTS AND DISCUSSION

The chemical structure of SiO-PETA was characterized using FT-IR, ¹H NMR, and ¹³C NMR spectroscopy. In the FT-IR spectrum shown in Figure 1b, the characteristic peaks corresponding to Si–O, Si–C, and C=C bonds in SiO-PETA are observed at 1100, 840, and 1640 cm⁻¹, respectively.²⁸ The ¹H and ¹³C NMR spectra of the reactants and the product are presented in Figure S1. As shown in Figure S1a, the proton signal corresponding to the trimethylsilane group in TMS-Cl appears at approximately 0.4 ppm, whereas this signal shifts to 0.06 ppm in SiO-PETA. In addition, the peaks associated with the hydroxyl groups in PETA (CH₂–OH at 3.55 ppm and –OH at 2.8 ppm) shift (CH₂–O–Si at 3.6 ppm) or disappear in the SiO-PETA, indicating successful silylation. The ¹³C NMR spectrum in Figure S1b further confirms the formation of Si–C bonds, along with the disappearance of carbon signals associated with C–OH groups in PETA. In Figure S1c, the LC–MS spectrum shows a protonated molecular ion peak for SiO-PETA ([M + H]⁺) at *m/z* = 371.2, which is consistent with its theoretical molecular weight of 370.2. These results collectively confirm the successful synthesis of SiO-PETA. To further verify the HF-scavenging ability of the synthesized cross-linker, DFT calculations were performed to evaluate the thermodynamic feasibility of the reaction between SiO-PETA and HF. The Gibbs free energy change (Δ*G*) was calculated as the difference between the total Gibbs free energies of the products and reactants, and the calculated Δ*G* value was –76.4 kcal·mol⁻¹ (Figure S2), indicating that the HF-scavenging reaction is highly spontaneous. Figure 1c shows photographic images of the prepared GPEs containing different amounts of SiO-PETA. After thermal curing of the precursor for 2 h, a nonfluidic GPE was formed from 4 wt-% SiO-PETA, whereas 2 wt-% was insufficient to form a stable GPE. The FT-IR spectra in Figure 1d (with magnified spectra shown in Figure S3) reveal the disappearance of the C=C double-bond peak around 1630 cm⁻¹, indicating the polymerization of SiO-PETA during thermal curing. To further quantify the conversion, ¹H NMR analysis was performed, and the results are presented in Figure 1e. Before thermal curing, the acrylate proton peaks of SiO-PETA in the GPE precursor are clearly observed in the range of 5.8–6.3 ppm. These peaks disappear after thermal curing, confirming the consumption of the acrylate groups. The conversion of SiO-PETA was calculated to be 99.67% by comparing the intensity of the acrylate peaks with that of the *p*-xylene internal standard.²⁹ These findings suggest that most of the SiO-PETA underwent free-radical polymerization, leading to the formation of a three-dimensional cross-linked polymer network within the GPE. The ionic conductivities of the LE and GPE were measured over a temperature range of 25–70 °C, and the results are shown in Figure 1f. At room temperature, the GPE exhibited an ionic

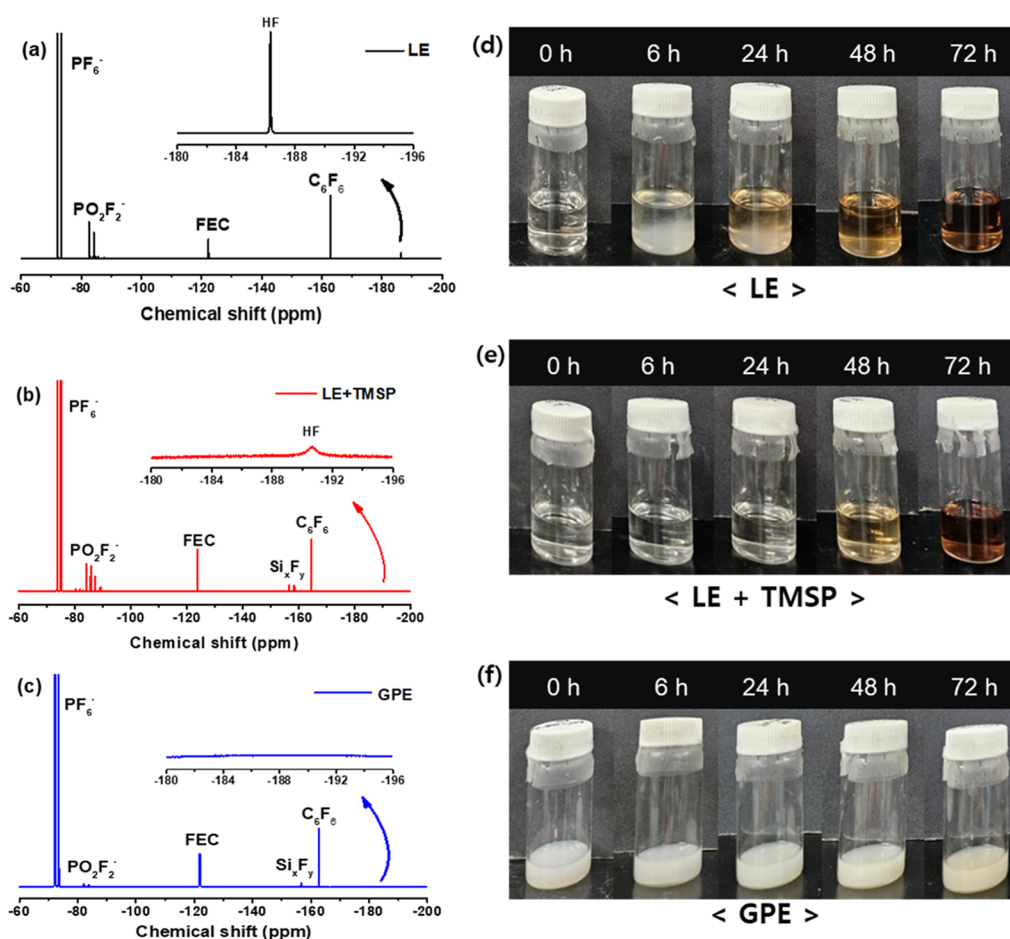


Figure 2. High-temperature storage test results for various electrolytes. ^{19}F NMR spectra of (a) LE, (b) LE + TMSP, and (c) GPE after storage at 70°C for 3 days. Optical images showing the color changes of (d) LE, (e) LE + TMSP, and (f) GPE during storage at 70°C for up to 72 h.

conductivity of $5.1\text{ mS}\cdot\text{cm}^{-1}$, while the LE showed $6.5\text{ mS}\cdot\text{cm}^{-1}$. Although the liquid electrolyte components were confined within the cross-linked polymer network, the GPE exhibited ionic conductivities comparable to those of the LE over the entire temperature range. The Li^+ transference numbers of the electrolytes were determined using the Bruce–Vincent method.³⁰ The AC impedance spectra and DC polarization curves used for the calculations are presented in Figure S4, and the resulting Li^+ transference numbers are summarized in Figure 1g. Because the cross-linked polymer network hinders anion transport, the GPE exhibits a slightly higher Li^+ transference number than the LE.^{31,32} Linear sweep voltammetry was conducted to evaluate the electrochemical stability of the electrolytes. Figure 1h presents the linear sweep voltammograms of the two electrolyte systems. In the cathodic scan, no additional peak was observed for the GPE compared with the LE, indicating that SiO-PETA does not undergo reductive side reactions at the anode. In the anodic scan, the oxidation onset of the LE occurs at approximately 4.9 V, whereas the GPE exhibits a higher onset potential of about 5.4 V, indicating improved oxidative stability. This behavior can be attributed to the confinement of the liquid electrolyte components within the cross-linked polymer network, which suppresses their oxidative decomposition. Electrochemical measurements were further conducted at 70°C to evaluate the high-temperature properties of the electrolytes (Figure S5). The Li^+ transference numbers slightly increased for both electrolytes at elevated temperature, likely due to facilitated Li^+

desolvation (0.35 for LE and 0.47 for GPE at 70°C).³³ Furthermore, the LSV results show that the oxidative stability of the LE decreased, with the onset of oxidation current appearing at around 4.5 V. In contrast, the GPE remained stable up to 5.3 V, demonstrating its superior electrochemical stability under high-temperature conditions. The HOMO and LUMO energy levels of the GPE components were determined using DFT calculations, as shown in Figure S6. SiO-PETA exhibits HOMO and LUMO levels comparable to those of the carbonate solvents in the LE, which is consistent with the linear sweep voltammetry results. In addition, the effect of SiO-PETA content on the properties of the GPE was systematically investigated. As shown in Figure S7, the mechanical strength increases progressively with increasing SiO-PETA content. The GPE containing 2 wt-% SiO-PETA remains in a fluidic state and exhibits very weak mechanical strength, whereas a mechanically stable gel is formed at contents of 4 wt-% and above. In contrast, the ionic conductivity decreases with increasing SiO-PETA content (Figure S8a). At 25°C , the GPE with 4 wt-% SiO-PETA shows an ionic conductivity of $5.1\text{ mS}\cdot\text{cm}^{-1}$, while the value significantly decreases to $1.9\text{ mS}\cdot\text{cm}^{-1}$ for the GPE with 6 wt-% SiO-PETA. Based on this trade-off between mechanical stability and ionic conductivity, 4 wt-% SiO-PETA was determined to be the optimal composition. Furthermore, the LSV results in Figure S8b reveal no additional decomposition peaks with varying composition, although the overall current value decreases gradually, which can be attributed to decreased ionic conductivity.

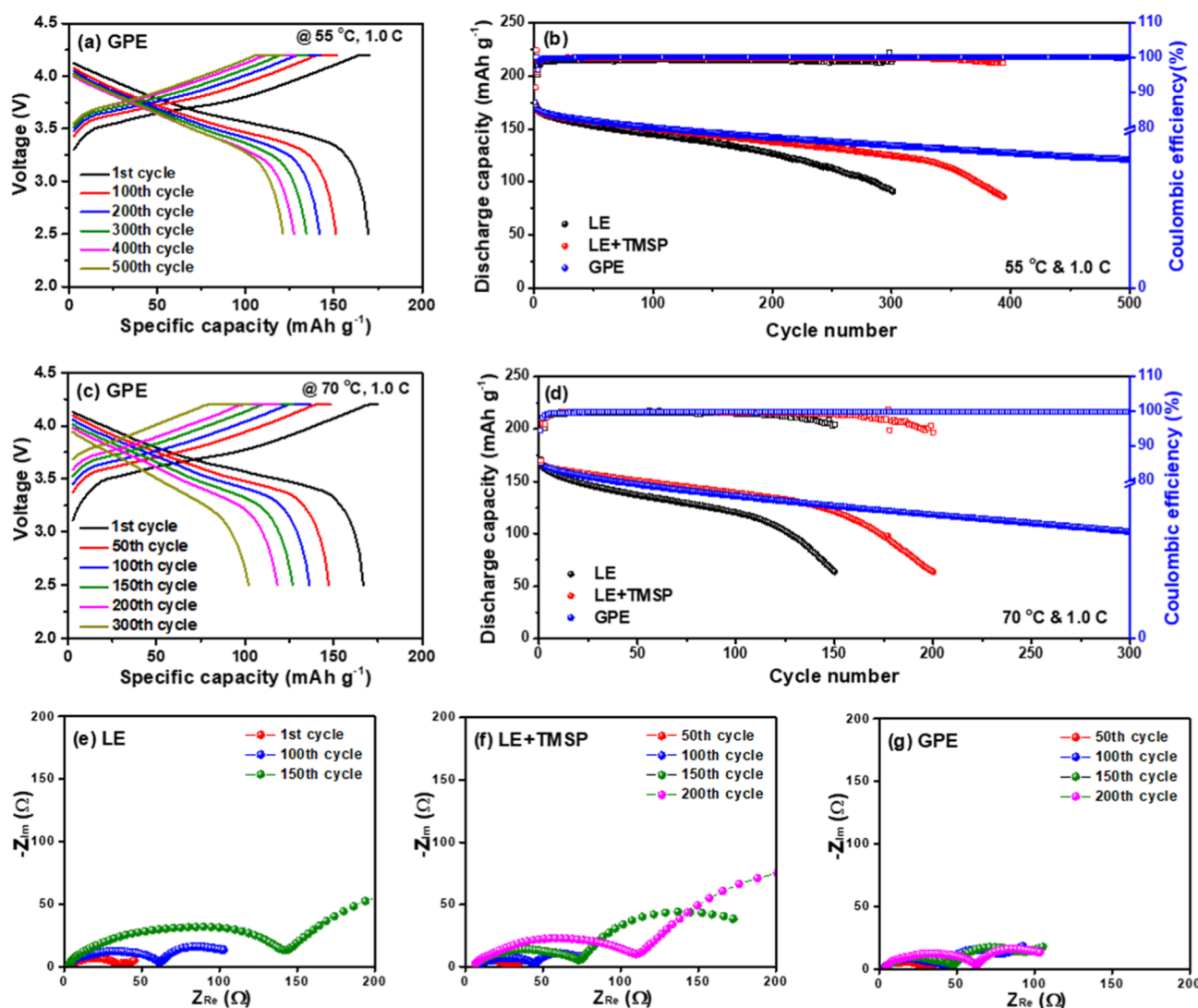


Figure 3. Voltage profiles of the GPE-based cells at (a) 55 °C and (c) 70 °C. Cycling performance of cells with different electrolytes at (b) 55 °C and (d) 70 °C. AC impedance spectra of cells with (e) LE, (f) LE + TMSP, and (g) GPE during cycling at 70 °C. Cycling was conducted at 1.0 C rate.

It is well-known that LiPF₆ undergoes thermal decomposition to form LiF and PF₅ at elevated temperatures. The generated PF₅ readily reacts with trace amounts of H₂O present in the electrolyte to produce HF. The resulting HF can attack cathode active materials and electrolyte components, thereby accelerating interfacial degradation and transition metal dissolution. To investigate the HF-scavenging ability of SiO-PETA within GPE, ¹⁹F NMR analysis was conducted using C₆F₆ as an internal standard. For comparison, a liquid electrolyte (denoted as LE + TMSP) containing 2 wt-% TMSP, a conventional HF-scavenging additive, was also tested. As shown in Figure S9, before storage at 70 °C, all electrolytes exhibited three peaks at -75.0, -122.0, and -163.9 ppm, corresponding to PF₆⁻, FEC, and C₆F₆, respectively.^{34,35} After storage at 70 °C for 3 days, a distinct HF peak appeared in the LE, as shown in Figure 2a, indicating HF generation due to the thermal decomposition of LiPF₆. In contrast, the HF peak was significantly suppressed in LE + TMSP (Figure 2b) and completely disappeared in the GPE (Figure 2c). In addition, peaks corresponding to Si_xF_y species were observed around -155 ppm, demonstrating HF scavenging by the trimethylsilyl-

lane groups.³⁶ Accordingly, the complete disappearance of the HF peak in the GPE is attributed to effective HF scavenging by SiO-PETA within the polymer matrix, which can mitigate transition metal dissolution and suppress cell performance degradation at elevated temperatures. Figures 2d–f and Figure S10 present optical images of the different electrolytes during storage at 70 °C. As the storage time increased, the LE and LE + TMSP gradually turned dark yellow, which is attributed to the thermal decomposition of liquid electrolyte containing LiPF₆.³⁷ In contrast, the GPE maintained its original white appearance for up to 72 h, indicating that HF-induced side reactions were effectively suppressed during high-temperature storage. To further evaluate the persistence of the HF-scavenging capability, the ¹⁹F NMR analysis was conducted after 10 days of storage at 70 °C (Figure S11). As shown in the figure, the intensity of the Si_xF_y peak slightly increases after prolonged storage, while the PO₂F₂⁻ peak, attributed to the decomposition of PF₆⁻, becomes more clearly observable. Nevertheless, the HF signal remains barely detectable, indicating that the GPE retains effective HF-scavenging capability even after long-term storage. These observations

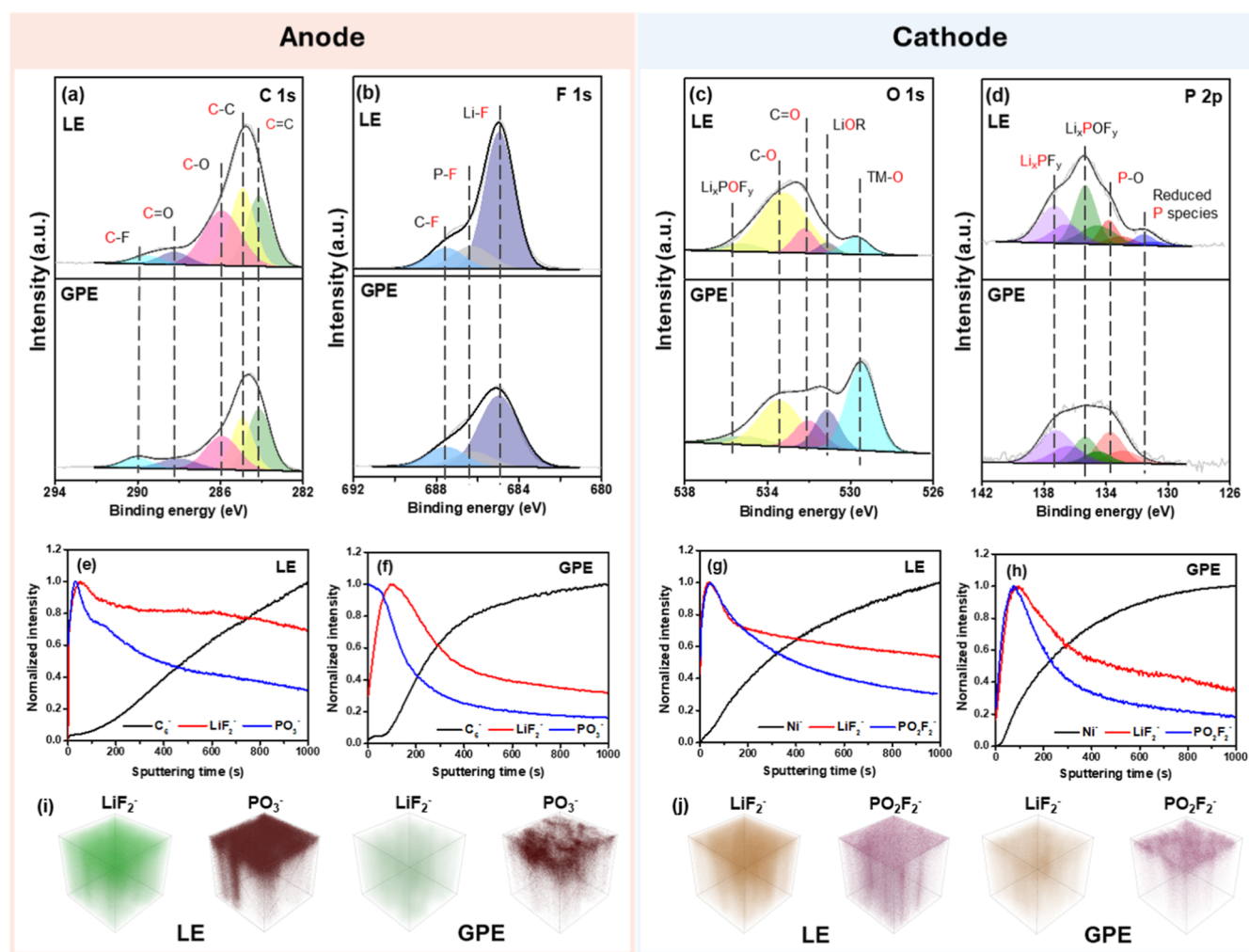


Figure 4. (a–d) XPS spectra of electrodes with different electrolytes after 100 cycles at 70 °C: (a) C 1s and (b) F 1s spectra of graphite anodes, and (c) O 1s and (d) P 2p spectra of NCM cathodes. TOF-SIMS depth profiles of (e,f) graphite anodes and (g,h) NCM cathodes. 3D reconstructed TOF-SIMS images of (i) graphite anodes and (j) NCM cathodes.

further support the superior persistence of HF capture capability in the GPE compared with other electrolyte systems.

The cycling performance of graphite/NCM cells was evaluated under various cycling conditions. The rate capability of the cells employing different electrolytes was assessed at 25 °C (Figure S12). Due to the lower ionic conductivity of the GPE, the GPE-based cell exhibited a marginally reduced discharge capacity at high C rates compared with the LE and LE + TMSP cells. Specifically, at 3.0 C rate, the LE and LE + TMSP cells showed capacity retentions of 87.1 and 86.3%, respectively, relative to their capacities at 0.2 C, while the GPE cell exhibited a lower retention (84.6%). The cycling performances of the cells with different electrolytes at 25 °C and 1.0 C rate are compared in Figure S13. Although the GPE cell showed a lower initial discharge capacity compared with the LE and LE + TMSP cells, all cells exhibited comparable capacity retention over 500 cycles. However, under high-temperature conditions, markedly different results were observed. The voltage profiles of the cell employing GPE at 55 and 70 °C are presented in Figure 3a–c, respectively. High-temperature cycling performance of the cells with different electrolytes is compared in Figure 3b,d. Unlike the room-temperature performance, the three types of cells exhibited distinctly different cycling behaviors at elevated temperatures.

As shown in Figure 3b, the GPE cell retained 71.5% of its initial capacity after 500 cycles at 55 °C, whereas the LE and LE + TMSP cells reached 60% capacity retention at the 284th and 370th cycles, respectively. When the temperature was increased to 70 °C, the LE and LE + TMSP cells exhibited rapid capacity decay, reaching 60% retention at the 141st and 175th cycles, respectively. By comparison, the GPE cell achieved a higher capacity retention of 61.2% after 300 cycles (Figure 3d), indicating that the GPE more effectively suppresses high-temperature degradation than the conventional TMSP additive. Both the LE and LE + TMSP cells exhibited a noticeable decline in Coulombic efficiency during cycling at 70 °C. Specifically, the Coulombic efficiency of the LE cell gradually decreases, falling below 95% after 149 cycles. The LE + TMSP cell exhibits a similar trend, with the Coulombic efficiency dropping below 95% after 194 cycles. In contrast, the GPE cell maintains high Coulombic efficiencies above 99.8% throughout cycling. These results clearly demonstrate that the GPE effectively suppresses parasitic side reactions, thereby ensuring superior cycling stability and high Coulombic efficiency even under harsh high-temperature conditions. To investigate resistance evolution during cycling at 70 °C, EIS analysis was performed, and the results are presented in Figures 3e–g. The spectra were fitted using the

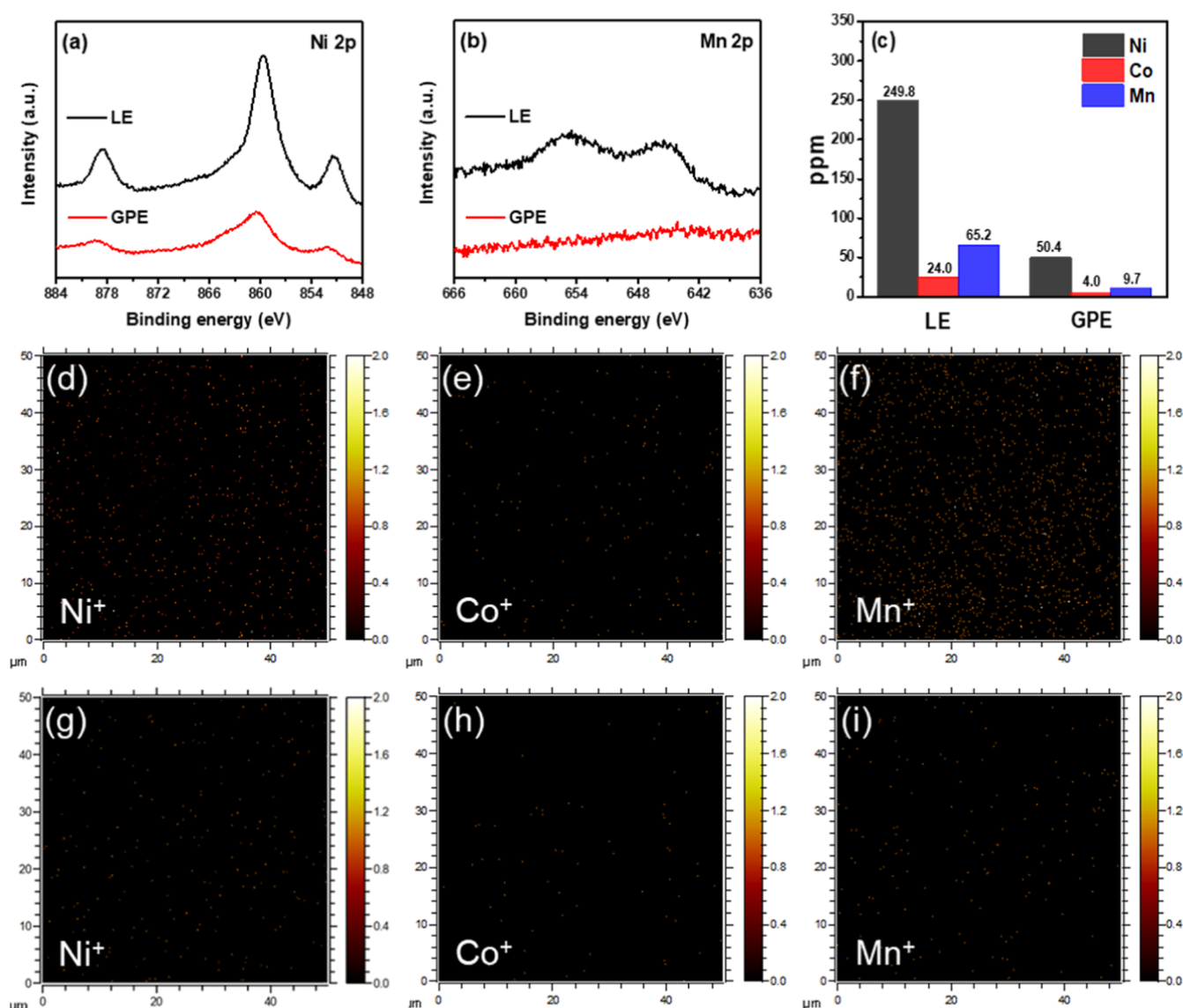


Figure 5. (a) Ni 2p and (b) Mn 2p XPS spectra of the graphite anode surfaces. (c) Concentrations of transition metals on the graphite anodes measured by ICP-MS. TOF-SIMS ion maps of Ni⁺, Co⁺, and Mn⁺ on the graphite anodes with (d–f) LE and (g–i) GPE. All graphite anodes were retrieved after the 100th cycle at 70 °C.

equivalent circuit shown in Figure S14, and the fitting results are summarized in Figure S15. At the initial charged state at 70 °C, no significant differences in cell resistance were observed among the different electrolyte systems, indicating comparable initial interfacial and bulk properties. However, upon cycling, the LE cell exhibited a pronounced increase in bulk resistance (R_b), film resistance (R_f), and charge transfer resistance (R_{ct}). The increases in R_b and R_f can be attributed to the electrolyte depletion and the formation of a thick SEI layer, respectively.³⁸ In particular, R_f is closely associated with the composition and thickness of the SEI. On the other hand, R_{ct} predominantly reflects the degradation behavior of the cathode active material. The degradation of the cathode induced by HF attack contributes to an increase in the charge-transfer resistance (R_{ct}), as its structural damage hinders Li⁺ intercalation and deintercalation kinetics.³⁹ Accordingly, the overall increase in resistance indicates progressive electrolyte decomposition, interfacial degradation, and the accumulation of resistive components in the SEI layer at elevated temperatures. In

contrast, the GPE-based cells showed only minimal increases in these resistance components during cycling. For the GPE-based cells, the HF-scavenging of SiO-PETA and the suppression of side reactions result in more stable interfacial chemistry, thereby limiting the growth of internal resistances at elevated temperatures. Thus, the suppressed increases in R_b , R_f , and R_{ct} indicate that the GPE effectively stabilizes both the electrolyte and the electrode–electrolyte interfaces under high-temperature conditions, mitigating parasitic reactions and preserving interfacial integrity.

The Si 2p XPS analysis of the GPE was conducted after formation and after 100 cycles, and the corresponding results are presented in Figure S16. As shown in the figure, following the formation cycle, the relative proportion of Si–C species is dominant, while the Si–F component remains relatively minor. In contrast, after 100 cycles at 70 °C, the intensity of the Si–F peak increases, whereas Si–O and Si–C species are still observed.⁴⁰ These results suggest that the silane groups react with HF to form Si–F species during cycling, while preserving

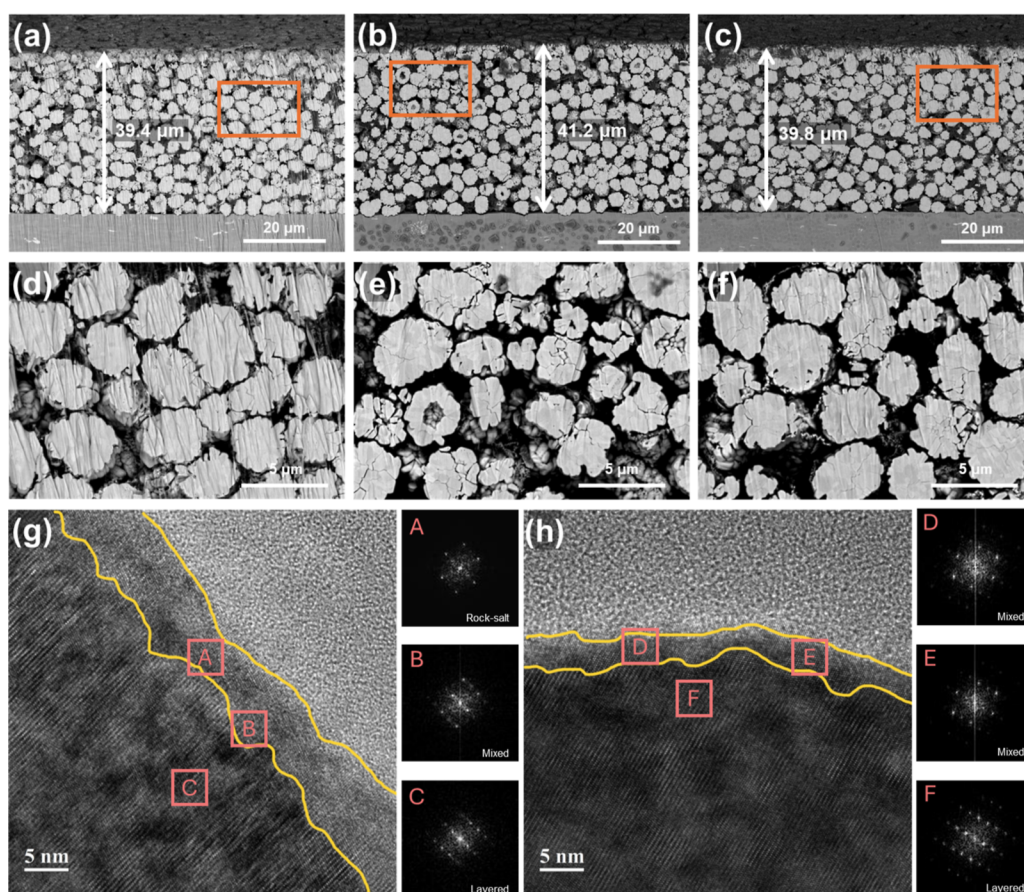


Figure 6. (a,d) Cross-sectional SEM images of the pristine NCM cathode. Cross-sectional SEM images of the NCM cathodes after 100 cycles at 70 °C with (b,e) LE and (c,f) GPE. HR-TEM images and corresponding FFT patterns of NCM cathodes retrieved from the cells with (g) LE and (h) GPE after 100 cycles at 70 °C.

the Si–O–C bonds under harsh thermal and electrochemical conditions. Figures 4 and S17 present the XPS spectra of the graphite anodes and NCM cathodes after 100 cycles. On the anode side, the GPE system showed clearer detection of intrinsic electrode components compared with the LE system. In the C 1s spectra (Figure 4a), the intensity of the graphite (sp^2 carbon) peak at 284.0 eV was relatively higher in the GPE cell, whereas peaks associated with electrolyte decomposition products, such as C–O (286.0 eV) and C=O (288.2 eV),⁴¹ were more pronounced in the LE cell. Consistent with this trend, the C–F peaks at 289.5 eV in the C 1s spectrum and at 687.5 eV in the F 1s spectrum, corresponding to the PVdF binder,^{42,43} were more clearly observed in the GPE system than in the LE system (Figure 4a,b). In addition, the O 1s and P 2p spectra shown in Figure S17a,b exhibit less intense byproduct-related peaks in the electrode cycled with GPE. These results indicate that the SiO-PETA-based GPE effectively suppresses thermally induced electrolyte decomposition, thereby minimizing the accumulation of decomposition products on the anode surface at elevated temperatures. For the cathode side, the O 1s spectra (Figure 4c) reveal pronounced differences in the surface-layer composition. The GPE cell exhibits a distinct M–O peak at 529.5 eV, corresponding to the lattice oxygen of the NCM active material.⁴⁴ In contrast, this peak is significantly attenuated in the LE cell, indicating the formation of a thick cathode electrolyte interphase (CEI) layer resulting from the electrolyte decomposition. The presence of this resistive CEI is consistent

with the increased internal resistance observed in the EIS analysis. Consistent with the O 1s results, the P 2p spectra (Figure 4d) further clarify the chemical composition of the degraded cathode surface. The LE cell shows a distinct peak at 131.5 eV, assigned to reduced phosphorus species such as C–P and Li_xP . The formation of these species is indicative of transition-metal dissolution.⁴⁵ Dissolved transition metal ions can coordinate with PF_6^- fragments and act as catalytic sites, thereby accelerating electrolyte decomposition. In contrast, this peak is negligible in the GPE cell. Moreover, the overall intensities of peaks associated with electrolyte decomposition products, such as P–O (133.8 eV), Li_xPOF_y (135.3 eV), and Li_xPF_y (137.3 eV),⁴⁶ are considerably lower in the GPE system. Additional evidence is provided by the C 1s and F 1s spectra (Figure S17c,d), where the relative intensity of C–F peak originating from the binder is higher in the GPE cell, suggesting limited surface coverage by decomposition products. Overall, these XPS results indicate that the GPE effectively suppresses parasitic reactions at the electrode surface, leading to the formation of a thinner and less resistive surface layer. To further elucidate the distribution of surface species, TOF-SIMS depth profiling was performed, and the corresponding depth profiles and three-dimensional (3D) reconstructed images are presented in Figures 4e–j. On the anode side, the depth profiles of C_6^- , LiF_2^- , and PO_3^- were analyzed. The C_6^- signal represents the graphite substrate, whereas LiF_2^- and PO_3^- originate from electrolyte decomposition products. As shown in the figure, the LiF_2^- and PO_3^-

signals are markedly stronger in the LE cell than in the GPE cell. In addition, the C_6^- signal reaches its plateau more slowly in the LE cell, indicating a thicker SEI layer formed by extensive electrolyte decomposition at elevated temperatures. A similar tendency is observed on the cathode side. The LE cell exhibits stronger LiF_2^- and $PO_2F_2^-$ signals, which are associated with decomposition products, whereas the Ni^- signal corresponding to the NCM active material emerges more rapidly in the GPE cell.^{47,48} This behavior suggests that the cathode surface in the GPE system is covered by a thinner interphase layer. The 3D reconstructed images further confirm that the accumulation of decomposition byproducts on both electrodes is significantly reduced in the GPE cell compared with the LE cell (Figure 4i,j). Overall, these results demonstrate that the GPE effectively suppresses electrolyte decomposition at both electrodes under high-temperature conditions, thereby limiting interphase growth and mitigating the increases in both film resistance (R_f) and bulk resistance (R_b) observed in the AC impedance spectra.

To investigate the suppression of transition metal (TM) dissolution induced by HF, the surfaces of graphite anodes after 100 cycles at 70 °C were analyzed. Figure 5a,b present the XPS spectra of Ni 2p and Mn 2p collected from the anode surfaces. In the LE system, distinct peaks corresponding to Ni and Mn were clearly observed, indicating that metal ions dissolved from the cathode migrated through the electrolyte and were subsequently deposited on the anode surface. In contrast, these peaks were significantly suppressed in the GPE system, suggesting reduced TM dissolution and deposition. To quantitatively verify this protective effect, ICP–MS analysis was conducted (Figure 5c). The LE system exhibited high concentrations of deposited TM ions (Ni, Co, and Mn), indicating severe TM dissolution and cathode degradation. However, in the GPE system, the concentrations of all detected TMs were markedly lower than those in the LE system. This substantial reduction in metal dissolution demonstrates that the GPE effectively scavenges HF and suppresses structural degradation of the cathode, thereby mitigating TM migration to the anode. The distribution of deposited TMs on the anode surface was further characterized using TOF-SIMS ion mapping (Figures 5d–i). As shown in the images, the anode from the LE system exhibited a dense distribution of secondary ions corresponding to Ni^+ , Co^+ , and Mn^+ , indicating significant TM deposition. In contrast, the anode from the GPE system showed markedly weaker signal intensities for all corresponding metal ions, suggesting substantially reduced TM crossover. These imaging results are consistent with the ICP–MS analysis, collectively confirming that the SiO-PETA-based GPE suppresses the dissolution and migration of transition metals, thereby mitigating anode degradation.

The SEM images of the graphite anodes were obtained to examine surface morphology after 100 cycles at 70 °C. As shown in Figure S18, the graphite electrode from the LE cell is covered with a substantial amount of surface byproducts, whereas the GPE-based cell exhibits a comparatively clean and well-preserved surface morphology. These results indicate that the GPE effectively suppresses side reactions at the anode under elevated temperature conditions, consistent with the EIS, XPS, and TOF-SIMS results, which suggest a greater accumulation of decomposition products in the LE system.

To investigate the effect of the GPE on the structural stability of the cathode during high-temperature cycling, NCM

cathodes obtained after 100 cycles at 70 °C were characterized by FE-SEM. Figure 6a–c present cross-sectional SEM images of the pristine cathode and the cathodes cycled with LE or GPE. Notably, the cathode cycled with LE exhibited a pronounced thickness increase, expanding from 39.4 to 41.2 μm after cycling. In contrast, the cathode cycled with GPE showed a much smaller dimensional change, increasing only slightly to 39.8 μm . This cathode expansion can be ascribed to microcracking and pulverization of NCM secondary particles.⁴⁹ Consistently, as shown in Figures 6d–f, microcracking of NCM particles was substantially suppressed in the GPE system, indicating improved mechanical and structural integrity. This enhancement is attributed to effective HF scavenging and the suppression of deleterious interfacial reactions by the GPE. In the LE system, HF generated at elevated temperatures continuously attacks the cathode surface and propagates along grain boundaries, accelerating intergranular cracking. The resulting cracks expose reactive surfaces to electrolyte decomposition, which promotes anisotropic volume changes and unstable cathode electrolyte interphase (CEI) growth. In contrast, in the GPE system, SiO-PETA scavenges HF and supports the formation of a thin, stable CEI, thereby preserving the mechanical integrity of the secondary particles even under high-temperature cycling. The microstructural evolution of the NCM cathodes was further examined by HR-TEM coupled with fast Fourier transform (FFT) analysis. Under harsh conditions, side reactions with HF and anodic decomposition can reduce highly oxidized Ni^{4+} to Ni^{2+}/Ni^{3+} . These reduced species can migrate into vacant Li slabs within the layered structure, triggering layered-to-rock-salt reconstruction and forming an electrochemically inactive phase that leads to irreversible capacity loss.⁵⁰ As shown in Figure 6g, a thick rock-salt layer was observed on the cathode active material cycled with LE. In contrast, the cathode cycled with GPE predominantly retained the layered structure with only a limited mixed-phase region (Figure 6h), demonstrating that the GPE mitigates cathode surface reconstruction by providing a chemically stabilized interfacial environment.

XRD patterns and DSC thermograms of the cycled NCM cathodes were analyzed in the charged state. To quantify the degree of cation mixing, the intensity ratio of the (003) to (104) peaks was calculated from the XRD patterns, as shown in Figure S19a.⁵¹ For the NCM cycled in LE at 25 °C (first cycle), the (003)/(104) ratio was 1.602, indicating a well-ordered layered structure. However, after 100 cycles at 70 °C, the ratio for the NCM in LE decreased markedly to 1.282, suggesting substantial structural disorder and increased cation mixing. In contrast, the NCM cycled in GPE retained a high ratio of 1.585 even after high-temperature cycling, demonstrating that the GPE effectively preserves the layered ordering of NCM and suppresses cation mixing under harsh conditions. The DSC thermograms of the cycled NCM cathodes are presented in Figure S19b. The sharp exothermic peak observed around 250 °C is associated with oxygen release from the destabilized layered structure, which typically occurs when the cathode undergoes severe structural degradation. In the cathode cycled with LE, this exothermic reaction was more pronounced, indicating substantial structural collapse and higher reactivity of the delithiated NCM toward liquid electrolyte at elevated temperatures. In contrast, the cathode cycled with the GPE exhibited a markedly reduced heat release, along with a shift of the exothermic peak toward higher temperatures. These results demonstrate that the GPE

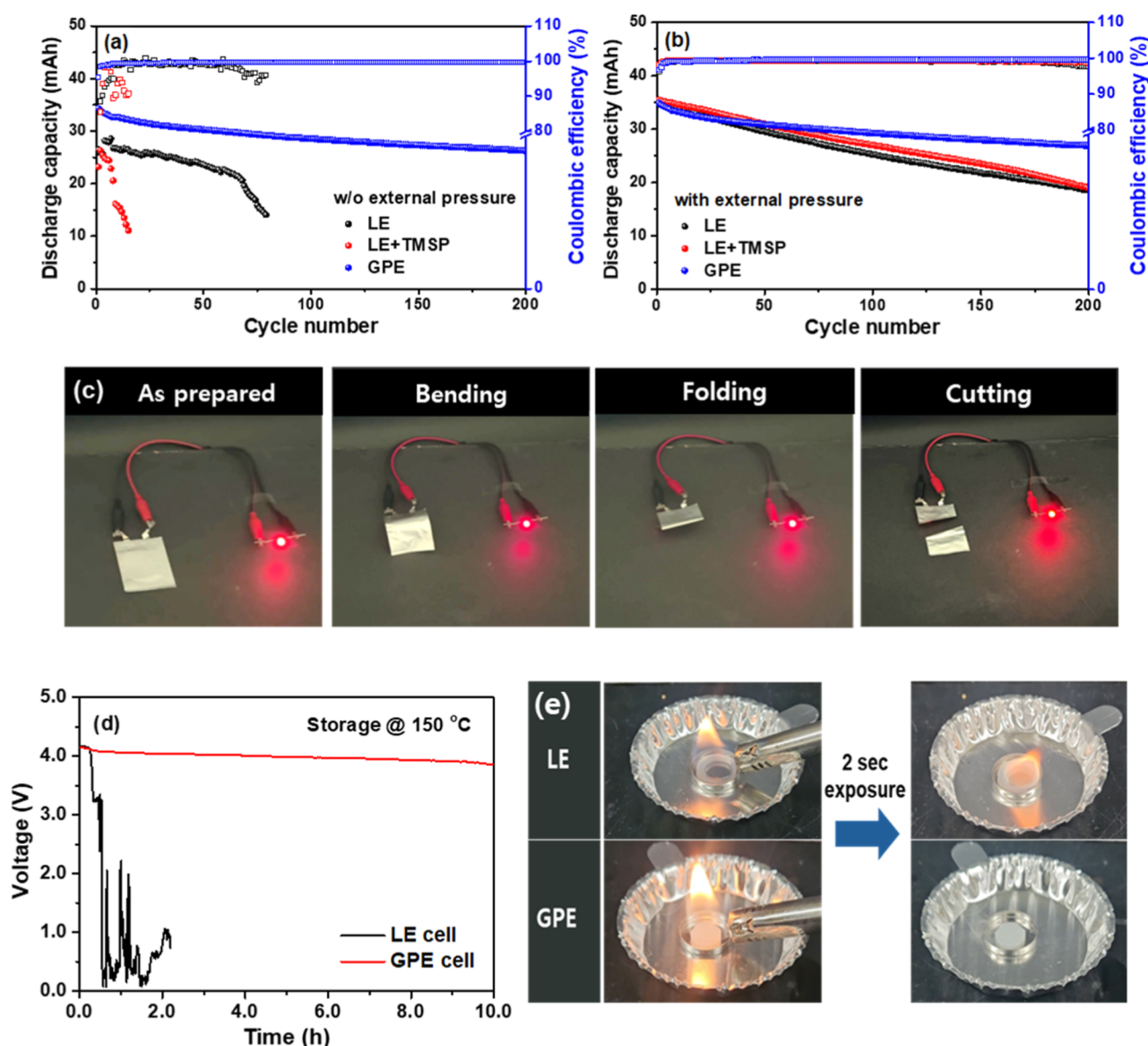


Figure 7. Cycling performance of pouch-type cells (a) without and (b) with external pressure at 70 °C and 1.0 C rate. (c) Photographs of the GPE-based pouch cell under bending, folding, and cutting while powering an LED. (d) Open-circuit voltage variation of the cells with different electrolytes during storage at 150 °C. (e) Flammability test results of LE and GPE.

effectively stabilizes the cathode structure during high-temperature cycling, leading to reduced lattice degradation and suppressed oxygen release.⁵² Consequently, the GPE enhances both the structural integrity and thermal stability of the NCM cathode under harsh operating conditions.

Pouch-type cells were fabricated and their cycling behavior was evaluated at 70 °C and 1.0 C. Figure 7a shows the cycling performance of the pouch cells operated without external pressure. As shown in the figure, the LE and LE + TMSP cells delivered low initial discharge capacities and exhibited rapid capacity fading, whereas the GPE cell maintained stable cycling over 200 cycles. The severe capacity decay observed in the LE and LE + TMSP cells is attributed to gas generation from parasitic side reactions and electrolyte vaporization at elevated temperatures. These processes lead to electrolyte depletion and interfacial degradation, ultimately causing rapid performance deterioration. Figure S20 presents optical images of the pouch cells before and after 50 cycles at 70 °C. The cells with LE and LE + TMSP showed noticeable swelling after cycling,

indicating significant gas evolution. In particular, the LE + TMSP cell exhibited the most pronounced expansion, which is likely associated with gas generation from TMSP decomposition, resulting in accelerated capacity fading at high temperatures.^{19,20} In contrast, the GPE cell retained its original shape without noticeable swelling, suggesting that gas evolution was effectively suppressed. This behavior is attributed to the encapsulation of organic solvents within cross-linked polymer network, which stabilizes the electrolyte and mitigates side reactions under high-temperature operating conditions. The cycling performance of the pouch cells tested under external pressure is shown in Figure 7b. Because external pressure helps maintain interfacial contact and suppresses interface deterioration, all three types of cells were able to operate at 70 °C. Nevertheless, the LE and LE + TMSP cells still exhibited more rapid capacity fading than the GPE cell. These results indicate that, even under conditions where mechanical liquid electrolyte is assisted by external pressure, the conventional liquid electrolyte systems remain susceptible to

interfacial degradation and side reactions at high temperatures. In contrast, the SiO-PETA-based GPE system maintains stable interfaces and suppresses these degradation processes, resulting in superior high-temperature cycling performance in pouch-type cells. The mechanical and thermal stability of the GPE-based cell was evaluated using pouch-type configurations. As shown in Figure 7c, the pouch cell employing the GPE continued to operate normally under bending, folding, and cutting conditions, demonstrating its mechanical robustness and strong resistance to internal short-circuiting. This behavior indicates that the polymer matrix provides structural integrity and maintains interfacial contact even under severe mechanical deformation. Figure 7d presents the open-circuit voltage (OCV) variation of fully charged pouch cells during storage at 150 °C. In the LE cell, the OCV dropped rapidly due to melting and thermal shrinkage of the PE separator, which likely caused internal short-circuiting. In contrast, the GPE cell maintained a stable OCV for up to 10 h, indicating superior thermal stability and effective suppression of internal failure under extreme temperature conditions. The flammability test shown in Figure 7e confirms the enhanced safety of the GPE system. The GPE exhibited reduced flammability compared to the liquid electrolyte, which can be attributed to the confinement of organic solvents within the cross-linked polymer network. This structural encapsulation effectively suppresses solvent volatilization and limits the supply of flammable species during ignition, thereby delaying ignition and resulting in reduced flammability compared to the liquid electrolyte. Overall, these results demonstrate that the GPE not only improves electrochemical performance at elevated temperatures but also provides substantial enhancements in mechanical resilience, thermal stability, and fire-related safety compared with conventional liquid electrolyte systems.

CONCLUSIONS

In this work, a multifunctional gel polymer electrolyte (GPE) based on a siloxy-functionalized cross-linker, SiO-PETA, was developed to enable stable and safe battery operation at elevated temperatures. The trimethylsilane groups in SiO-PETA effectively scavenged HF generated from the thermal decomposition of liquid electrolyte, thereby suppressing transition metal dissolution and interfacial degradation. Simultaneously, the chemically cross-linked polymer network encapsulated the liquid electrolyte components, mitigating solvent vaporization and parasitic reactions at high temperatures. As a result, graphite/NCM cells employing the GPE exhibited significantly improved cycling stability at 55 and 70 °C compared with cells using conventional liquid electrolyte or liquid electrolyte containing TMSP additive. Surface analyses confirmed reduced electrolyte decomposition, thinner interphase layers, and suppressed transition metal crossover in the GPE system. In addition, pouch-type cells demonstrated stable cycling at 70 °C even without external pressure, along with enhanced mechanical robustness, thermal stability, and reduced flammability. Overall, the SiO-PETA-based GPE provides dual chemical and physical stabilization of the electrolyte system, effectively suppressing degradation pathways under harsh thermal conditions. This strategy offers a practical and scalable approach to improving the high-temperature performance and safety of next-generation lithium-ion batteries.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.6c03585>.

¹H and ¹³C NMR spectra of TMS-Cl, PETA, and SiO-PETA, LC-MS spectrum of SiO-PETA, ΔG of the reaction between SiO-PETA and HF, Magnified FT-IR NMR spectra of the LE, GPE precursor and GPE, AC impedance spectra and DC polarization current profiles of the Li/electrolyte/Li cells, Li⁺ transference numbers and LSV curves of the electrolytes at 70 °C, HOMO and LUMO energy levels of the components in the GPE, Compressive stress-strain curves of GPEs, Ionic conductivities and LSV curves of GPEs with different SiO-PETA contents, ¹⁹F NMR spectra of LE, LE + TMSP, and GPE before storage test, Optical images of the GPE, LE, and LE + TMSP during storage at 70 °C, ¹⁹F NMR spectrum of GPE after storage at 70 °C for 10 days, Discharge capacities of the graphite/NCM cells with different electrolytes as a function of C rate, Cycling performance of the graphite/NCM cells with different electrolytes at 25 °C, An equivalent circuit for fitting the experimental AC impedance spectra, Evolution of internal resistances in cells with different electrolytes during cycling at 70 °C, Si 2p XPS spectra of the GPEs after formation and 100 cycles at 70 °C, XPS spectra of graphite anodes and NCM cathodes after 100 cycles at 70 °C, SEM images of graphite anodes after 100 cycles at 70 °C, XRD patterns and DSC thermograms of charged NCM cathodes after 100 cycles at 70 °C. Photographs of pouch-type cells with LE, LE + TMSP, and GPE before cycling and after 50 cycles at 70 °C (PDF)

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Notes

The authors declare no competing financial interest.

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