

500 Wh kg⁻¹-Class Safe Lithium Metal Batteries Enabled by a Sequentially Responsive Localized High-Concentration Gel Polymer Electrolyte

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Article

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Abstract

Practical application of high-energy-density lithium metal batteries (LMBs) is limited by interfacial parasitic reactions and thermal runaway risks. We develop a localized high-concentration gel polymer electrolyte (LGPE) featuring a pre-programmed sequential response, enabled by an electrophilic fluorinated crosslinked network derived from perfluorophenyl acrylate (PFPA), which integrates interfacial regulation and thermal defense within a single molecular framework. During routine cycling, the electrophilic PFPA preferentially adsorbs on the lithium anode and redirects interfacial film formation from free-solvent decomposition to controlled LiFSI defluorination, in-situ forming a LiF-rich gradient solid electrolyte interphase that stable Li plating/stripping. Under thermal abuse, the low-energy-barrier C–F bonds cleave preferentially to release fluorinated reactive species for gas-phase radical scavenging, while the residual backbone promotes condensed-phase char formation, achieving staged defense against combustion-chain propagation. Therefore, LGPE achieves non-flammability, with a high limiting oxygen index of 49.10%. Li||LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ cells retain 80.80% capacity after 430 cycles at 4.3 V. A 10.5 Ah pouch cell assembled with an N/P ratio of 2.6 and an E/C ratio of 1.6 g Ah⁻¹ delivers 504 Wh kg⁻¹ energy density, retaining 96.32% capacity after 80 cycles. This work provides a viable route toward concurrently enhancing interfacial electrochemical stability and intrinsic thermal safety in LMBs.

Introduction

Lithium metal batteries (LMBs) are widely regarded as promising candidates for next-generation high-energy-density energy storage because lithium metal offers an ultrahigh theoretical capacity of 3860 mAh g⁻¹ and an ultralow electrochemical potential of – 3.04 V versus the standard hydrogen electrode^{1,2,3,4,5}. However, their practical deployment remains hindered by two tightly coupled challenges, namely unstable interfacial chemistry and insufficient thermal safety. Continuous parasitic reactions between lithium metal and electrolyte components lead to fragile solid electrolyte interphase (SEI) formation, nonuniform lithium deposition, and dendrite growth, while the flammability of conventional liquid electrolytes greatly increases the risk of thermal runaway^{6,7,8,9,10,11,12}. Addressing these two issues simultaneously is therefore essential for the practical implementation of LMBs.

Considerable efforts have been devoted to electrolyte engineering to stabilize lithium metal and improve battery safety. Solid-state electrolytes can mitigate flammability, but their practical use is often limited by low room-temperature ionic conductivity and large solid-solid interfacial resistance^{13,14,15}. Gel polymer electrolytes (GPEs) provide an attractive intermediate platform by confining liquid electrolytes within polymer networks, thereby suppressing leakage while preserving liquid-like ion transport^{16,17,18,19}. Incorporating localized high-concentration electrolyte (LHCE) chemistry into gel frameworks further offers a route to regulate Li⁺ solvation structures and promote the formation of inorganic-rich interphases^{20,21}. However, integrating LHCEs into gel systems remains challenging because the polymer matrix can perturb the localized coordination environment. More importantly, most reported GPEs still

function primarily as passive hosts or barriers. They immobilize liquid components, but do not actively direct interfacial reactions during cycling or dynamically respond to thermal abuse^{22,23}.

Improving thermal safety introduces a further complication. Although LHCE-based systems can enhance interfacial stability, their constituent solvents often remain combustible, and the addition of conventional flame-retardant additives rarely resolves the underlying interfacial instability^{24,25,26}. Flame-retardant phosphate solvents offer a direct route to reducing flammability in electrolyte systems^{27,28,29}. However, their poor reductive stability on lithium metal tends to disrupt controlled interphase formation and compromise the development of robust SEIs^{30,31,32}. As a result, current electrolyte strategies often face an intrinsic trade-off between interfacial electrochemical stability and fire resistance. This limitation arises in part because interfacial regulation and thermal protection are usually introduced as physically mixed but functionally decoupled features, which leads to competing reaction pathways during electrochemical cycling and insufficient responsiveness under thermal abuse^{33,34,35}. Overcoming this bottleneck therefore requires a shift from component-level combination to molecular-level integration, in which electrochemical and thermal functions are encoded within a unified framework and activated sequentially under different operating conditions³⁶.

Here we report a localized high-concentration gel polymer electrolyte (LGPE) enabled by an electrophilic fluorinated crosslinked network derived from perfluorophenyl acrylate (PFPA). This design molecularly integrates interfacial regulation and thermal defense while preserving the anion-dominated solvation characteristics of the LHCE. During electrochemical cycling, PFPA preferentially interacts with the lithium surface and redirects interfacial film formation from uncontrolled solvent decomposition toward regulated LiFSI-derived defluorination, leading to the in-situ formation of a LiF-rich gradient composite SEI. Under thermal abuse, the low-energy-barrier C–F bonds within the network cleave preferentially to release fluorinated reactive species for gas-phase radical quenching, while the residual framework promotes condensed-phase char formation. This programmed sequential response enables the electrolyte to stabilize the lithium metal interface under normal operation and to suppress combustion-chain propagation under abusive conditions without requiring any external trigger. As a result, the LGPE simultaneously delivers improved interfacial stability, intrinsic flame retardancy, and durable high-energy full-cell performance in LMBs.

Results

Pre-programmed construction of LGPE with preserved anion-dominated solvation

A prerequisite for implementing the proposed sequential-response design is to introduce electrophilic interfacial functionality into the gel framework while minimizing perturbation to the anion-dominated solvation structure of the parent LHCE. To this end, LGPE was prepared by in-situ thermal polymerization of a low-content polymer network in the LHCE. PFPA and pentaerythritol tetraacrylate (PETEA) were

used as the fluorinated monomer and crosslinker, respectively, each at 2 wt%, with 2,2'-azobis(2-methylpropionitrile) (AIBN) as the initiator at 70°C (Fig. 2a). In this configuration, PFPA-derived fluorinated units are incorporated into a crosslinked matrix, while the liquid electrolyte phase remains the dominant component. The LHCE consists of 1.2 M LiFSI dissolved in TEP, BTFE, and TTE with a molar ratio of 1:1:2. After curing, the precursor is converted into a free-standing LGPE membrane (Figs. 2b and S1). The disappearance of the characteristic C = C stretching band at 1630 cm⁻¹ in the Fourier transform infrared (FTIR) spectra is consistent with the formation of the crosslinked polymer network (Fig. 2c).

Retention of the localized high-concentration coordination environment after gelation is important for preserving the solvation characteristics associated with the LHCE. Raman spectroscopy shows that LGPE remains dominated by contact ion pairs (CIPs) and cation-anion aggregates (AGGs), whereas the conventional carbonate electrolyte BE, consisting of 1 M LiPF₆ in EC:DEC = 1:1 by volume, is characterized mainly by solvent-separated ion pairs (SSIPs) (Figs. 2d and 2e)³⁷. These results suggest that incorporation of the three-dimensional polymer network does not substantially alter the anion-rich coordination environment during in-situ curing. Consistently, the downfield shift of the Li⁺ resonance in the ⁷Li nuclear magnetic resonance (NMR) spectra suggests strengthened coordination between Li⁺ and FSI⁻ in LGPE relative to BE (Fig. 2f), which may help facilitate interfacial Li⁺ desolvation³⁸.

To further examine the microscopic coordination environment, molecular dynamics (MD) simulations were performed. The simulation snapshots show that Li⁺ in LGPE are predominantly surrounded by FSI⁻ anions, with relatively limited solvent distribution within the first solvation shell (Figs. 2g and 2h). Quantitative coordination analysis gives a coordination number of 3.29 between Li⁺ and the O atoms of FSI⁻, which is higher than that between Li⁺ and TEP at 1.02. In addition, the calculated coordination interaction between Li⁺ and PFPA is minimal (Figs. 2i, 2j, S2, and S3), suggesting that PFPA contributes little to the primary Li⁺ solvation sheath. This result is consistent with a design in which PFPA-derived units are incorporated into the gel framework without becoming major components of the first-shell Li⁺ coordination structure. Under these conditions, the electrolyte shows an ionic conductivity of 1.29 mS cm⁻¹ and a Li⁺ desolvation energy of 2.03 eV (Figs. 2k and S4)³⁹.

The bulk structural and electrochemical characteristics of LGPE are also consistent with this interpretation. X-ray diffraction (XRD) shows broad amorphous scattering features, indicating that the crosslinked framework is predominantly disordered in the bulk phase (Figure S5). In addition, LGPE exhibits a lithium-ion transference number (t_{Li^+}) of 0.66, which may be associated with the anion-rich solvation environment together with restricted motion of bulky anionic species within the polymer-constrained medium. Such a coordination environment is expected to reduce the population of highly reactive free solvent species at the polarized interface and is accompanied by an electrochemical stability window of up to 4.70 V (Fig. 2m). Overall, these results indicate that the gelation strategy preserves key solvation features of the parent LHCE while incorporating fluorinated electrophilic motifs into the polymer framework, thereby providing the structural basis for the subsequent interfacial and thermal studies.

Macroscopic safety evaluation and thermal protection characteristics

To assess the thermal safety characteristics of LGPE at the macroscopic level, a series of combustion and thermal analyses were conducted. As shown in Fig. 3a, LGPE does not ignite under direct exposure to an open flame under the tested conditions, whereas the liquid BE undergoes vigorous combustion. Infrared thermal imaging and separator-heating tests further show that the separator containing LGPE retains its overall structure at 160°C, while that containing BE exhibits pronounced thermal deformation and melting (Fig. 3b). Thermogravimetric analysis (TGA) provides additional quantitative comparison. At 200°C, the mass loss of LGPE is 13.78%, substantially lower than that of BE at 53.96% (Figure S7). Together, these results indicate that gelation with the PFPA-containing crosslinked framework is associated with improved thermal tolerance and reduced flammability at the macroscopic level.

The combustion behavior of LGPE was further evaluated by limiting oxygen index (LOI) and self-extinguishing time (SET) measurements. LGPE exhibits an LOI of 49.10% and a SET of 0 s g⁻¹ under the tested conditions, and compares favorably with the reported flame-retardant electrolyte systems summarized in Fig. 3c and Table S1 (Figs. 3c, S8, and S9). To further examine heat-release behavior during combustion, microscale combustion calorimetry (MCC) was performed. LGPE shows a peak heat release rate (pHRR) of 272.00 W g⁻¹ and a total heat release (THR) of 10.30 kJ g⁻¹, both lower than those of BE and the conventional LHCE (Figs. 3d and 3e). These data suggest that LGPE not only shows reduced ignitability in the macroscopic flame test, but also releases less heat during combustion than the control electrolytes.

To gain insight into the possible molecular basis of the observed flame-retardant behavior, density functional theory (DFT) calculations were performed (Figs. 3f and 3g). The calculated reaction energies between the pentafluorophenyl radical (C₆F₅·), considered here as a representative PFPA-derived pyrolysis fragment, and the combustion-chain radicals H· and HO· are - 0.72 and - 1.01 eV, respectively, both lower than the corresponding values for EC, DEC, and TEP. These calculations suggest that fluorinated PFPA-derived fragments may interact more favorably with reactive radical species than the conventional electrolyte components considered here. From this perspective, PFPA may contribute not only to formation of the gel framework but also to thermal protection through radical-quenching reactions at elevated temperature. This interpretation is consistent with the improved flame-retardant characteristics observed for LGPE, although the detailed reaction pathways during combustion likely remain more complex.

Sequential triggering mechanism of staged thermal protection

To examine how the staged thermal response of LGPE may be initiated, thermogravimetric-differential scanning calorimetry (TG-DSC) was first performed on PFPA (Fig. 4a). After excluding the contribution of early mass loss associated with adsorbed moisture and residual volatile species, PFPA exhibits a

distinct pre-pyrolysis mass-loss region between 100 and 147°C, with an onset temperature (T_{onset}) of approximately 100°C and a peak decomposition temperature (T_{peak}) of approximately 147°C, as identified from the differential thermogravimetric curve. This behavior suggests that PFPA-derived units may begin to decompose at relatively low temperature, before more extensive thermal degradation of the overall electrolyte system occurs.

The possible origin of this early thermal response was further examined by DFT calculations of bond dissociation in representative electrolyte components on the lithium surface (Fig. 4b). The calculated activation energy for C–F bond cleavage in PFPA is $E_a = 0.42$ eV, with a reaction energy of -4.10 eV, whereas cleavage of the P–O–C bond in TEP requires a substantially higher activation energy of $E_a = 2.13$ eV and a reaction energy of $+1.85$ eV. This difference in calculated bond dissociation energetics suggests that PFPA-derived moieties may undergo bond cleavage more readily than the phosphate solvent under thermal perturbation. This interpretation is consistent with the lower-temperature mass-loss feature observed in the TG-DSC results.

To probe whether species released at the early stage affect combustion-related radicals, in-situ variable-temperature electron paramagnetic resonance (EPR) spectroscopy was combined with thermogravimetric infrared-mass spectrometry (TG-IR-MS). The EPR results track the evolution of HO· radicals during programmed heating (Figs. 4c and 4d). In BE, the HO· signal increases continuously with temperature. By contrast, the corresponding signal in LGPE remains markedly lower over the measured temperature range, suggesting that radical generation, radical persistence, or both are reduced in the gel electrolyte during heating.

TG-IR analysis provides further information on the evolution of volatile species during thermal decomposition (Figs. 4e and S10). In a lower-temperature region corresponding approximately to 100–147°C, volatile fluorinated species are detected near the PFPA decomposition range. At a later stage centered around approximately 240°C, the HO· radical concentration increases substantially, and the mass spectrometric signal assigned to pentafluorophenol (HOC_6F_5), taken here as a representative radical-quenching product, reaches its maximum. The temperature separation between these two signals is consistent with a scenario in which fluorinated species generated at an earlier stage remain available for subsequent radical-involved reactions at higher temperature. By comparison, BE releases appreciable amounts of POF_3 at lower temperature. In addition, the gas-phase signals assigned to combustible species, including CO and hydrocarbons, as well as the combustion product CO_2 , are lower for LGPE than for BE, which is consistent with less extensive combustion-chain propagation in the LGPE system⁴⁰.

Additional support for this interpretation is provided by thermogravimetric mass spectrometry (TG-MS) fragment analysis (Figs. 4f and 4g). Fragment ions at $m/z = 168$, assigned to C_6F_5^+ , and $m/z = 69$, assigned to CF_3^+ , are observed during LGPE pyrolysis, supporting the formation of fluorinated decomposition products. Meanwhile, the intensities of fragment ions associated with combustible gases

at $m/z = 27$ and 28 are lower than those of BE (Figs. 4h and 4i), in agreement with the EPR and TG-IR results.

In addition to possible gas-phase radical interception, the pyrolyzed residual framework may also contribute to thermal protection in the condensed phase. At elevated temperature, phosphorus-containing species derived from TEP decomposition may participate in residue formation. These species may facilitate further crosslinking and aromatization of the degraded polymer framework together with the LHCE components, leading to formation of a carbonaceous layer. X-ray photoelectron spectroscopy (XPS) shows the presence of C–F-containing species in the char residue (Figs. 4j, 4k, and S11). Fourier transform infrared (FTIR) spectra further show the coexistence of $P=O$, $P-O-C$, and C–F-related features in the residue (Fig. 4l), which is consistent with the incorporation of phosphorus- and fluorine-containing species into the condensed products. Raman spectroscopy shows that the I_D/I_G ratio of the LGPE-derived char is 0.93, lower than that of BE at 1.33 (Fig. 4m), suggesting a relatively higher degree of structural ordering in the carbonaceous residue. Such a residue may help limit heat feedback and the continued release of combustible volatiles during thermal decomposition.

Taken together, these results support a staged thermal-protection scenario in LGPE. In this picture, fluorinated PFPA-derived species formed at an earlier stage may participate in gas-phase radical-related reactions, while the residual framework together with phosphorus-containing decomposition products contributes to condensed-phase char formation. This combined behavior is consistent with the improved thermal tolerance and flame-retardant characteristics observed for LGPE.

Electrochemical response and lithium deposition behavior of LGPE

To evaluate the electrochemical behavior of LGPE and its influence on lithium deposition, a series of electrochemical and microscopic characterizations were carried out. In $Li||Li$ symmetric cells, $Li||LGPE||Li$ shows stable voltage polarization over 2000 h, whereas BE exhibits a pronounced increase in polarization after approximately 420 h (Fig. 5a). Rate tests further show that LGPE retains comparatively low overpotentials over a range of current densities (Fig. 5b). Taken together, these results indicate improved interfacial stability during repeated lithium plating and stripping in the LGPE-based cells.

The improved cycling behavior is accompanied by changes in interfacial kinetic parameters. Tafel analysis shows that the exchange current density of LGPE is 0.42 mA cm^{-2} , approximately twice that of BE at 0.20 mA cm^{-2} , consistent with faster interfacial charge-transfer kinetics (Fig. 5c). Arrhenius analysis further gives an activation energy of $23.47 \text{ kJ mol}^{-1}$ for lithium-ion transport in LGPE, lower than that of BE (Figs. 5d and S12), suggesting reduced resistance for interfacial Li^+ transport. In $Li||Cu$ half-cells operated at 0.5 mA cm^{-2} and 0.5 mAh cm^{-2} , LGPE supports cycling for 230 cycles with an average Coulombic efficiency of 98.6% and relatively stable overpotential evolution, whereas BE shows obvious Coulombic-efficiency fluctuation and rapid decay after about 60 cycles (Figs. 5e and S13). These results

are consistent with more reversible lithium deposition and stripping in the LGPE system over extended cycling.

The influence of LGPE on deposition morphology was further examined by post-cycling structural characterization and in-situ optical microscopy. Scanning electron microscopy (SEM) images of lithium metal after 100 cycles show that BE leads to a porous and dendritic surface morphology, whereas LGPE yields a denser and smoother deposited layer (Figs. 5f and S14). In agreement with these observations, in-situ optical microscopy shows that during the early stage of polarization, BE rapidly forms irregular nuclei that evolve into loose mossy lithium within 10 min, while LGPE maintains a comparatively dense and smooth deposition front over the observation period (Fig. 5g). Atomic force microscopy (AFM) further shows that the electrode cycled with LGPE has a surface roughness of 21.20 nm, lower than that of BE (Fig. 5h). Together, these observations suggest that LGPE is associated with more uniform lithium deposition and reduced accumulation of dendritic or highly porous lithium structures.

To further examine the possible origin of this morphological difference, finite element simulations were performed from the perspectives of mechanical stress and electrochemical mass transport. The simulated interfacial stress evolution shows that BE is more prone to local stress concentration, which is accompanied by the development of surface protrusions during deposition (Fig. 5i). By contrast, LGPE shows a lower peak von Mises stress at the interface, consistent with more spatially uniform mechanical constraint from the gel electrolyte environment. In addition, simulations of ion concentration and electric-field distribution show that the LiF-rich interphase considered for LGPE is associated with a more gradual Li^+ concentration gradient and a more uniform local electric field, whereas BE exhibits stronger field distortion and more localized ion accumulation (Figs. 5j, S15 and S16)⁴¹. These results provide a plausible basis for the more uniform lithium growth observed experimentally in the LGPE system.

Formation and microscopic characteristics of the polymer-inorganic composite SEI

The improved interfacial behavior of LGPE appears to be associated with differences in the initial film-forming process on the lithium surface. To examine this possibility, DFT calculations were performed to evaluate the adsorption energies of representative electrolyte components on lithium (Figs. 6a and S17). PFPA adopts a flat-lying configuration on the lithium surface, with a calculated adsorption energy of -4.01 eV, which is stronger than those of LiFSI at -1.90 eV, TEP at -1.91 eV, TTE at -1.10 eV, and BTFE at -1.00 eV. These results suggest that PFPA has a stronger tendency to interact with the lithium surface than the other components considered here, and may therefore influence the earliest stages of interfacial film formation.

To further examine how PFPA may affect the initial interfacial reduction pathway, transition-state calculations were carried out on the lithium surface (Fig. 6b). The calculated activation energy for C–F bond dissociation in PFPA is $E_a = 0.42$ eV (Figure S18), lower than the corresponding barriers considered for the other electrolyte components. In addition, the presence of adsorbed PFPA lowers the calculated

defluorination barrier of neighboring LiFSI from $E_a = 1.13$ eV in the isolated state to $E_a = 0.50$ eV in the PFPA-associated configuration. These results suggest that PFPA may participate in early interfacial reduction and may also alter the reduction pathway of nearby LiFSI, increasing the likelihood of LiF-forming decomposition reactions. This interpretation is further supported by lowest unoccupied molecular orbital (LUMO) analysis (Fig. 6c), which shows that PFPA has the lowest LUMO energy among the components considered, whereas TEP has a higher LUMO energy than both PFPA and LiFSI. Together, these calculations are consistent with preferential reduction of PFPA- and LiFSI-related species before substantial phosphate-solvent reduction, providing a plausible basis for the interfacial chemistry observed in LGPE.

The morphology of the resulting interphase was further examined by cryogenic transmission electron microscopy (cryo-TEM) (Figs. 6d and S19). The SEI formed in BE appears relatively loose and largely amorphous, with Li_2CO_3 as a major component. By contrast, the interphase formed in LGPE appears denser and exhibits a polymer-inorganic composite character, with a thickness of about 10.8 nm on the lithium surface. Fast Fourier transform (FFT) analysis identifies lattice fringes assignable to LiF (111), Li_2O (111), and Li_3PO_4 (111), suggesting that nanoscale inorganic domains are distributed within an amorphous matrix. Such an interfacial structure is consistent with reduced exposure of fresh lithium to continued electrolyte decomposition.

To further probe the compositional distribution within the interphase, time-of-flight secondary ion mass spectrometry (TOF-SIMS) and XPS depth profiling were performed (Figs. 6e, 6f, and S20). In the TOF-SIMS results, LiF^- and LiF_2^- signals are more prominent in the LGPE-derived SEI, whereas the organic fragment C_2HO^- , associated here with solvent decomposition, is comparatively weaker, suggesting a larger contribution from anion-derived decomposition products in SEI formation⁴². XPS depth profiling further indicates compositional heterogeneity across the SEI thickness. The C–F signal in the surface C 1s spectrum is consistent with fluorinated polymer-containing species in the outer region of the LGPE-derived SEI (Figs. 6g and S21). The F 1s spectra show that LiF remains an important component throughout the sputtering depth (Fig. 6h). In addition, the Li 1s depth profile suggests progressive enrichment of inorganic species such as LiF and Li_3PO_4 toward the inner region, whereas Li_2CO_3 becomes more prominent in the inner layer of the BE-derived SEI (Fig. 6i)⁴³. Taken together, these results are consistent with formation of a gradient composite SEI in LGPE, comprising a fluorinated polymer-containing outer region and a more inorganic-rich inner region. Such a structure may help balance interfacial compliance and mechanical robustness, and may contribute to the improved cycling stability observed for the LGPE system.

Comprehensive full-cell performance evaluation and thermal runaway protection assessment

To assess the full-cell applicability of LGPE, Li||NCM811 cells were evaluated under high-voltage, elevated-temperature, and lean-electrolyte conditions. Electrochemical floating analysis (EFA) shows

that LGPE maintains a relatively low and stable oxidation current over a polarization range of 3.8–4.8 V, whereas BE exhibits apparent anodic decomposition above 4.3 V (Figure S22). Cyclic voltammetry (CV) further shows good overlap of the redox peaks over repeated scans (Figure S23), consistent with reversible Li^+ intercalation and deintercalation in the LGPE-based full cells. Together, these results suggest that the electrolyte formulation of LGPE provides oxidative stability compatible with high-voltage operation.

The cycling behavior of $\text{Li}||\text{LGPE}||\text{NCM811}$ full cells further supports this interpretation. At 25°C and 0.5 C, the cell retains 80.80% of its initial capacity after 430 cycles (Figs. 7a and S24). At 60°C, a capacity retention of 78.80% is maintained after 300 cycles (Fig. 7b). The cell also shows reversible rate performance from 0.1 to 2 C (Figure S25), indicating stable charge-storage behavior over a broad operating range. Galvanostatic intermittent titration technique (GITT) analysis shows that LGPE gives a higher apparent lithium-ion diffusion coefficient than BE, with $D_{\text{Li}}^+ = 16.25 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ (Figures S26 and S27). In-situ electrochemical impedance spectroscopy (EIS) combined with distribution of relaxation times (DRT) analysis further shows that LGPE is associated with lower interfacial resistance at both the SEI and cathode electrolyte interphase (CEI), together with lower charge-transfer resistance than BE (Figure S28). These results are consistent with improved ion-transport characteristics and interfacial stability in the LGPE-based full-cell configuration.

The high-voltage compatibility of LGPE was further examined in more demanding cathode systems. When paired with a 4.5 V NCM811 cathode and a 4.6 V LiCoO_2 cathode, the cells retain 82.7% and 81.5% of their initial capacities, respectively, over the tested cycling periods (Figs. 7c and S29). The evolution of the differential capacity (dQ/dV) curves shows reduced peak broadening and attenuation in the LGPE-based cells during high-voltage cycling (Figs. 7d and 7e), which is consistent with mitigated polarization and less pronounced structural degradation of the cathode. A broader comparison with previously reported electrolyte systems shows that LGPE compares favorably in long-term cycling under combined wide-temperature and high-voltage conditions (Fig. 7f and Table S2). Taken together, these results indicate that the interfacial and transport characteristics identified in symmetric-cell and half-cell tests are also reflected in full-cell performance.

To further examine practical cell-level performance, $\text{Li}||\text{NCM811}$ pouch cells with a nominal capacity of 10.5 Ah were assembled under lean-electrolyte and high-areal-capacity conditions, with a cathode loading of 4 mAh cm^{-2} , an N/P ratio of 2.6, and an E/C ratio of 1.6 g Ah^{-1} . Based on a total device mass of 78.7 g, the pouch cell delivers an energy density of 504 Wh kg^{-1} at a cutoff voltage of 4.30 V, while retaining 96.32% of its initial capacity after 80 cycles with stable charge-discharge profiles (Figs. 7g and S31). Benchmarking against recently reported pouch cells under similar conditions shows that the LGPE system achieves competitive energy density (Fig. 7h). When subjected to nail-penetration tests (Fig. 7i), the $\text{Li}||\text{LGPE}||\text{NCM811}$ pouch cell maintained stable voltage and temperature profiles without any visible smoke, combustion, or explosion, and sustained continuous and reliable operation, indicating enhanced abuse tolerance at the device level. Full-cell thermal behavior was further assessed by accelerating rate

calorimetry (ARC) in adiabatic mode (Figure S32). The onset temperature of exothermic reaction for LGPE (180.70°C) is notably higher than that of BE (160.36°C), and the thermal runaway trigger temperature follows the same trend, confirming that the staged thermal defense mechanism remains effective at the full-cell level. COMSOL Multiphysics simulations were further performed to visualize the thermal runaway evolution (Figs. 7j and 7k). At $t_2 = 2713$ min, the BE cell had already entered thermal runaway with temperatures exceeding 416°C throughout the cell volume, whereas the LGPE cell remained at approximately 252°C under the same conditions. The LGPE cell ultimately triggered thermal runaway at $t_4 = 2928$ min with a peak temperature of $\sim 444^\circ\text{C}$, in excellent agreement with the ARC-measured value (deviation $< 0.1\%$), validating the reliability of the simulation.

Discussion

This work presents a gel electrolyte design featuring a preprogrammed sequential response, in which PFPA is incorporated into an electrophilic fluorinated crosslinked network to integrate interfacial regulation and thermal protection within a single molecular framework. Experimental and computational results indicate that, during electrochemical cycling, PFPA preferentially participates in the initial interfacial processes and shifts the interfacial reaction pathway from extensive free-solvent decomposition toward LiFSI-associated defluorination, thereby promoting the formation of a LiF-rich gradient composite SEI with a fluorinated polymer-containing outer layer and an inorganic-rich inner layer. Under thermal abuse, PFPA-derived fluorinated species are likely involved in gas-phase radical-scavenging reactions, while the residual framework, together with phosphorus-containing decomposition products, contributes to char formation in the condensed phase. This staged thermal-response behavior is consistent with the high limiting oxygen index of 49.10% observed for the LGPE. In full-cell configurations, Li||NCM811 cells retain 80.80% of their initial capacity after 430 cycles at 4.3 V. Moreover, a 10.5 Ah pouch cell with an N/P ratio of 2.6 and an E/C ratio of 1.6 g Ah^{-1} delivers a high energy density of 504 Wh kg^{-1} and retains 96.32% of its capacity after 80 cycles. These results suggest that molecularly integrating interfacial and thermal functions within the electrolyte framework is a promising strategy for simultaneously improving interfacial stability and thermal tolerance in lithium metal batteries.

Methods

Materials

Perfluorophenyl acrylate (PFPA, 98%), pentaerythritol tetraacrylate (PETEA, stabilized with MEHQ), triethyl phosphate (TEP), bis(2,2,2-trifluoroethyl) ether (BTFE, 99%), 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether (TTE, 98%), poly(vinylidene fluoride) (PVDF), and N-methyl-2-pyrrolidone (NMP, 99.9%) were purchased from Aladdin Ltd. 2,2'-Azobis(2-methylpropionitrile) (AIBN, 98%), NCM811, LiCoO₂ (LCO), and Super P were purchased from Shanghai Macklin Biochemical Co., Ltd. Lithium

bis(fluorosulfonyl)imide (LiFSI, 99.9%) was purchased from Canard Technology Co., Ltd. All chemicals were used as received without further purification.

Preparation of electrolytes

The precursor solution was prepared by adding PFPA and PETEA to the localized high-concentration electrolyte (LHCE) at 2 wt% each, giving a total LHCE content of 96 wt%. The molar ratio of PFPA to PETEA was 1.48:1. The LHCE was prepared by dissolving 1.2 M LiFSI in a mixed solvent of TEP, BTFE, and TTE with a molar ratio of 1:1:2. AIBN was then added to the precursor solution as the thermal initiator, and the mixture was heated at 70°C for 3 h. The LGPE was obtained after in-situ polymerization.

Preparation of cathodes and battery assembly

The cathode slurry was prepared by mixing NCM811, Super P, and PVDF in N-methyl-2-pyrrolidone at a weight ratio of 8:1:1. The slurry was cast onto aluminum foil and dried under vacuum at 60°C for 12 h. The dried electrodes were punched into discs with a diameter of 12 mm and an active-material loading of approximately 3.8 mg cm^{-2} . Polypropylene separators of the Celgard 2500 type were used. Li||Li symmetric cells with different electrolytes were assembled in argon-filled gloveboxes using CR2032 coin cells. Li||Cu half-cells, Li||NCM811 full cells, and Li||LiCoO₂ full cells were assembled using CR2025 coin cells. The electrolyte volume in each coin cell was 60 μL . Li||NCM811 pouch cells were assembled in an argon-filled glovebox. The anode consisted of lithium metal foil, and the cathode consisted of NCM811 coated on carbon-coated aluminum foil. The cathode and anode were separated by a polypropylene separator. Nickel and aluminum tabs were ultrasonically welded to the lithium and aluminum current collectors, respectively, for external electrical connection. The cell stack was then packaged in aluminum-plastic film. The electrolyte precursor solution containing AIBN was injected into the pouch cell, followed by vacuum sealing. The LGPE-based pouch cells were obtained after heating at 70°C for 3 h. Electrochemical measurements were carried out using electrochemical workstations (CHI660E and Bio-Logic VMP3) and battery testing systems from Wuhan LAND Electronic Co., Ltd. and NEWARE. The calculation formula for ionic conductivity, lithium transference number, activation energy can be found in Supplementary Method S1.

Characterizations

The solvation structures of the electrolytes were characterized by nuclear magnetic resonance (NMR) spectroscopy using a Bruker 600 MHz spectrometer. Inductively coupled plasma mass spectrometry (ICP-MS) was used to determine elemental concentrations in the electrolytes and separators. For ex-situ electrode characterization, cycled electrodes were repeatedly rinsed with dimethyl carbonate (DMC) to remove residual salts and then vacuum-dried. Surface morphology and internal structures were characterized by scanning electron microscopy (SEM, ZEISS GeminiSEM 300), transmission electron microscopy (TEM, FEI Talos F200x), and focused ion beam scanning electron microscopy (FIB-SEM), the latter being used for cross-sectional analysis of NCM811 particles. Surface topography and roughness of Li anodes were measured by atomic force microscopy (AFM, Hitachi E-sweep). The chemical composition and depth-dependent distribution of the solid electrolyte interphase (SEI) were analyzed by

X-ray photoelectron spectroscopy (XPS, Thermo Scientific Nexsa), XPS depth profiling (Thermo Scientific K-Alpha, sputtering times of 0, 60, and 120 s), and time-of-flight secondary ion mass spectrometry (TOF-SIMS, PHI nanoTOF III). Synchrotron-based X-ray absorption fine structure (XAFS) measurements at the Ni K-edge were conducted at the KMC-2 beamline of BESSY-II, Germany, to probe the Ni oxidation state. Dynamic interfacial evolution was further examined using an in-situ optical microscope (Yuescope YM710R) and in-situ X-ray diffraction (XRD). The in-situ XRD measurements were collected during the first cycle over a 2θ range of 10° to 50° at a scan rate of 4° min^{-2} .

Theoretical simulations

All the DFT calculations were performed using the DMol³ module in Materials Studio. The exchange-correlation functional was described within the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) functional. Grimme’s DFT-D3 correction was included to account for van der Waals interactions. Core electrons were treated using DFT semi-core pseudopotentials. The calculations were carried out with a global orbital cutoff of 3.4 Å and a Fermi smearing of 0.005 Ha, where 1 Ha = 27.211 eV. The convergence criteria for geometry optimization and energy calculations were set to an energy tolerance of $1.0 \times 10^{-5} \text{ Ha atom}^{-1}$, a self-consistent field tolerance of $1.0 \times 10^{-6} \text{ Ha atom}^{-1}$, a maximum force tolerance of 0.002 Ha Å^{-1} , and a maximum displacement tolerance of 0.005 Å.

The binding energy (ΔE) was calculated according to Eq. (4):

$$\Delta E = E_{AB} - E_A - E_B$$

4

where E_{AB} is the total energy of the combined system, and E_A and E_B are the energies of the isolated adsorbate and radical species, respectively.

MD simulations were performed using the Forcite module in Materials Studio. The molecular structures of TEP, BTFE, TTE, PFPA-PETEA, and LiFSI were first geometry-optimized. The LHCE model was constructed using the Amorphous Cell module with 67 TEP, 67 BTFE, 133 TTE, and 50 LiFSI molecules. The LHCE-GPE model was constructed with 67 TEP, 67 BTFE, 133 TTE, 3 PFPA-PETEA units, and 50 LiFSI molecules. The COMPASS III force field was used for all MD simulations. Each system was first pre-equilibrated in the NPT ensemble at 298 K for 200 ps, followed by equilibration in the NVT ensemble at 298 K for 2 ns. The final 1 ns of the NVT trajectory was used for radial distribution function (RDF) analysis and coordination-number statistics.

Finite element simulation

Finite element simulations were performed using COMSOL multiphysics 6.3. A mechano-electrochemical model was established to analyze lithium deposition behavior, including the evolution of deposition morphology, interfacial ion concentration, and current-density distribution in different

electrolyte systems. For computational simplicity, a $5\text{ }\mu\text{m} \times 6\text{ }\mu\text{m}$ electrolyte region was used in the simulation domain. Three electrolyte systems were considered for comparison, namely the baseline electrolyte (BE), the localized high-concentration electrolyte (LHCE), and the localized gel polymer electrolyte (LGPE). The detailed simulation process can be found in Supplementary Method S2.

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Figures

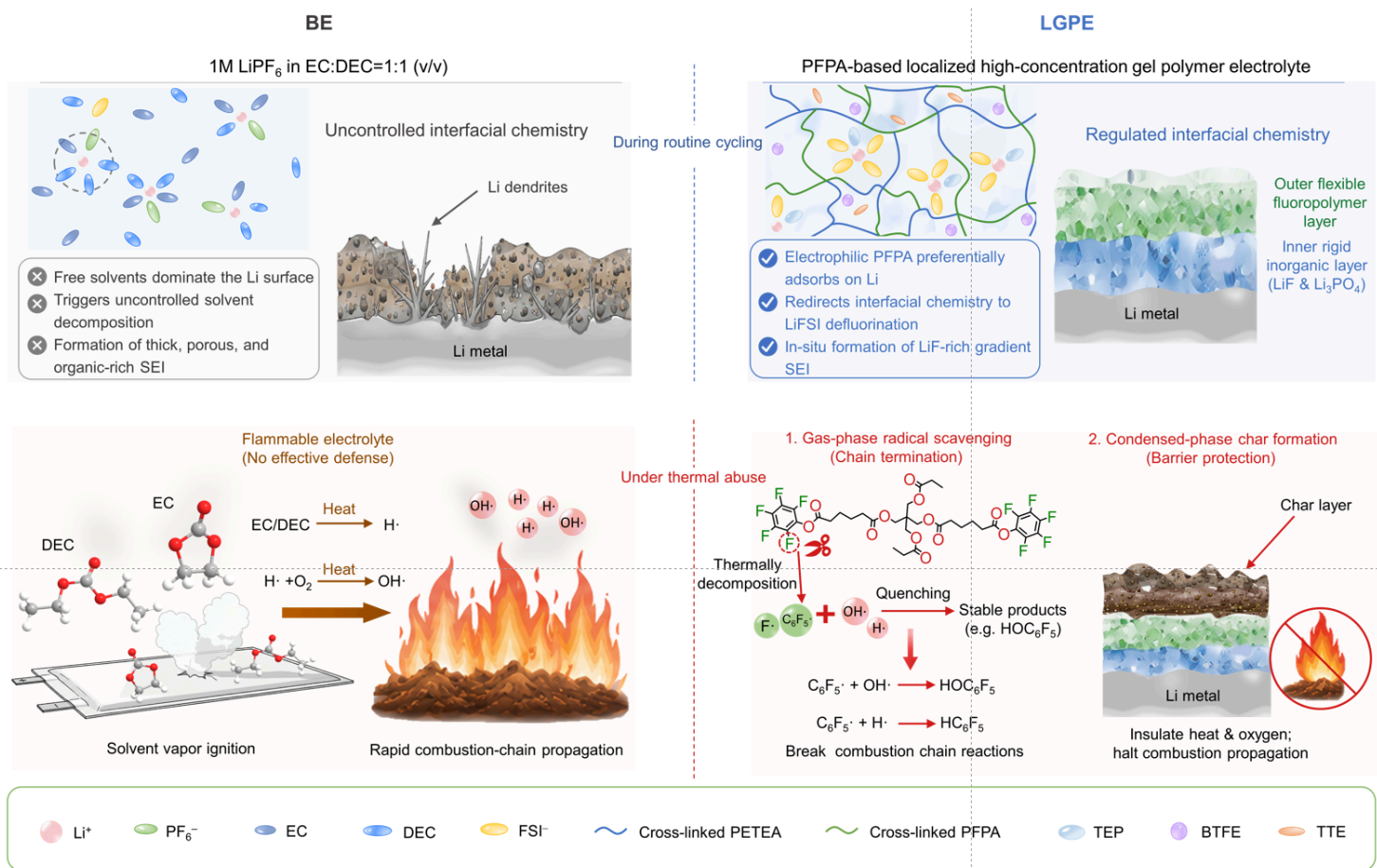


Figure 1

Schematic illustration of the working mechanism of the designed LGPE. During routine cycling, the functionalized LGPE network redirects interfacial chemistry to construct a robust LiF-rich gradient SEI for stable Li deposition; under thermal abuse, it halts combustion propagation through simultaneous gas-phase radical scavenging and condensed-phase char formation.

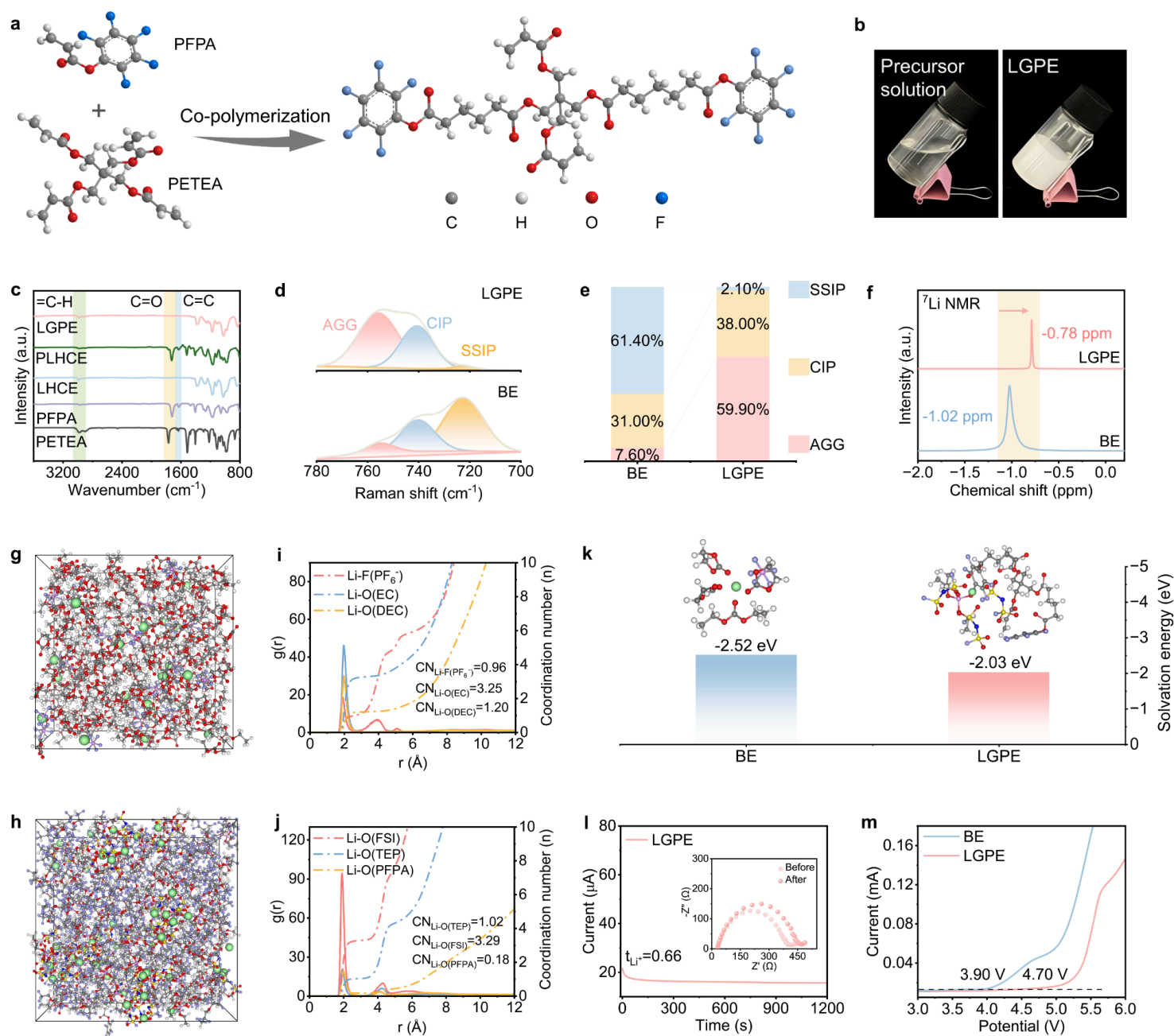


Figure 2

a) Chemical structures of PFPA and PETEA, and the proposed polymer matrix for LGPE. b) Optical images of the precursor solution and LGPE. c) FTIR spectra of PETEA, PFPA, LHCE, PLHCE, and LGPE. Raman spectra (d) and the corresponding quantitative distributions of solvation species (e) for the BE and LGPE. f) Room-temperature ⁷Li solid-state NMR spectra. MD simulation snapshots, corresponding radial distribution functions (solid lines), and coordination numbers (dashed lines) for BE (g, i) and LGPE (h, j). k) DFT-optimized Li⁺ solvation structures (Color code: C, grey; O, red; H, white; Li, green; P, purple; S, yellow; N, dark blue; F, light blue). l) Chronoamperometry profile and impedance spectra (inset) for t_{Li}⁺ measurement. m) Linear sweep voltammetry curves of BE and LGPE.

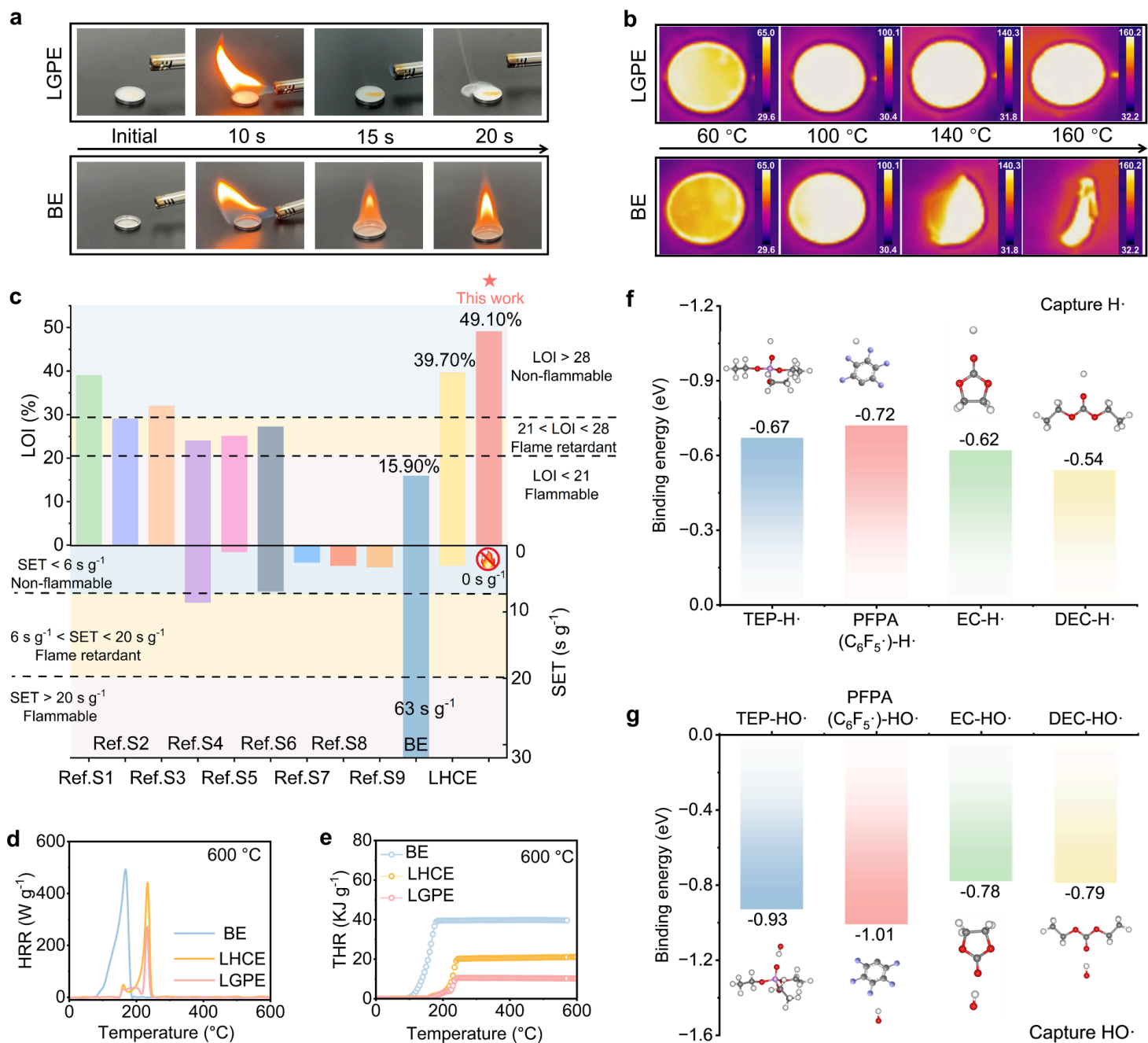


Figure 3

a) Combustion tests of LGPE and BE. b) Infrared thermal imaging information of LGPE and BE on PP membrane at different temperatures. c) Comparison of LOI and SET between LGPE and reported flame-retardant electrolytes. d) HRR and e) THR curves of BE, LHCE and LGPE during combustion. Comparison of binding energies between PFPA, TEP, EC, and DEC and (f) H[·] radicals and (g) HO[·] radicals.

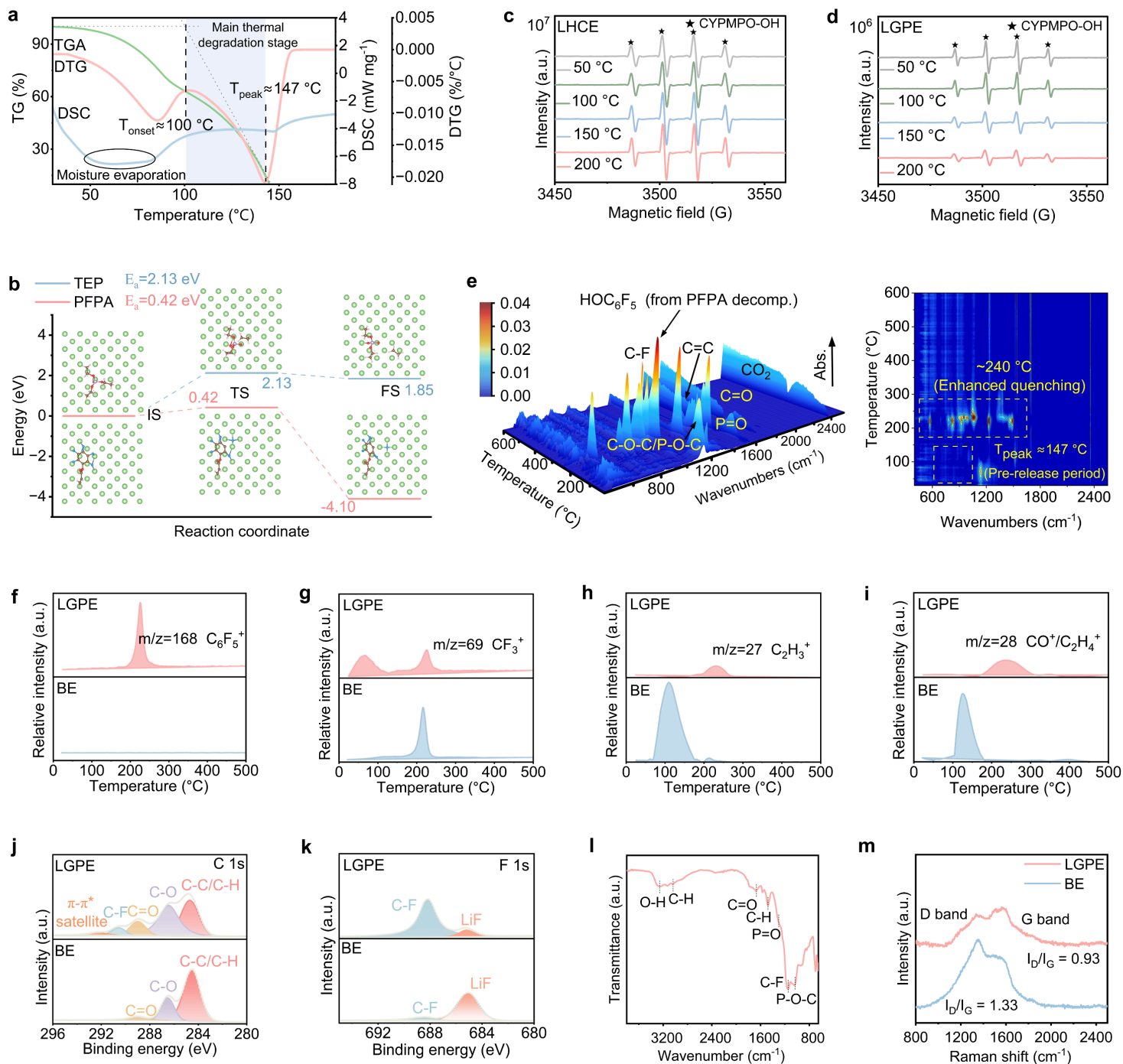


Figure 4

a) TG-DSC analysis curves of PFPA skeleton during programmed heating. b) DFT-calculated energy profiles for the dissociation of the C-F bond in PFPA and the P-O-C bond in TEP on the Li anode surface. Color code: C, brown; O, red; H, pink; Li, green; P, purple; S, yellow; N, dark blue; F, blue. In-situ EPR spectra of (c) LHCE and (d) LGPE at different temperatures. e) 3D TG-IR spectra and corresponding contour maps of the LGPE. f-i) Ionized fragments in the escaping gases of LGPE and BE during thermogravimetric experiment. j-k) XPS spectra of char residue for LGPE and BE. l) FTIR curve of the residual carbon layers of LGPE. m) Raman analysis of the residual carbon layers of LGPE and BE.

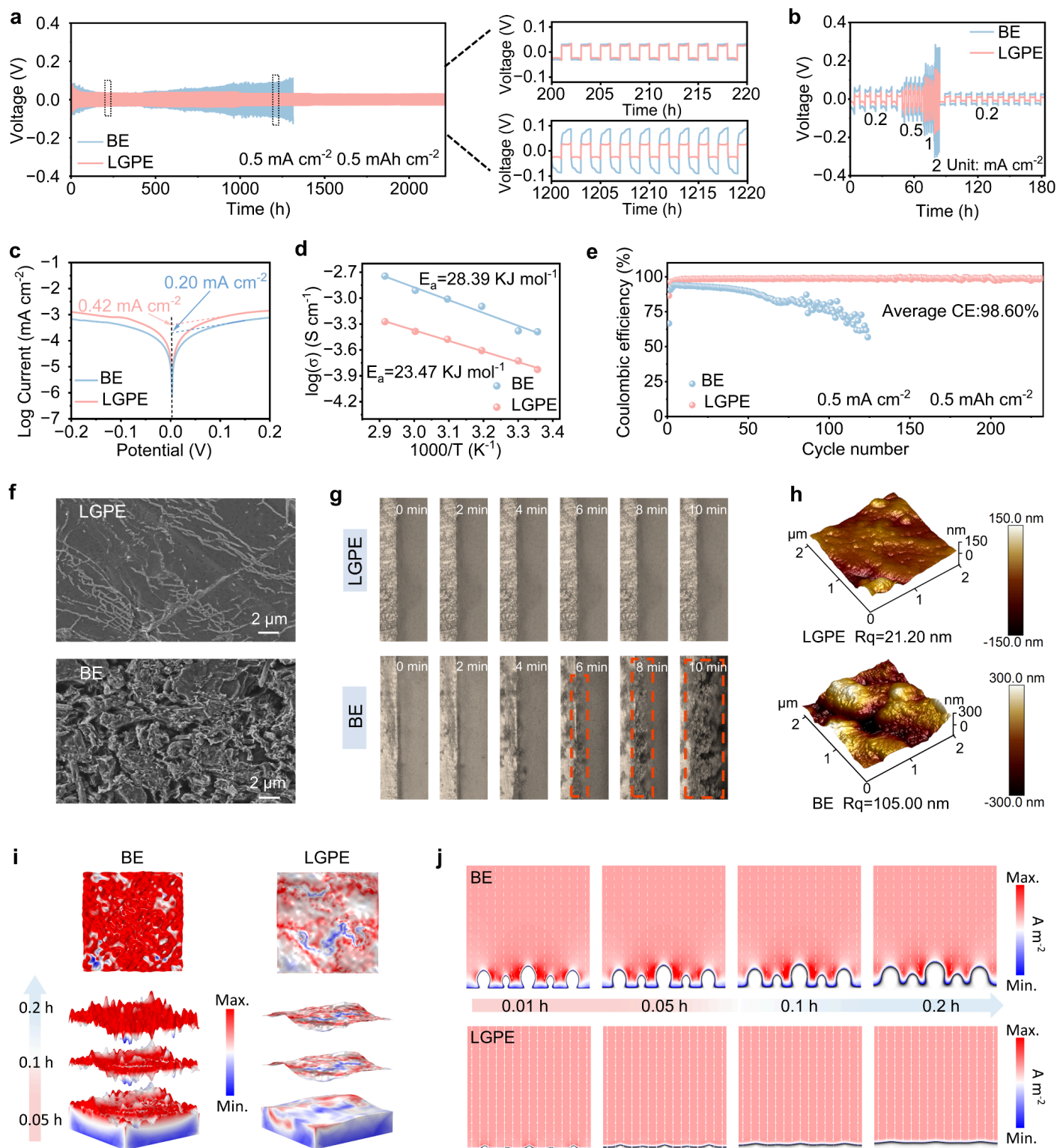


Figure 5

a) Voltage curves and their local magnifications of lithium deposition/stripping in lithium||lithium symmetric cells using LGPE and BE. b) Rate performance at current densities of 0.2, 0.5, 1, and 2 mA cm^{-2} . c) Tafel plots and derived exchange current density for the Li||Li cells using LGPE and BE. d) Arrhenius plots for activation energy (E_a) calculation. e) Coulombic efficiency (CE) tests at 0.5 mA cm^{-2}

and a fixed capacity of 0.5 mAh cm^{-2} . f) SEM images of the cycled lithium anodes with the LGPE and BE. g) In-situ optical microscopy snapshots of Li anode surfaces during plating with LGPE and BE. h) AFM images of LGPE and BE. i) Simulated stress distribution on the lithium anode at different deposition stages. j) Simulated Li deposition morphology and electric field distribution for BE and LGPE.

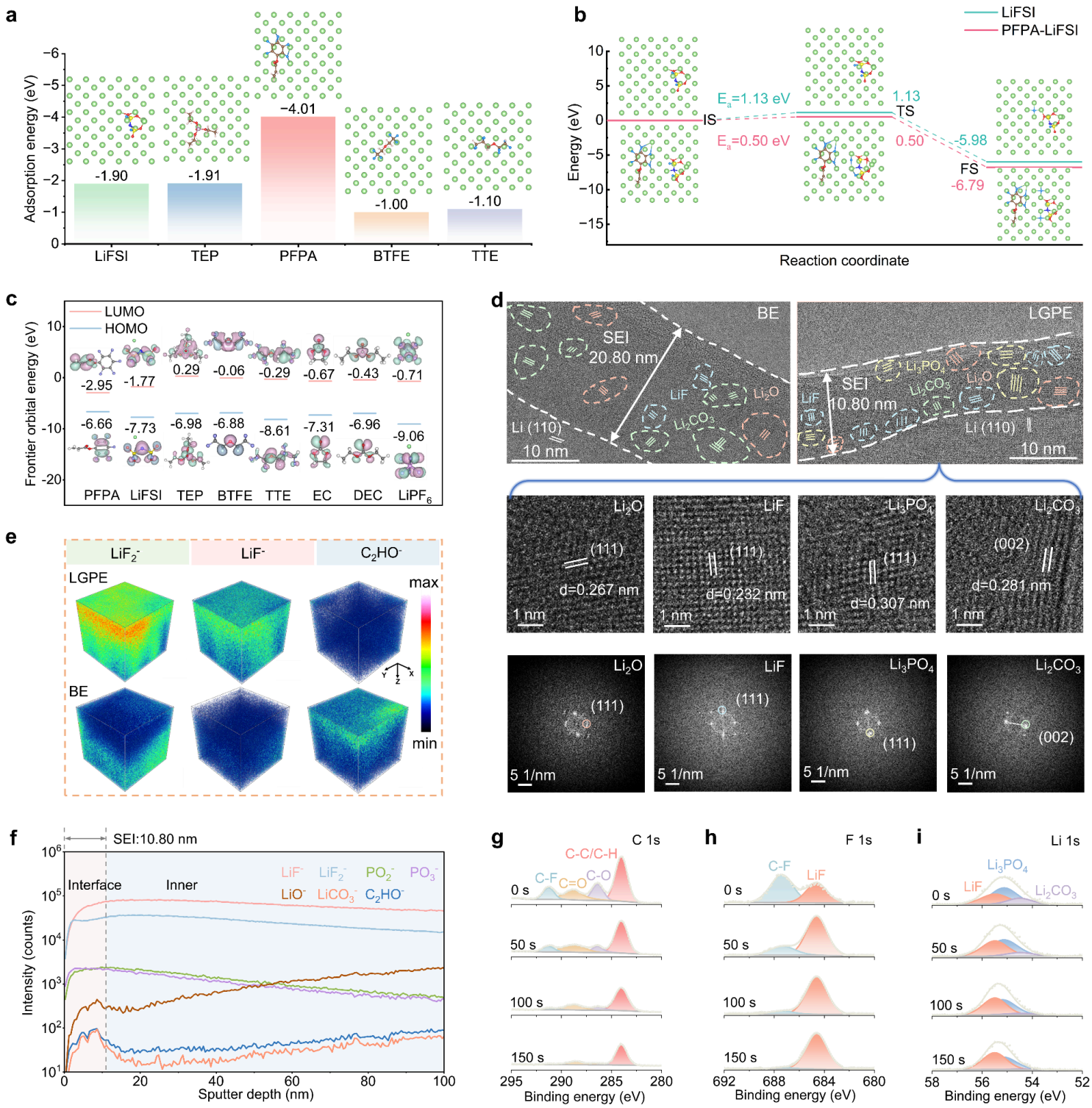


Figure 6

a) Adsorption energies of each component in LGPE. b) Energy profiles and corresponding activation barriers (E_a) for the reduction and dissociation of isolated LiFSI, and the PFPA-assisted LiFSI complex on the lithium anode. c) HOMO and LUMO energy levels of PFPA, LiFSI, TEP, BTFE, TTE, EC, DEC, and LiPF₆. d) Cryo-TEM images of SEI on lithium metal anode associated with BE and LGPE. Cryogenic HRTEM images and FFT of Li₂O, LiF, Li₃PO₄ and Li₂CO₃ of LGPE. e) 3D views of LiF₂⁻, LiF⁻ and C₂HO⁻ distributions in the SEI that formed in Li||NCM811 cells with the LGPE and BE. TOF-SIMS depth profiling of secondary ion fragments on the SEI using f) LGPE. XPS spectra of the Li anode in Li||Li batteries with LGPE at different etching times after 50 cycles: g) C 1s, h) F 1s and i) Li 1s .

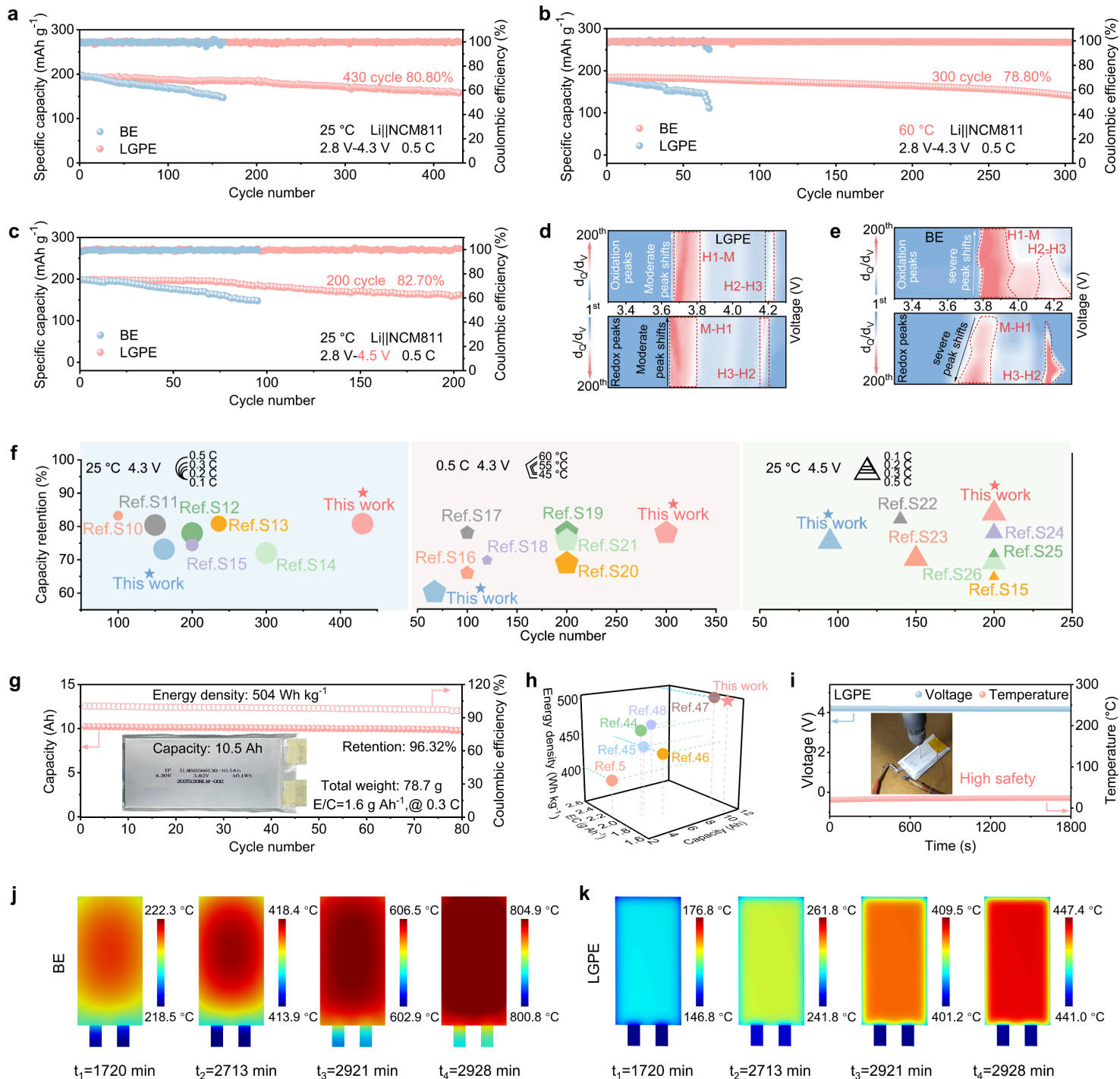


Figure 7

Cycling performance of Li||NCM811 cells using LGPE and BE at 2.8-4.3 V, a) at 25 °C, b) at 60 °C. c) Cycling performance of Li||NCM811 cells using LGPE and BE at 2.8-4.5 V. Corresponding dQ/dV curves of d) LGPE and e) BE with different cycles at 0.5 C. f) Electrochemical performance comparison of LGPE-based full cells with reported electrolytes under diverse conditions. g) Cycling performance of the 10.5 Ah NCM811 pouch cell over the voltage range of 2.8-4.3 V. The inset exhibits the optical image. h) Comparison of Li-metal pouch cells in previous reports and this work^{3,44,45,46,47,48}. i) The acupuncture experiment of Li||NCM811 pouch cells in LGPE and the corresponding changes in battery voltage and temperature. COMSOL simulation of the thermal runaway temperature distribution in j) BE and k) LGPE.

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