Batteries

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Practical High-Voltage Lithium Metal Batteries Enabled by the In-Situ Fabrication of Main-Chain Fluorinated Polymer Electrolytes

Jie Zhu, Peiran Bian, Guolin Sun, Jinping Zhang, Genglin Lou, Xingchen Song, Ruiqi Zhao, Jie Liu, Nuo Xu, Aihong Li, Xiangjian Wan, Yanfeng Ma, Chenxi Li, Hongtao Zhang,* and Yongsheng Chen*

Abstract: Polymer electrolytes are crucial for advancing safe, high-energy-density lithium batteries. Therefore, such electrolytes must possess stability with high-voltage cathodes and lithium metal, ensuring efficient interfacial contact and high room-temperature ionic conductivity. In this study, we present a novel main-chain fluorinated polymer electrolyte, FEOP, synthesized through cationic ring-opening polymerization. FEOP integrates high oxidative resistance of polytetrafluoroethylene with lithium metal compatibility of polyether, achieving an oxidation potential of up to 5.6 V and an anion-involved solvation structure. The exceptional stability enables NCM811 cells to deliver an impressive cycling life of 2000 cycles at 1 C up to 4.5 V. Furthermore, at ultrahigh cut-off voltages of 4.7 and 4.9 V, both NCM811 and LNMO cells demonstrate stable cycling over 700 cycles, marking the longest lifespan for polymer-based batteries under these challenging conditions. Moreover, 4.7 V solid-state lithium metal pouch cells incorporating FEOP exhibit an energy density of 405.3 Whkg⁻¹ and maintain stable cycling over 70 cycles, while successfully passing industry-standard nail penetration tests. Moreover, FEOP demonstrate excellent compatibility with ultra-high-loading electrode (70 mg cm^{-2}) , achieving an exceptional areal capacity of 16.2 mAh cm⁻². These results provide a solid foundation for designing practical electrolytes that enable next-generation high-energydensity and high-safety solid-state batteries.

[*] J. Zhu, P. Bian, G. Sun, J. Zhang, X. Song, R. Zhao, J. Liu, N. Xu, X. Wan, Y. Ma, C. Li, H. Zhang, Y. Chen The Centre of Nanoscale Science and Technology and Key Laboratory of Functional Polymer Materials, Institute of Polymer Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China

State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China

Introduction

The rapidly expanding renewable energy storage market has driven substantial demand for next-generation batteries combining high energy density and enhanced safety features. Among various anode materials, lithium metal batteries (LMBs) are particularly promising due to lithium metal's ultrahigh theoretical specific capacity $(3860 \text{ mAh g}^{-1})$ and the lowest reduction potential (-3.04 vs. SHE).^[1] On the cathode side, the utilization of Ni-rich LiNi_{1-x-v}Co_xMn_vO₂ (NCM, $1-x-y \ge 0.6$) with high specific capacity and extended charging cut-off voltage, can further enhance the energy density of LMBs.^[2] Specifically, increasing the charging cutoff voltage of the NCM cathode from the conventional 4.3 to 4.7 V (vs. Li/Li⁺) can lead to a 15-35% theoretical increase in discharge capacity.^[3] Furthermore, replacing the conventional liquid electrolyte with nonvolatile and nonleakable polymer electrolytes can significantly improve battery safety. This approach maintains compatibility with the existing lithium-ion batteries (LIBs) manufacturing infrastructure, rendering it highly promising for the largescale production of solid-state batteries. Consequently, highvoltage LMBs employing Ni-rich cathodes and polymer electrolytes are considered as compelling alternatives for advanced battery systems requiring high energy density and superior safety. However, the practical implementation of these batteries imposes stringent requirements on the polymer electrolytes, necessitating high ionic conductivity, compact interfacial contact, and compatibility with both high-voltage cathode and highly reactive lithium metal anode.^[4]

Among the diverse array of polymer electrolytes, mainchain fluorinated polymers, particularly polytetrafluoroethylene (PTFE) and polyvinylidenefluoride (PVDF),^[5] stand out due to their excellent oxidative stability, which makes

J. Zhu, P. Bian, G. Sun, J. Zhang, X. Song, R. Zhao, J. Liu, N. Xu, X. Wan, Y. Ma, C. Li, H. Zhang, Y. Chen Renewable Energy Conversion and Storage Center (RECAST), Nankai University, Tianjin 300071, China E-mail: s: E-mail: yschen99@nankai.edu.cn htzhang@nankai.edu.cn G. Lou, A. Li Tianjin Plannano Technology Company Limited, Tianjin 300071, China

Y. Ma, Y. Chen

them highly suitable for applications with high-voltage cathodes.^[6] This stability arises from their high degree of fluorination; the presence of highly electronegative fluorine atoms and the robustness of carbon–fluorine bonds provide remarkable resistance to oxidation.^[6b,7] Nonetheless, these polymers exhibit significant drawbacks despite their advantages. They are highly crystalline, which leads to poor ionic conductivity.^[8] Moreover, the fabrication of main-chain fluorinated polymer electrolytes often requires complex exsitu methods, such as blading and hot pressing. These procedures not only increase costs but also elevate interfacial resistance, attributed to the intricate manufacturing process involved.

In contrast to main-chain fluorinated polymers, polyether-based electrolytes, exemplified by the widely used polyethylene oxide (PEO), stand out for their exceptional reductive stability when supporting Li anode and high Li⁺ -conductivity, making them among the most promising candidates for solid-state LMBs.^[8-9] These polyether-based electrolytes can be directly fabricated within the battery through in situ cationic ring-opening polymerization, thereby enhancing interfacial contact.^[10] However, the strong electro-donating nature of the lone pair electrons on ether oxygen limit their oxidative stability to approximately 4 V vs. Li⁺/Li, particularly when used with transition metal oxide cathodes, which hinders their application in highvoltage LMB.^[11] To address this issue, various strategies have been explored, including the incorporation of inorganic fillers into the electrolytes or chemical modification with antioxidant functional groups.^[12] Approaches such as fluorine termination or side-chain fluorination have demonstrated potential by using electron-withdrawing fluorinated groups to reduce the electron cloud density on ether oxygen.^[13] Nevertheless, the degree of fluorination in these polymers is often insufficient, leading to suboptimal cycling performance of high-voltage LMBs, especially at high cutoff voltages exceeding 4.5 V. While some studies have explored the use of fluorinated acrylate crosslinkers to fabricate polymer electrolytes containing multiple -CF₂bonds, the main chain C-C bonds formed during the polymerization of acrylate monomers lead to lithium-ion conductivity that is inferior to that of polyether-based electrolytes.^[7c] Consequently, designing polyether-based polymer electrolyte that maintain both redox stability and compatibility with high-voltage LMBs continues to be a significant challenge and an area of urgent research focus.

Based on the molecular-level understanding of polyether and main-chain fluorinated polymers, we are inspired to explore the potential of integrating the ultra-stable carbonfluorine bond with the electron-donating ether bond within a singular polymer framework through an in situ fabrication method. This strategy seeks to harness the synergistic benefits of both polymer types to develop a new polymer electrolyte suitable for practical high-voltage LMBs. In this study, we successfully conceptualized and in situ synthesized a main-chain fluorinated and crosslinked polymer electrolyte, designated as FEOP, which features a polymer matrix composed of tetrafluoroethylene and ethylene oxide polymer chain segments. FEOP exhibits high ionic conductivity, compact interfacial contact, and exceptional redox stability, with an ultrahigh oxidation potential of up to 5.6 V. Its compatibility with high-voltage cathodes and lithium metal is significantly enhanced, attributed to the formation of an inorganic-rich solid electrolyte interface (SEI) and a cathode electrolyte interface (CEI), both of which are reinforced by the highly fluorinated polymer chain segments and the modulated solvation structure within FEOP. As a result, the assembled Li||LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (NCM811) battery demonstrates ultra-long cycling stability, achieving 2000 cycles at 4.5 V with the FEOP electrolyte. At even higher voltages of 4.7 V and 4.9 V, FEOP-based batteries achieve the best cycling performance of 700 cycles reported to date for polymer electrolyte-based batteries. Moreover, FEOP enables stable operation with an ultra-high-loading NCM811 cathode $(70 \text{ mg cm}^{-2}, 16 \text{ mAh cm}^{-2})$ at 4.7 V in high-voltage LMBs. Remarkably, a 5.6 Ah Li | NCM811 pouch cell at 4.7 V exhibits an outstanding energy density of 405.3 Whkg⁻¹, and a 2.6 Ah 18650 cylindrical LIB at 4.6 V achieve 85.4% capacity retention after 200 cycles, while concurrently demonstrating excellent safety performance under mechanical abuse. This study not only provides crucial insights into the design of polymer electrolytes compatible with high-voltage cathodes and lithium metal anode but also advances the development of practical, high-energy-density battery systems.

Results and Discussion

Synthesis of Main-Chain Fluorinated and Ethylene Oxide Polymer Electrolyte (FEOP)

In the synthesis of our designed main-chain fluorinated and ethylene oxide polymer electrolyte (FEOP), we introduced a novel fluorinated bifunctional epoxy compounds, 1,4bis(2',3'-epoxypropyl)perfluorobutane (BEPFB), as the crosslinker. Figure 1a shows that BEPFB crosslinker enables the seamless integration of tetrafluoroethylene units into the polymer main-chain backbone. The synergy of fluorine's electron-withdrawing properties and the carbon-fluorine (C-F) bonds in BEPFB endows the obtained polymer with remarkable oxidation stability. Simultaneously, the terminal epoxide groups on BEPFB facilitate the in situ fabrication of FEOP through cationic ring-opening polymerization (CROP). Incorporated ethylene oxide segments within the polymer matrix provide optimal compatibility with lithium metal, boosting Li⁺ ionic conductivity. During synthesis, lithium salt such as LiBF₄ and LiDFOB were employed as Lewis acid sources. Upon heating at 60°C for 24 h, these salts initiated the polymerization of precursor with BEPFB, yielding a solidified gel electrolyte (denoted as FEOP). This polymerization process occurs in situ within the battery, enabling the electrolyte to achieve a thickness of 25 µm, matching that of the PE separator. By contrast, as shown in Figure 1b, under identical condition, using the non-fluorinated crosslinker ethylene glycol diglycidyl ether (EGDE) resulted in an uncured, liquid oxide electrolyte (denoted as OLE). Additionally, as shown in Figure S1, the stress-strain



Figure 1. (a) Schematic illustration of the FEOP design. (b) Photographs of solidified FEOP and uncured OLE after heating the precursor solution at $60 \,^{\circ}$ C for 24 h, using BEPFB and EGDE as crosslinkers, respectively. (c) Temperature dependence of the ionic conductivity for FEOP and OLE, with data fitted using the Arrhenius transport model to calculate activation energies. (d) Linear sweep voltammetry (LSV) curves of FEOP and OLE.

curve of FEOP highlights the enhanced mechanical properties conferred by the fluorinated network.

The temperature dependence of the ionic conductivity of the fluorinated polymer electrolyte FEOP and the nonfluorinated OLE is shown in Figure 1c. At room temperature (25 °C), FEOP achieves an ionic conductivity of 1 mS cm⁻¹, which is sufficient for practical applications in LMBs. Based on the Arrhenius equation, the activation energy (E_a) of FEOP was calculated to be 15.68 kJ mol⁻¹, lower than that of OLE $(20.19 \text{ kJmol}^{-1})$. This reduced activation energy in FEOP indicates enhanced Li⁺ transportation within the polymer electrolyte. Further characterization reveals that the main-chain fluorinated FEOP achieves a transference number (t_{Li}^{+}) of 0.51 (Figure S2), thereby facilitating uniform lithium deposition and suppressing both electrolyte decomposition and dendrite formation.^[14] Notably, increasing the polymer-to-solvent weight ratio from 1:10 to 1:5 further raises the t_{1i}^{+} from 0.51 to 0.61, demonstrating that fluorination enhances the rapid transport of Li⁺ (Figure S3). The electrochemical stability of FEOP and OLE electrolytes was further evaluated using linear sweep voltammetry (LSV) and density functional theory (DFT) calculations. Figure 1d reveals that FEOP exhibits a remarkable oxidation potential up to 5.6 V, surpassing OLE. This enhanced stability is crucial for ensuring compatibility with high-voltage cathode materials. Additionally, DFT calculations (Figure S4) demonstrate that FEOP has a reduced highest occupied molecular orbital (HOMO) level, indicative of improved antioxidation properties. These advantageous characteristics can be attributed to the stability of the carbon-fluorine (C–F) bonds and the electron-withdrawing properties of the fluorine atoms within the polymer's main chain. Differential electrochemical mass spectrometry (DEMS) was further employed on Li||NCM811 cells using both FEOP and the control OLE electrolytes to assess the stability of these electrolyte systems and identify oxidative decomposition products. As illustrated in Figure S5, cycling the Li FEOP NCM811 cell at a high voltage of 4.6 V generated only a minimal amount of CO₂ gas, highlighting the superior oxidative stability of FEOP. In stark contrast, the Li|OLE| NCM811 cell released a significant amount of CO₂ and exhibited signs of overcharging once the voltage exceeded 4 V.

The lithium metal compatibility of polymer electrolytes was evaluated using both Li || Li symmetric cells and Li || Cu cells. As shown in Figure S6, at a current density of 0.5 mA cm⁻², the Li | FEOP | Li symmetric cell delivers extended cycling stability of 2000 h. In contrast, the OLEbased cell exhibits a steep voltage increase within 180 h due to the persistent side reactions. Additionally, as depicted in Figure S7, FEOP achieves a superior critical current density of 3.25 mA cm⁻², surpassing the 2 mA cm⁻² of OLE, indicating the FEOP's superior capability to suppress lithium dendrite formation. The Li|FEOP|Li symmetric cell also displays superior rate performance with minimal overpotentials of 38.1, 56.7, 108.7, and 172.7 mV at current densities of 0.5, 1, 2, and 3 mA cm⁻², respectively (Figure S8). Morphological analysis reveals that metallic lithium deposition in the Li | FEOP | Cu cell exhibits a dense and coarsely granular structure, in stark contrast to the loose and elongated tubular structure observed in the Li|OLE|Cu cell (Figure S9). This compact lithium deposition in the FEOP system, with a lower surface-to-volume ratio, effectively mitigates side reactions between the Li anode and the electrolyte while suppressing Li dendrite growth. Consequently, the Li | FEOP | Cu cell achieves a stable cycling over 200 cycles with a high Coulombic efficiency (CE) of 96.3 %. In comparison, OLE exhibited pronounced side reactions, yielding a CE of only 93.0% (Figure S10). These results demonstrate the enhanced compatibility of the fluorinated polymer electrolyte FEOP with the lithium metal anode compared to OLE.

Characterization of Solvation Structure and Solid Electrolyte Interphase (SEI)

The coordination environments of solvents and anions in electrolytes were initially investigated using Raman spectroscopy. Figure 2a reveals an absorption band ranging from 730-750 cm⁻¹ corresponding to the S-N-S stretching vibration of the bis(trifluoromethanesulfonyl)imide anion (TFSI⁻). The FEOP electrolyte displays a blue shift relative to OLE, indicating enhanced coordination between TFSIanions and Li⁺ ions. This indicates an increased tendency to form contact ion pairs (CIPs) and aggregated ion pairs (AGGs) in the FEOP electrolyte, promoting the formation of an inorganic-rich SEI and enhancing lithium anode stability.^[15] Further analysis of solvent molecules revealed distinctive vibrational patterns. As shown in Figure 2b and Figure S11, free fluoroethylene carbonate (FEC) molecule exhibits C-F stretching vibration, while free fluoroethylene methyl carbonate (FEMC) molecule shows O-CH₃ stretching vibration, both in the range of 905-935 cm^{-1.[16]} Compared to OLE, FEOP showed reduced peak intensity for free solvent (FEC and FEMC) molecules and increased intensity for those coordinated, indicating enhanced oxidative stability.^[17] This optimized coordination structure significantly enhanced the oxidative stability of FEOP, which is crucial for maintaining long-term battery performance and safety. To further explore the solvation structure of electrolytes, molecular dynamics (MD) simulations were employed, as detailed in Figure 2c and Figures S12 and S13. These simulations revealed that the FEOP electrolyte exhibited higher peak intensities for Li–O (DFOB⁻), Li–O (TFSI⁻), and Li–F (BF₄⁻), indicating enhanced coordination between anions and Li⁺ ions.^[18] The MD simulations corroborate the Raman spectroscopy findings, confirming stronger Li⁺-anion interactions in the FEOP electrolyte and accounting for its enhanced lithium anode stability.

The main-chain fluorinated polymer network and unique solvation structure of FEOP significantly influence electrolyte-Li metal anode interfacial chemistry. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) measurements were employed to investigate the SEI component distribution. As shown in Figure 2d-f, key compounds such as LiF2-, C2H3O-, and Li3N were identified in the FEOP electrolyte. Notably, Li₃N is only present in FEOP, indicating increased anion involvement, especially TFSI-, in SEI formation. This finding aligns with the solvation structure analysis of FEOP that the increased CIPs and AGGs promote anion decomposition. The presence of Li₃N significantly enhances the interfacial properties due to its high Li⁺ conductivity, which improvs diffusion kinetics and enables uniform lithium ions deposition.^[19] Moreover, the enrichment of LiF at the SEI surface, attributed to both the fluorinated polymer network and the anion-enriched solvation structure, strengthens the interface's mechanical stability.^[20] In contrast, an inhomogeneous, thick SEI, characterized by an organic components-rich outer layer and inorganic components-rich inner layer, was formed in OLE. This distinct structure primarily results from OLE decomposition with limited TFSI- reduction. X-ray photoelectron spectroscopy (XPS) analysis at varying etch depths provided quantitative insights into SEI composition, as shown in Figure S14-S16. The higher ratio of C=O suggests that organic components dominate the OLE-derived SEI, whereas the FEOP-derived SEI shows more inorganic content, as evidenced by increased levels of LiF, Li₃N, and B-O species. Additionally, as shown in Figure S17a-d, although the components of the LE electrolyte also contribute to the formation of a stable interface, the SEI composition in the FEOP system exhibits stronger LiF and Li-N XPS signals compared to the LE electrolyte system. This suggests that the polymer backbone of FEOP facilitates the formation of a more stable Li anode/electrolyte interface.

Performance of FEOP-Based Batteries using High-Voltage Cathodes

Our findings reveal that FEOP offers dual benefits: stability with lithium metal anodes and exceptional oxidation resistance up to 5.6 V. With these properties, FEOP is compatible with high-voltage cathode materials, including high-nickel NCM811 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO), making it suitable for application in advanced high-voltage LMBs. To evaluate

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Figure 2. (a-b) Raman spectra of FEOP and OLE. (c) Radial distribution function of the FEOP obtained by molecular dynamics simulation. (d) Time-of-flight secondary ion mass spectrometry (TOF-SIMS) depth profiling of selected secondary ion fragments of the SEI in FEOP and OLE. TOF-SIMS 3D spatial distribution of LiF⁻, $C_2H_3O^-$, and Li_3N fragments of the SEI in (e) FEOP and (f) OLE. Relative composition of SEI at different sputtering times in (g) FEOP and (h) OLE, obtained by XPS analysis.

performance under demanding conditions, coin-type Li|| NCM811 batteries were tested at elevated cut-off voltages (4.5–4.7 V). When operating at 4.5 V and 1 C, as illustrated in Figure 3a and Figure S18a, the Li|FEOP|NCM811 battery demonstrates remarkable cycling stability, enduring 2000 cycles with a capacity retention of 74.1 % (a minimal decay rate of 0.013 % per cycle). In contrast, OLE- and LEbased cells without the main-chain fluorinated polymer network displayed rapid capacity decay, with 79.0 % and 55.8 % capacity retention after only 500 cycles, respectively. When elevated to an operating voltage of 4.7 V, the FEOPbased Li||NMC811 battery delivered an impressive specific capacity of 206.6 mAh g⁻¹ (at 1 C) and exceptional cycling stability of 700 cycles (68.1 % capacity retention). FEOP not only surpasses OLE- and LE-based cells but also represents the longest lifespan reported for polymer electrolytes-based cells with NCM811 cathode at this ultra-high voltage of 4.7 V, as evidenced in Figure 3b, Figure S18b and Table S1. Moreover, FEOP also exhibits exceptional electrochemical performance across a wide range of temperatures (from -14to 60 °C). As shown in Figure S19 and S20, Li|FEOP| NCM811 cells deliver a high specific capacity of 185.8 mAh g⁻¹ at -14 °C and an impressive specific capacity of 228.5 mAh g⁻¹ at 60 °C.

The exceptional oxidation stability of FEOP enables its application in ultra-high-voltage LNMO cathodes at 4.9 V.



Figure 3. Cycling performances of Li | NCM811 batteries with FEOP and OLE at 1 C with the charge cut-off voltage of (a) 4.5 V and (b) 4.7 V. (c) Cycling performances of Li | LNMO batteries with FEOP and OLE at 1 C with the charge cut-off voltage of 4.9 V. Rate performances of Li | NCM811 batteries with FEOP and OLE at 1 C with the charge cut-off voltage of 4.9 V. Rate performances of Li | NCM811 batteries with FEOP and OLE at 1 C with the charge cut-off voltage of 4.9 V. Rate performances of Li | NCM811 batteries with FEOP and OLE at 1 C with the charge cut-off voltage of 4.9 V. Rate performances of Li | NCM811 batteries with FEOP and OLE at 1 C with the charge cut-off voltage of 4.9 V. Rate performances of Li | NCM811 batteries with FEOP and OLE with the charge cut-off voltage of (d) 4.5 V and (e) 4.7 V. (f) Comparison of Li | NCM811 batteries at room temperature between this work and recently reported polymer electrolytes in terms of cycle numbers and specific capacity. The related references were given in Table S1.

As shown in Figure 3c, the Li |FEOP|LNMO cell achieved an ultra-long cycling performance of 700 cycles, delivering a discharge capacity of 145.6 mAh g⁻¹ and maintaining a high capacity retention of 78.0 %, which is the best result among polymer electrolyte-based LNMO batteries (Table S1). Conversely, the OLE system, with its non-fluorinated polyether, showed poor compatibility with the 4.9 V–LNMO cathode, displaying a first-cycle CE of only 50.5 % due to severe electrolyte decomposition. By contrast, the incorporation of tetrafluoroethylene segments into the polyether main chain of FEOP significantly enhanced stability at 4.9 V, achieving

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87.7% first-cycle CE and notable improvements in both capacity and cycling stability. The outstanding electrochemical performance of FEOP-based LNMO cells at 4.9 V can be attributed to the stable fluorinated polymer backbone structure of FEOP and the formation of a uniform and inorganic-rich CEI layer on the LNMO surface (Figure S21 and S22). Moreover, Figure 3d-e reveal that at both 4.5 and 4.7 V, the Li|FEOP|NCM811 cells exhibit superior capacities compared to OLE-based counterparts across all testing rates. Even at an aggressive rate of 10 C, the cells achieve capacities of 151.2 mAh g^{-1} at 4.5 V and 180.4 mAh g⁻¹ at



4.7 V. FEOP's outstanding rate performance at high cut-off voltage was further validated by Li|FEOP|LNMO cells operating at 4.9 V (Figure S23). Figure 3f, S24–S26 and Table S1 provide a comparative assessment of the cycling performance for various polymer-based cells, supported by statistical data. These results particularly highlight FEOP's superior compatibility with high-voltage cathodes at elevated cut-off voltages.

Characterization of Cathode Electrolyte Interphase (CEI)

The detailed investigation into the chemical composition and interface structure of the cycled cathode in high-voltage LMBs using FEOP electrolyte offers valuable insights into its enhanced performance. Surface analysis of the NCM811 cathode after 50 cycles at 4.5 V was conducted using TOF-SIMS, as depicted in Figure 4a–c. The results revealed that, compared to OLE electrolyte, the FEOP system exhibited lower signals for $-C_2H_3O$, indicating decreased electrolyte oxidation on the cathode surface.^[21] Additionally, the CEI formed in the FEOP system was notably thinner, suggesting



Figure 4. (a) TOF-SIMS depth profiling of several secondary ion fragments of the CEI in FEOP and OLE. TOF-SIMS 3D spatial distribution of LiF⁻, $C_2H_3O^-$, and LiB₂O₄ fragments of the CEI in (b) FEOP and (c) OLE. Relative composition of CEI at different sputtering times in (d) FEOP and (e) OLE, obtained by XPS analysis. TEM images and diffraction patterns of NCM811 cathodes harvested from Li || NCM811 cells using (f) FEOP and (g) OLE after 50 cycles at 1 C.

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reduced electrolyte decomposition. More importantly, TOF-SIMS analysis revealed elevated concentrations of inorganic components, such as LiF_2^- and LiB_2O_4 , within the CEI of FEOP.^[22] These inorganic components form a protective layer that preserves cathode structural integrity and enhances interface stability during cycling.^[23] Complementary XPS analysis, as shown in Figure 4d-e and Figure S27–S29, further confirms that FEOP, compared to OLE and LE, generates a LiF- and B-rich protective layer. This advantageous property stems from FEOP's fluorinated backbone and its anion-involved solvation structure, which facilitates the generation of a stable inorganic layer at the interface.

Transmission electron microscopy (TEM) analysis revealed the thickness of the CEI on the NCM811 cathode. As shown in Figure 4f-g, the uniform CEI formed on the surface of the cycled NCM811 with FEOP exhibited a thickness of approximately 1.9 nm, significantly thinner than that formed with conventional OLE electrolytes. This thin yet robust CEI effectively preserves the structural integrity of the cathode during cycling, thereby leading to improved rate performance and cycling stability.^[24] Moreover, the NCM811 cathode cycled in FEOP maintains its original layered structure, with an interplanar distance indexed to the planar (003) crystal plane at 0.204 nm, showing no evidence of the detrimental rock-salt phase transition typically observed with thicker CEIs.[5b] This structural preservation can be attributed to the protective properties of the inorganic-rich CEI formed in the FEOP system. Additionally, as shown in Figure S30, electrochemical floating analysis (EFA) further confirmed the superior compatibility of FEOP with NCM811. The Li|FEOP|NCM811 battery demonstrated remarkable stability, maintaining a low leakage current of just 2.1 µA even at 4.9 V (across the 4.2-4.9 V range). In contrast, the Li|OLE|NCM811 battery exhibited significantly higher and progressively increasing current at 4.8 V. These results validate the superior high-voltage stability achieved through the formation of the inorganic-rich CEI in FEOP.

Practical Batteries, Ultra-High Loading Cathode and Safety Test

The outstanding compatibility of FEOP with both lithium anodes and NCM811 cathodes enabled the development of high-voltage (4.6 and 4.7 V) practical batteries in solidified 18650 cylindrical and pouch configurations. Industrystandard 18650 cylindrical LIBs were fabricated with in situ fabricated FEOP electrolyte, with specifications detailed in Figure 5a and Table S2 and S3. As shown in Figure 5b, the assembled NCM523 | FEOP | Graphite cylindrical cell exhibited excellent performance, achieving a high capacity of 2.60 Ah at 0.1 C with a cut-off voltage of 4.6 V, surpassing the 2.01 Ah capacity at 4.2 V (Figure S31). These 4.6 V FEOPbased 18650 cylindrical cells achieved an energy density of 216.0 Wh kg⁻¹ and maintained excellent cycling stability over 200 cycles with a high capacity retention of 85.4%. Energy density was further improved by incorporating a siliconbased anode material, as illustrated in Figure 5c, Figure S32, and Table S3. The assembled 3-Ah-level LIB with NCM811

cathode and Si/C anode achieved a remarkable capacity of 3.50 Ah at 4.6 V, resulting in an exceptional energy density of up to 274.1 Whkg⁻¹ (including the overall weight with steal packaging). These values surpass those of currently available commercial 18650 cells (Figure 5d and Table S4), underscoring the significant advantages of FEOP's high-voltage stability in enhancing energy density for practical applications.

Moreover, increasing cathode mass loading is an effective strategy for maximizing energy density.^[25] However, implementing high-loading cathodes in solid-state batteries has historically proven to be challenging .^[26] Leveraging our previously developed dry-processed technology, we successfully integrated the FEOP electrolyte with an ultra-thick (500 µm) cathode and a 50 µm Li foil, as illustrated in Figure 5e.^[27] This innovative approach enabled the development of the first polymer-based solid-state battery with such a high cathode loading. Remarkably, the Li|FEOP| NCM811 battery, featuring an unprecedented cathode loading of 70 mg cm⁻², exhibited an ultrahigh areal capacity of 16.2 mAh cm⁻² while maintaining a capacity retention of 87.4% after 40 cycles (Figure 5f). This performance at an operating voltage of 4.7 V surpasses all previously reported polymer-based electrolyte systems, establishing a new benchmark for high-loading solid-state batteries, as shown in Figure 5g and Table S5. Additionally, cross-sectional scanning electron microscopy (SEM) was employed to confirm the excellent compatibility between the in situ polymerized FEOP and the ultra-thick (500 µm) cathode. As shown in Figure S33, energy-dispersive X-ray spectroscopy (EDS) mapping of element B, originating from the electrolyte salts LiBF₄ and LiDFOB, clearly demonstrates that the FEOP electrolyte has uniformly infiltrated the ultra-thick electrode, forming a robust interface with the electrode material. This highlights the significant potential of FEOP for future high-energy-density solid-state batteries.

To achieve higher energy density, FEOP was employed in multilayer lithium metal pouch cells with optimized parameters (20 μ m Li, 3.34 mAh cm⁻² NCM811, N/P=1.3, E/C=3 gAh⁻¹, detailed in Table S6). As depicted in Figure 6a and b, the 4.7 V FEOP-based Li metal pouch cell delivered a capacity of 1.19 Ah and achieved a high energy density of 332.1 Whkg⁻¹ (based on the total weight of the pouch cell, Figure S34), while maintaining 77.2% capacity retention over 70 cycles. In addition, when operated 4.3 V, the FEOP-based pouch cell also delivered an energy density of 298 Whkg⁻¹ with a capacity of 1.01 Ah (Figure S35 and Table S6). Furthermore, an advanced configuration was developed with the goal of achieving 400 $Wh kg^{-1}$ (Figure 6c and Table S7). This FEOP-based LMB incorporated an NCM811 cathode (19 mg cm⁻²), a thin lithium anode (40 μ m, N/P ratio is 1.0), and low electrolyte content (3.8 g Ah^{-1}). As shown in Figure 6d and 6e, the resulting 5.6 Ah pouch cell, operating at 4.7 V, delivered an initial discharge energy of 21.83 Wh with a total weight of 53.86 g (Figure S36), achieving an impressive practical energy density of 405.3 Wh kg⁻¹. The energy densities and comparative analysis of these assembled solid-state LMBs and LIBs are summarized in Figure S37, highlighting the significant

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Figure 5. (a) Configurations of 1.9-Ah and 3.3-Ah solid-state 18650 cylindrical LIBs for practical application. (b) Cycling performances of the 1.9-Ah solid-state 18650 cylindrical LIB (anode: Graphite) at 0.1 C under 4.6 V. (c) Cycling performances of the 3.3-Ah solid-state 18650 cylindrical LIB (anode: Silicon + Carbon) at 0.1 C under 4.6 V. (d) The comparison of commercial cylindrical LIBs and cylindrical LIBs using FEOP in terms of energy density and charge voltage. (e) Configurations of the ultrahigh-mass-loading Li | FEOP | NCM811 full cells. (f) Cycling performance of the ultrahigh-mass-loading Li | FEOP | NCM811 full cells between this work and recently reported polymer electrolyte-based batteries in terms of areal capacity and mass loading of active material. The related references are given in Table S5.

advancements enabled by FEOP in solid-state battery technology.

To evaluate the practical safety of FEOP-based LMBs under extreme short-circuit conditions, industry-standard nail penetration tests were performed on pouch cells and 18650 cylindrical batteries under a fully charged state. As shown in Figure 6f-h and Video S1, the Ah-level FEOPbased solid-state pouch cell exhibits outstanding safety, with no electrolyte leakage or combustion during nail penetration, attributed to the solidified polymer electrolyte. Moreover, as shown in Figure 6i and Video S2, the 18650 Li FEOP NCM811 cylindrical cell also remained intact, without explosion or leakage after nail penetration. Notably, an overcharging test was conducted on a 5-Ah FEOP-based pouch cell (Figure S38), where the battery was initially charged to 4.7 V and then continuously charged at this ultrahigh voltage for over 10 hours. Impressively, the battery achieved a 7-Ah overcharged capacity without any explosion or fire. Consequently, the FEOP-based batteries demonstrate exceptional safety and adaptability under a broad range of harsh conditions and configurations, rendering them highly suitable for commercial applications.

Conclusion

In this work, a main-chain fluorinated polymer electrolyte FEOP was successfully in situ fabricated using a novel polyfluorinated crosslinker through cationic ring-opening polymerization. The integration of ultra-stable C-F bonds and numerous electron-withdrawing fluorine atoms into the polymer network significantly bolstered the oxidation stability of the electrolyte, achieving an impressive oxidation potential of 5.6 V. Combined with the anion-involved solvation structure, the resulting inorganic-rich SEI and CEI contribute to the exceptional compatibility of FEOP with both lithium metal anode and high-voltage cathodes. Consequently, the developed FEOP, combining the high oxidation resistance of PTFE and the lithium metal compatibility of polyether, is exceptionally suitable for high-voltage LMBs. When paired with 4.5 V-NCM811 cathode, the battery achieved an ultra-long cycling of 2000 cycles at 1 C rate with a capacity retention of 74.1 %. Upon increasing the cut-off voltage to 4.7 V for NCM811 and 4.9 V for LNMO, the FEOP-based cells demonstrate remarkable stability of 700 cycles, representing the longest lifespan for polymer electrolyte-based batteries at such high voltages. Remark-

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Figure 6. (a) Charge-discharge curves of the 1-Ah solid-state LMB at 0.1 C under 4.7 V. (b) Cycling performances of the 1-Ah solid-state LMB at 0.1 C under 4.7 V. (c) Configuration of the 5-Ah solid-state LMB. (d) Charge-discharge curves of the 5-Ah solid-state LMB at 0.1 C under 4.7 V. (e) Cycling performances of the 5-Ah solid-state lithium metal batteries at 0.1 C under 4.7 V. (f) Photograph of the 1-Ah solid-state LMB lighting up the light board. (g-h) Nail penetration test for 1-Ah solid-state LMB using FEOP. (i) Nail penetration test for solid-state 18650 cylindrical cell using FEOP.

ably, FEOP-based batteries can even pair with an ultra-thick cathode (500 µm) and stably cycle at 4.7 V, achieving a record-high cathode mass loading of 70 mg cm^{-2} (areal capacity of 16.2 mAh cm⁻²). Consequently, by leveraging the developed FEOP, we achieved a 4.7 V lithium metal pouch cell with an energy density exceeding 400 Wh kg⁻¹. Additionally, the assembled 18650 cylindrical batteries achieve an energy density of over 270 Wh kg⁻¹, significantly surpassing commercial cylindrical LIBs. These high-energy-density solid-state batteries using FEOP have successfully passed the strict nail penetration test, demonstrating their practical viability. This research effectively addresses the challenges of polymer electrolytes in terms of ionic conductivity, interfacial contact, lithium metal anodes, and high-voltage cathodes, providing a promising strategy for the practical implementation of high-voltage solid-state LMBs.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

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

Keywords: polymer electrolyte · main-chain fluorinated polymer · in situ crosslinking · long cycling · high-voltage

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Batteries

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Practical High-Voltage Lithium Metal Batteries Enabled by the In-Situ Fabrication of Main-Chain Fluorinated Polymer Electrolytes



A main-chain fluorinated polymer electrolyte that integrates high oxidative resistance of polytetrafluoroethylene with lithium metal compatibility of polyether (FEOP) was developed, enabling the practical 4.7 V solid-state lithium metal pouch cells with an energy density of 405.3 Wh kg⁻¹ and maintain stable cycling over 70 cycles.