Supporting Information

In-situ Janus Polymerization of Cyclic Phosphate and Ethers Affording P/F

Copolymer Electrolyte for High-safety Lithium Metal Batteries with Long-

cycle Life

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1. Experimental

1.1. Materials

Lithium metal purchased from Tianjin Zhongneng Lithium Industry Co. Al current collector and CR 2032-type coin-cell cases were purchased from Guangdong Canrd New Energy Technology Co. Ltd. 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) was purchased from Shanghai Songjing New Energy Technology Co. Conductive carbon black SP, adhesive polyvinylidene fluoride (PVDF), LiFePO₄ (LFP), lithium bis(trifluoromethane) sulfonimide (LiTFSI), lithium difluoroxalate borate (LiDFOB), lithium hexafluorophosphate (LiPF₆), lithium trifluoromethanesulfonate (LiOTf) was purchased from Shanghai Songjing New Energy Technology Co. Ltd. LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC₈₁₁) cathode was purchased from Guangdong Canrd New Energy Technology Co., Ltd. The battery separator (Celgard 2325) was purchased from Celgard, LLC. N-methyl-2-pyrrolidone (NMP) was purchased from Tianjin Kermel Chemical Reagent Co. Ltd. tris(pentafluorophenyl)borane (TB), perchloric acid (HClO₄), Aluminum trifluoromethanesulfonate (Al(OTf)₃) was purchased from Adamas, and Scandium trifluoromethanesulfonate (Sc(OTf)₃), 2-chloro-2-oxo-1,3,2-dioxaphospholane (COP) was purchased from Aladdin.

1.2. Syntheses

The 2-methoxy-1,3,2-dioxaphospholane-2-oxide (methyl ethylene phosphate, MeOEP) were synthesized. To a stirred solution of methanol (0.32 g, 10 mmol) and triethylamine (1.01 g, 10 mmol) were added to anhydrous tetrahydrofuran (THF, 50 ml) in an ice-water bath. 2-chloro-2-oxo-1,3,2-dioxaphospholane (COP, 1.42 g, 1 mmol) in 30 mL of anhydrous THF was added dropwise to the above mixture over half hour, and the reaction mixture was stirred for 12 hours at room temperature. Thereafter, triethylamine hydrochloride was removed by filtration and THF was removed by rotary evaporation. The pure product was obtained as a colorless liquid after vacuum distillation with a yield of 70%.¹H NMR (600 MHz, D₆-DMSO, δ /ppm): 4.48 ~ 4.36 (m, 4H, -OCH₂CH₂O-), 3.74 ~ 3.70 (d, 3H, -OCH₃). ³¹P NMR (600 MHz, D₆-DMSO, δ /ppm): 17.9 ppm.

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1.3. Preparation of copolymer electrolytes

To ensure MeOEP polymerisation, Sc(OTf)₃ was first dissolved in MeOEP to obtain a solution, and the gel Sc-MeOEP was obtained after 12 hours of reaction. The conversion rate is about 40%, and then the mixed electrolyte of TFPO/DOL-LiTFSI is added to the Sc-MeOEP gel to obtain the liquid precursor Sc-MeOEP-TFPO/DOL, then Sc-MeOEP-TFPO/DOL is assembled in coin batteries. Specifically, dissolve 0.01 mmol Sc(OTf)₃ in 1 mmol MeOEP to obtain Sc-MeOEP, dissolve 2 mmol LiTFSI in 1 mL TFPO/DOL(1/9) to obtain electrolyte TFPO/DOL, add TFPO/DOL solution to gel Sc-MeOEP and stir to obtain the precursor Sc-MeOEP-TFPO/DOL, other proportions of electrolytes also follow a similar method, and the precursor was encapsulated in a button cell according to the method of using liquid electrolytes, the copolymer electrolytes is prepared after being placed at room temperature for a period of time.

1.4. Electrode materials preparation

The LFP cathode was prepared by mixing LFP powder with acetylene black and poly(vinylidene fluoride) (PVDF) mixer at a weight ratio of 80:10:10 in N-methyl-2- pyrrolidone (NMP). The slurry was then coated on an aluminum foil and dried under vacuum at 80 °C for 24 hours, the active mass loading of LFP cathode was controlled at ~2 mg cm⁻². LiNi_{0.8}MnO_{.1}Co_{0.1}O₂ (NMC₈₁₁) cathode was prepared by mixing NMC₈₁₁ powder with acetylene black and PVDF mixer at a weight ratio of 80:10:10 in NMP. The slurry was then coated on an aluminum foil and dried under vacuum at 80 °C for 24 h, the active mass loading of NMC₈₁₁ was controlled at 3 ~ 5 mg cm⁻².

1.5. Materials characterization

The instrument used for the electrolyte hydrogen nuclear magnetic resonance (¹H NMR) was performed on JNM-ECZ400S, the 600 MHz Nuclear Magnetic Resonance was performed on JNM-ECZ400S. (NMR spectra were measured using a Bruker Avance NED 600 MHz spectrometer, the chemical shifts in parts per million (ppm) were referenced to a tetramethylsilane standard.) Electrode surface topography was observed by a scanning electron microscope (SEM, Hitachi of Japan S-4800). Electrode surface composition was analyzed by X-ray photoelectron spectroscopy (XPS), the experiments were carried out on a Shimazu Axis Suprar, the calibration of the binding energy peak positions is applied according to C 1s located at 284.8 eV. All cells were disassembled in an argon-filled glove box with O_2 and H_2O kept at < 0.1 ppm. The cells were disassembled in an Ar-filled glove box, rinsed three times with DOL solvent, and then dried under vacuum, and thus it was assumed that no residual salt or solvent remained on the surface of the electrodes. Argon-filled sample transfer chamber was adopted to avoid the air exposure and surface modification for lithium during transferring process before characterization.

1.6. Electrochemical measurements

Using an Ar-filled glove box, Li||LFP cells, Li||NMC₈₁₁ and Li-Li cells were assembled in a standard 2032-type coin-cell, using a LAND CT2001A instrument (Wuhan Jinnuo Electronic Co. Ltd.), galvanostatic charge–discharge tests of coin cells were performed at different current densities. Electrochemical impedance spectroscopy (EIS) and Li⁺ transference number (t_{Li^+}) was carried out using Electrochemical workstation (CS310H, CorrTest). The LSV testing is carried out using Li-Al half-cells at a scan rate of 10 mV s⁻¹ from open circuit voltage (OCV) to 6.0 V. The EIS of the cell was tested with an electrochemical workstation in the frequency range $10^5 - 10^{-2}$ Hz.

1.7. Theoretical calculations

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of the MeOEP, TFPO and DOL were calculated using density functional theory calculation (DFT) at the Gaussian 16, Revision C.02 (b3lyp def2svp em=gd3bj). 2. Supplementary tables and figures



electrolytes. (a) A Yrmada group investigated a fluorapatite cyclic phosphate 2-(2,2,2-trifluoroethoxy)-1,3,2dioxaphospholane 2-oxide (TFEP) as ester-based electrolyte co-solvent.¹ (b) J. Chen et al. reported a monofluorinated cosolvent diethyl fluoridophosphate.² (c) M. Chen et al. reported F/P hybrid polyolefins with ether-based side chain.³ (d) Y. Chen et al. prepared F/P-containing gel polyester-based electrolyte by in-situ polymerization.⁴ (e) In this work, the synthesis of F/P gel polyether-based electrolyte via In-situ Janus polymerization of cyclic phosphate, fluoridated cyclic ether and 1,3-dioxolane.

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The MeOEP monomer was synthesized in a one-step reaction using 2-chloro-2-oxo-1,3,2-dioxaphospholane (COP) and methanol as starting materials (Scheme S2). In its ¹H NMR spectrum recorded in deuterated dimethyl sulfoxide (D₆-DMSO) (Figure R1), in addition to the solvent peak for DMSO (2.50 ppm; all deuterated solvent in this work is D₆-DMSO), the double peaks observed at 3.74–3.70 ppm corresponds to the three hydrogen atoms (a: -CH₃) of the methyl group on the cyclic side chain. These three hydrogen atoms are split into double peaks due to coupling with the phosphorus atom two bonds away. The multiple peaks in the 4.48–4.36 ppm region is assigned to the four methylene hydrogen atoms on the cyclic structure (b: $O-CH_2-CH_2-O$). The integration ratio of these two peaks is 4:3 (Fig. S1a), consistent with the proposed assignments, confirming the successful synthesis of MeOEP. Furthermore, the ³¹P NMR spectrum of MeOEP (Fig. S1b) displays a single peak at 17.9 ppm, with no residual peaks from the starting material COP (inset in Fig. 1b shows the COP peak at 22.7 ppm). This observation further corroborates the successful synthesis of MeOEP.



Fig. S1 MeOEP monomer (¹H NMR and ³¹P NMR in D₆-DMSO).

When MeOEP was polymerized into a gel (denoted as PMeOEP), its ¹H NMR spectrum (Fig. S2a) showed a new broad polymer peak (b') at 4.18 ppm. The combined integration of this broad peak and the peak at 4.42 ppm (b + b') exhibited a ratio of approximately 4:3 compared to the integration of the peaks at 3.74–3.70 ppm (a + a', assigned to -CH₃), indicating that the broad peak corresponds to the four methylene hydrogens on the PMeOEP polymer backbone (b': O-CH₂-CH₂-O). The methyl group peak on the polymer sidechain nearly overlaps with the monomer methyl peak, suggesting no significant change in the chemical environment of the methyl group after polymerization. In the ³¹P NMR spectrum of PMeOEP (Fig. S2b), a new peak emerges at -0.1 ppm alongside the monomeric peak at 17.9 ppm. This newly observed peak aligns with prior studies on MeOEP polymerization, ^[1] confirming the occurrence of the polymerization reaction.



Fig. S2 The ¹H NMR and ³¹P NMR of PMeOEP.

After Sc(OTf)₃ rapidly converted liquid DOL into a gel (denoted as PDOL), its ¹H NMR spectrum (blue line in Fig. S3) revealed single peak at 3.77 ppm and 4.78 ppm, corresponding to the hydrogen atoms of residual monomer DOL (labeled a: $-O-CH_2CH_2-O$ - and b: $-O-CH_2-O$ -). Additionally, single peaks at 3.58 ppm and 4.63 ppm were assigned to the hydrogen atoms on the polymer chain ($-O-CH_2CH_2-O$ - and $-O-CH_2-O$ -, a´ and b´ in Fig. S3).



Fig. S3 The ¹H NMR of DOL and PDOL.

In the 'H NMR spectrum of the TFPO monomer (black line in Fig. S4), the multiple peaks at the highest chemical shift of 6.15 ppm is assigned to the hydrogen atom on the carbon bonded to two fluorine atoms in the TFPO sidechain (a: $-CF_2-CF_2-H$). This hydrogen is split into a triplet peak by the two strongly electronegative fluorine atoms on the same carbon, which is further split into another triplet peak by the two fluorine atoms on the adjacent carbon. Aside from the DMSO peak at 2.50 ppm, the peaks at the lowest chemical shifts (2.58 ppm and 2.75 ppm) correspond to the two hydrogen atoms on the methylene group in the TFPO ring (e: $-CH_2-$). These hydrogens exhibit distinct chemical shifts due to their differing chemical environments caused by the adjacent chiral carbon. The multiple peaks at 3.15 ppm is assigned to the hydrogen atom on the chiral carbon in the TFPO ring (d: $-CH_2$). This hydrogen, located on the chiral carbon, is split into multiple peaks due to coupling with four hydrogens from the two adjacent carbons. Additionally, the two hydrogens on the branch chain carbon attached to the chiral carbon (c: $-CH_2-O_2$) exhibit distinct chemical environments. One hydrogens on the same carbon and hydrogens from the adjacent chiral carbon. The remaining unassigned hydrogens belong to the methylene group linked to the fluorinated sidechain (b: $-O-CH_2-CF_2-$). These hydrogens show a higher chemical shift due to reduced electron density around the carbon bonded to the highly electronegative fluorine groups. 'H NMR integration further corroborates these assignments.



Fig. S4 The ¹H NMR of TFPO and PTFPO.

When TFPO is converted into a gel using $Sc(OTf)_3$ (denoted as PTFPO), its ¹H NMR spectrum undergoes significant changes: the peak at 6.51 ppm (the highest chemical shift) transforms into broad peaks (labeled as a' in Fig. S4). Irregular broadened peaks emerge between 4.0–3.2 ppm, with an integration ratio of approximately 7:1 relative to the peak at 6.51 ppm (inset in Fig.S4), confirming the polymerization of TFPO.



Fig. S5 The ¹H NMR of F-GPE.

Introducing TFPO into DOL modulates the polymerization rate of the cyclic ether monomer initiated by Sc(OTf)₃. When Sc(OTf)₃ converts the TFPO/DOL liquid electrolyte into a gel-state (denoted as F-GPE), its ¹H NMR spectrum (Fig. S5) shows peaks at 4.78 ppm and 3.77 ppm, assigned to residual DOL hydrogens (a: -O-CH₂CH₂-O-, b: -O-CH₂-O-), the polymer peaks at 4.63 ppm and 3.58 ppm (labeled as b' and a') exhibit broadening compared to the PDOL homopolymer, indicating copolymerization between DOL and TFPO. Furthermore, a new proton NMR signal appears at 4.71 ppm, corresponding to the copolymer linkage unit (-O-CH₂-O-; this peak was discussed in our prior work). These observations confirm that Sc(OTf)₃ enables TFPO and DOL to copolymerize, successfully yielding the F-GPE electrolyte.



Fig. S6 The ¹H NMR of P-GPE.

Sc(OTf)₃ rapidly converts the MeOEP/DOL mixed electrolyte into a gel (denoted as P-GPE). In the ¹H NMR spectrum of P-GPE (Fig. S6), the peaks at 4.78 ppm and 3.77 ppm are assigned to residual DOL. The polymer peak at 4.63 ppm (b'_2) undergoes a minor shift and broadening compared to the PDOL homopolymer peak (b'_1), indicating copolymerization between DOL and MeOEP. Additionally, the four methylene hydrogens on the phosphate ester polymer backbone resonate at 4.23 ppm (a'_2), showing a 0.05 ppm shift relative to the PMeOEP homopolymer peak (a'_1). This further confirms that MeOEP and DOL copolymerize, resulting in a distinct chemical environment for the phosphate backbone hydrogens in the copolymer compared to the PMeOEP homopolymer.



Fig. S7 The ¹H NMR of F-GPE.

Sc(OTf)₃ converts the MeOEP/TFPO mixed electrolyte into a gel, denoted as P(MeOEP-TFPO). In the ¹H NMR spectrum of P(MeOEP-TFPO) (Fig. S7), the hydrogen on the chiral carbon of the PTFPO homopolymer resonates at 3.93 ppm (b_1 '). Upon copolymerization of TFPO with MeOEP, this hydrogen shifts to 3.97 ppm (b_2 '). Additionally, the peak corresponding to PMeOEP at 4.19 ppm broadens (a'). These observations collectively confirm the copolymerization of MeOEP and TFPO.



Fig. S8 The ¹H NMR comparisons of mixtures.

Conversion rate of MeOEP: The a-hydrogens in the monomer MeOEP exhibit a chemical shift at 4.42 ppm, which shifts to 4.18 ppm upon polymerization (Figure R11). The conversion rate was determined by integrating the hydrogen signals: the polymer peak (a') was divided by the sum of the monomer and polymer peaks (a + a'):



Fig. S9 The ¹H NMR spectrum and integration of MeOEP polymerized into gel PMeOEP, with a monomer conversion rate of approximately 40%.

Conversion rate of DOL: The b-hydrogens in the monomer DOL exhibit a chemical shift at 4.78 ppm, which shifts to 4.63 ppm upon polymerization (Fig. S9). Therefore, the conversion rate of DOL, denoted as C_{DOL} , is calculated as:

$$C_{\rm DOL} = \frac{b}{b+b}$$

While the conversion rate of DOL could also be determined using the a-hydrogens, this approach becomes less accurate in the ternary monomer polymerization system due to peak overlap between the polymer peaks of TFPO and the a/a' peaks of DOL. For this reason, the b-hydrogens were selected for calculating the DOL conversion rate in this study.



Fig.S10 The ¹H NMR spectrum and integration of DOL polymerized into gel PDOL, conversion rate >95%.

Conversion rate of TFPO: Due to the overlap of the polymer peaks with the a-hydrogens in monomer TFPO, which exhibit the largest chemical shift (6.4–6.62 ppm), and the distinct separation of the monomeric e_1 and e_2 hydrogens (chemical shifts at 2.75 and 2.58 ppm, respectively) from other peaks and polymer signals, we selected the e_1 or e_2 hydrogens for quantification. The monomeric TFPO contains three hydrogen environments (a, e_1 , e_2) in a 1:1:1 ratio (Fig. S11). Therefore, the TFPO conversion rate (C_{TFPO}) was calculated via ¹H NMR integration using the following approach:

$$C_{\rm TFPO} = \frac{a + a \ -e_1}{a + a \ } = \frac{a + a \ -e_2}{a + a \ }$$

By focusing on the non-overlapping e_1 or e_2 hydrogens, this method avoids ambiguity caused by peak overlap in the ahydrogen region, ensuring accurate determination of TFPO conversion.



Fig.S11 The ¹H NMR spectrum and integration of TFPO (a) polymerized into gel PTFPO (b), with a monomer conversion rate of approximately 30%.







Fig. S13 (a) The electrochemical impedance spectra analysis of the electrolytes F-GPE and FP-GPE yielded ionic conductivities of 1.7 and 2.0 mS/cm (25° C), respectively; (b) Electrochemical impedance spectra of the symmetric cell Li|FP-GPE|Li before and after polarization; (c) chronoamperometry curve of the symmetric cell Li|FP-GPE|Li at a voltage of 10 mV.



Fig. S14 Time-voltage profiles of Li||Li batteries containing FP-GPE at different current densities.



Fig. S15 (a) Electrochemical impedance spectra of Li|F-GPE|Li cell before and after cycling. (b) Electrochemical impedance spectra of Li|FP-GPE|Li cell before and after cycling. The Nyquist plots of Li|Li batteries display a semicircle at high frequency followed by a tail and are fitted to an equivalent circuit with a resistance and a constant phase element (CPE), ascribed to the electrolyte resistance (R_s), the bulk resistance (R_b) and the interphase resistance (R_i), respectively.



Fig. S16 Time-voltage profiles of Li||Li batteries containing FP-GPE at 0.2 mA cm⁻² current density.



Fig. S17 Chemical structures and the corresponding molecular orbital energies of various organic solvents.



Fig. S18 The composition of SEI on the anode surface after cycling of batteries containing FP-GPE electrolytes was analyzed by XPS test.





In the SEI formed between FP-GPE and lithium metal, the LiF intensity is significantly higher than that in the SEI formed with F-GPE, which is hypothesized to be the beneficial outcome of the synergistic interaction between MeOEP and TFPO derivatives (Figure S). In F-GPE, the reduction of TFPO derivatives on the lithium metal surface generates LiF and alkaline species (e.g., PPO-Li derivatives). In FP-GPE, however, these alkaline species further trigger the ring-opening polymerization of residual MeOEP, producing a phosphate-centered 3D cross-linked polymer through transesterification reactions. This polymer structure exhibits excellent mechanical properties. Consequently, the synergistic interplay of MeOEP/TFPO derivatives in FP-GPE facilitates the formation of an F/P-rich SEI, where the inorganic/organic hybrid components significantly enhance SEI stability.



Initial state

Move the fire

Final state





Fig. S21 Li||LFP batteries performance. (a) Charge and discharge curves of Li|DOL|LFP battery at different rates. (b) Charge and discharge curves of Li|F-GPE|LFP battery at different rates.



Fig. S22 Li||LFP batteries performance. (a) Charge and discharge curves of Li|F-GPE|LFP battery at 1 C current density. (b) Charge and discharge curves of Li|FP-GPE|LFP battery at 2 C current density.



Figure S23 The Li|FP-GPE|LFP batteries undergoes long cycles at current densities of 1 C, 2 C, and 3 C.



Fig. S24 Scanning electron microscope of lithium-metal surface after F-GPE and FP-GPE are circulated of the Li||LFP batteries.



Fig. S25 SEM of pristine LFP, SEM on the LFP cathode surface after batteries cycling of containing F-GPE and FP-GPE.



Fig. S26 SEM of pristine NCM, LFP after cycling in F-GPE, and LFP after cycling in FP-GPE.



Fig. S27 (a) C 1s spectra of XPS on the NCM cathode surface after cycling of cells containing F-GPE and FP-GPE. (b) F 1s spectra of XPS on the NCM cathode surface after cycling. (c) P 2p spectra of XPS on the NCM cathode surface after cycling.

Entry	Catalyst	Concentration (mol/L)	<i>T</i> /°C	Time	State	Conv.
1	LiTFSI	1	RT	30 d	Liquid	×
2	LiPF ₆	1	RT	2 d	Liquid	×
3	LiOTf	1	RT	2 d	Liquid	×
4	Al(OTf) ₃	0.1	50	2 d	Liquid	×
5	TB	0.05	50	2 d	Liquid	×
6	HClO ₄	1	50	2 d	Liquid	×
7	DBU	0.05	RT	1 h	Gel	80%
8	CH ₃ OLi	0.01	50	1 d	Gel	30%
9	Sc(OTf) ₃	0.01	RT	12 h	Gel	40%
The re	eaction was carried	out in a dry nitrogen at	mosphere with	out bulk polymeriz	ation with additio	nal solvent.

Table S1. Polymerization experiment of MeOEP.

Table S2. Polymer electrolytes (about containing 2 M LiTFSI) were prepared by mixing MeOEP, DOL and TFPO in different ratios at an initiator of 0.01 M Sc(OTf)₃. The details are shown in the following table:

Entry	Polymers	Monomer (MeOEP/TFPO/DOL)	Conditions	Conv.	Electrolytes
1	Sc-DOL	0/0/10	RT 1 min	Gel	-
2	Sc-TFPO	0/10/0	RT 3d	30 %	-
3	Sc-MeOEP	10/0/0	RT 12h	40 %	-
4	Sc-MeOEP/DOL	1/0/10	RT 1 min	Gel	-
5	F-GPE	0/1/10	RT 1d	85% (DOL)	\checkmark
6	FP-GPE	1/1/10	RT 1d	86% (DOL)	\checkmark

Electrolytes	Cycle	Rs	R _b /Ω	R _i /Ω
F-GPE	Before	9.2	10.8	166.9
	After	148.3	674.8	241.0
FP-GPE	Before	5.6	14.9	86.7
	After	16.0	68.1	25.5

 Table S3. The EIS fitting results before and after cycling of Li-Li symmetric batteries containing F-GPE and FP-GPE electrolytes.

References

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