Supporting Information

High-Performance Flame-Retardant Polyphosphate ester-based Solid Electrolyte via In-situ Ring-Opening Polymerization for Safe Li Metal Batteries

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Synthesis of 2-(2,2,2-trifluoroethoxy)-1,3,2-dioxaphospholane 2-oxide (TFEOP)

Under strict temperature control (0 ℃), a solution of 2-chloro-2-oxo-1,3,2-dioxaphospholane (5.0 g, 35.1 mmol) in anhydrous tetrahydrofuran (THF, 10 mL) was added dropwise to a mixture of 2,2,2-trifluoroethanol (2.78 mL, 3.86 g, 38.6 mmol) and triethylamine (5.0 mL, 3.63 g, 35.9 mmol) in anhydrous THF (50 mL). After complete addition, the reaction mixture was warmed to room temperature and stirred for 12 h. The resulting triethylammonium chloride precipitate was removed by vacuum filtration. The filtrate was concentrated via rotary evaporation and purified by reduced-pressure distillation (boiling point: 97 ℃ at 4 mmHg) to afford TFEOP as a colorless liquid.[1]

Synthesis of 5,5'-[oxybis(methylene)]bis[5-ethyl-1,3-dioxan-2-one] (BCM)

BCM was prepared according to the previously published procedure.[2] In a 250 mL round-bottom flask, DPC (85.6 g, 400 mmol) was melted at 140 ℃. DTMP (25.0 g, 100 mmol) was added slowly into the flask. The mixture was stirred at 140 ℃ for 36 h and then cooled to ambient temperature. The mixture was purified by column chromatography with ethyl acetate/n-hexane (v/v = 1/1 to 3/1) to remove an excess amount of DPC and the byproduct phenol. The crude product was purified by recrystallization from ethyl acetate/n-hexane (v/v = 3/1) to yield BCM as a white solid. Yield: 10.4 g, 34.4%.

Table S1 The material ratio of each component of polyphosphoester-based solid electrolyte

	SPE (Mole ratio)			**Additive (Mass fraction relative to SPE mass)**	
	TFEOP	**BCM**	**PEO-1000**	**LiTFSI**	**G4**
TFMPE-1	11	1.1	1	30 wt%	0
TFMPE-2	22	1.1	1	30 wt%	0
TFMPE-3	11	1.1	1	75 wt%	0
TFMPE-4	22	1.1	1	30 wt%	5 wt%

Table S2 Performance comparison between TFMPE and reported solid polymer electrolytes with similar construction

Electrolyte	Conductivity	Temperature	ESW	Reference
Polyphosphoester SPE	3.7×10^{-4} S cm^{-1}	30 ℃	4.9 V	This work
Polyphosphoester SPE	2×10^{-4} S cm^{-1}	70 ℃	-	[21]
Polyphosphoester SPE	1.14×10^{-5} S cm^{-1}	40 ℃	-	[22]
Poly(ether-ester) SPE	3.54×10^{-5} S cm^{-1}	30 ℃	5.1 V	[36]
Fluorinated blended SPE	2.26×10^{-5} S cm^{-1}	60 ℃	4.5 V	[37]
Fluorinated composite SPE	3.71×10^{-4} S cm^{-1}	30 ℃	4.65 V	[38]
Polyphosphoester SPE	1.25×10^{-5} S cm^{-1}	30 ℃	4.0 V	[39]
Fluorinated polycarbonate SPE	8.0×10^{-5} S cm^{-1}	30 ℃	4.6 V	[40]
Polyphosphoester SPE	~10^{-4} S cm^{-1}	30 ℃	-	[41]
Polyphosphoester SPE	5.5×10^{-4} S cm^{-1}	30 ℃	4.0 V	[42]

Supplementary Figures:

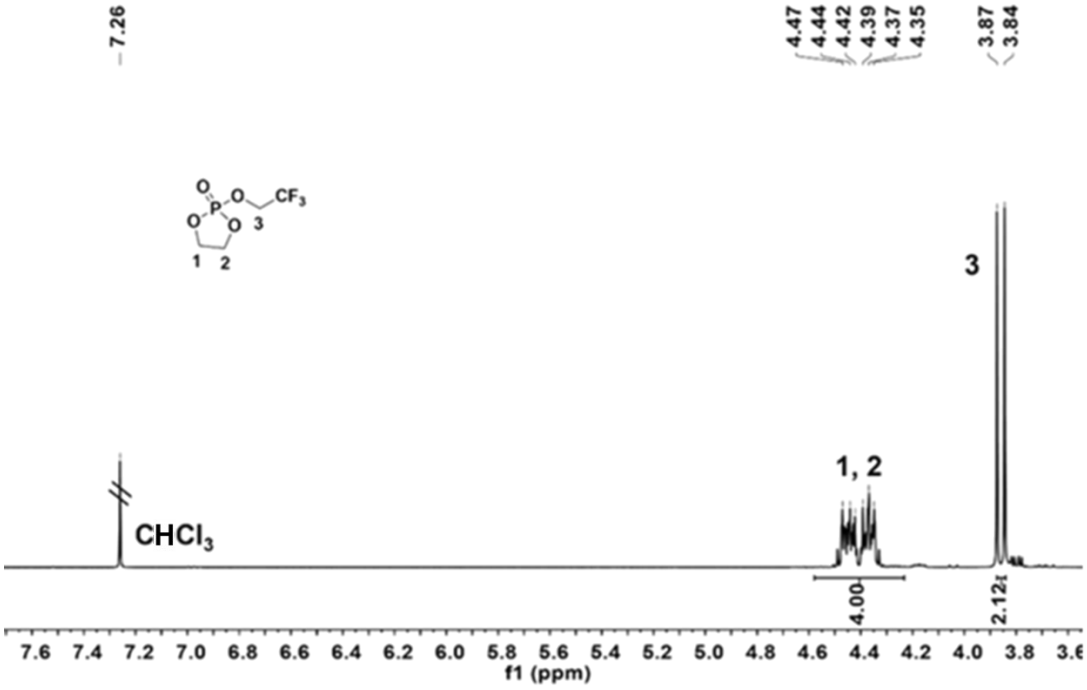

Figure S1 [1]H NMR spectrum of TFEOP.

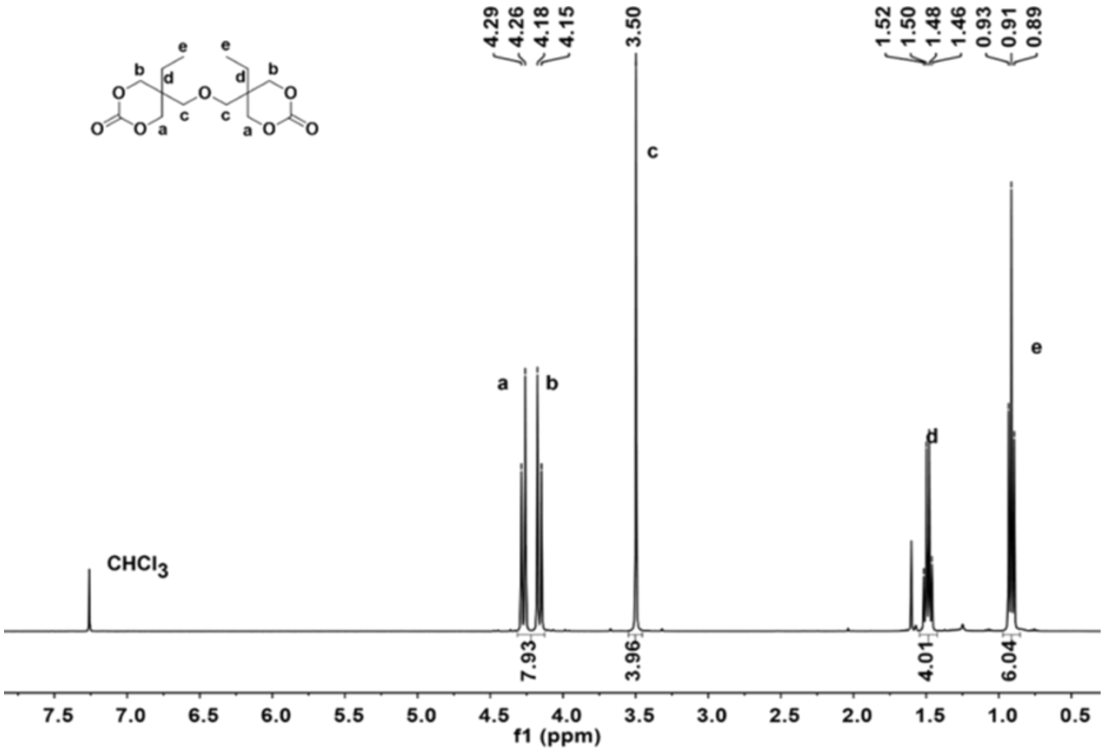

Figure S2 [1]H NMR spectrum of BCM.

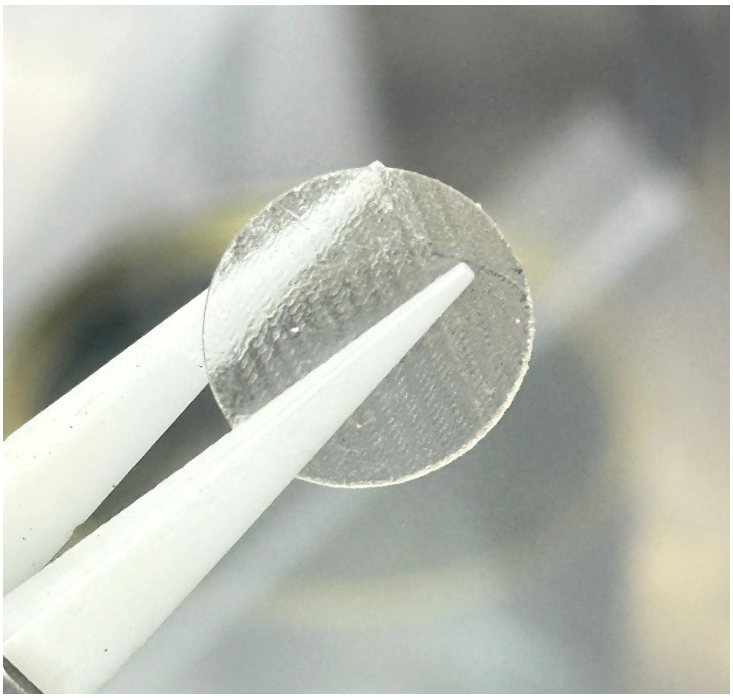

Figure S3 Photograph of the thermally polymerized TFMPE obtained without GF support.

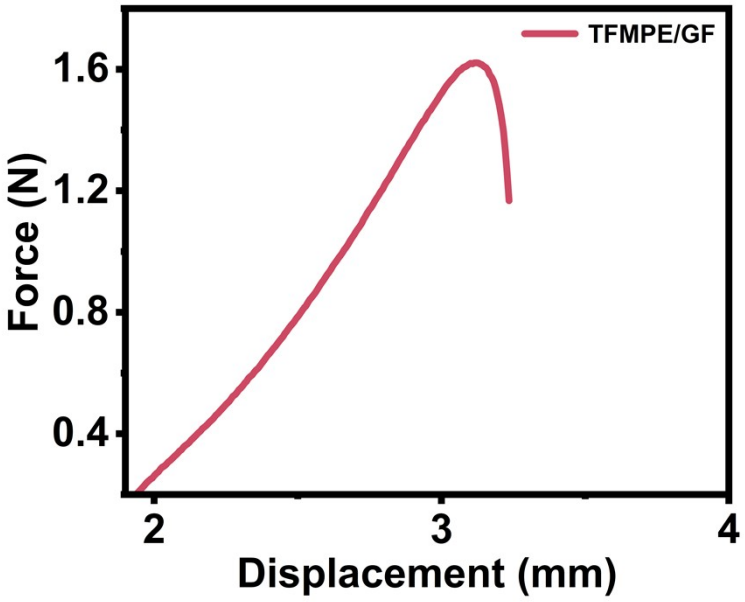

Figure S4 Puncture force-displacement curve of the TFMPE/GF composite membrane.

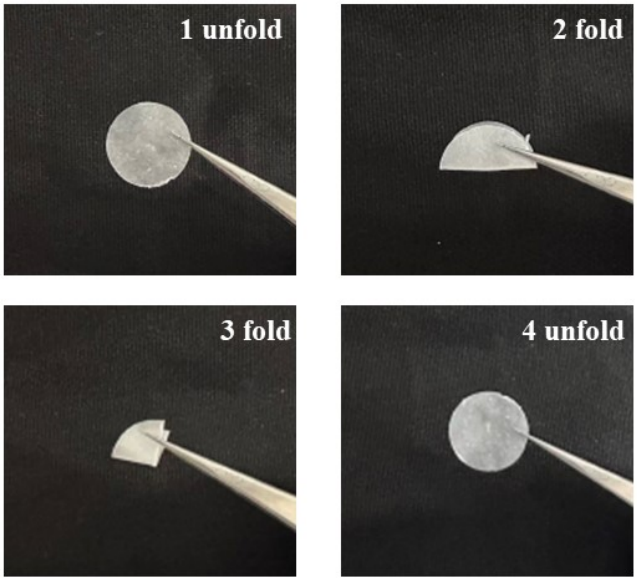

Figure S5 Photographs of the TFMPE membrane in the folded and unfolded states.

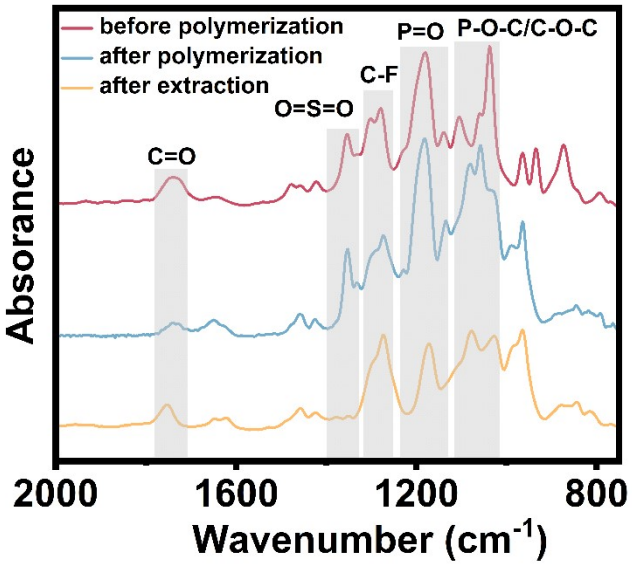

Figure S6 FTIR spectra of the samples before polymerization, after polymerization, and after extraction.

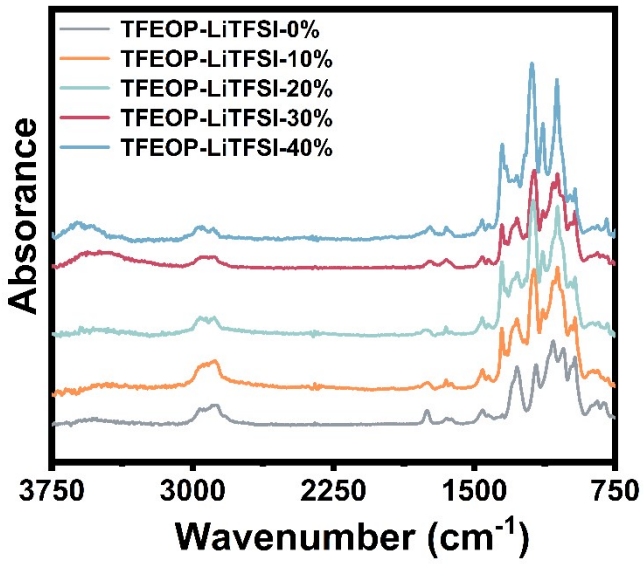

Figure S7 FTIR spectra of TFMPE with different LiTFSI contents.

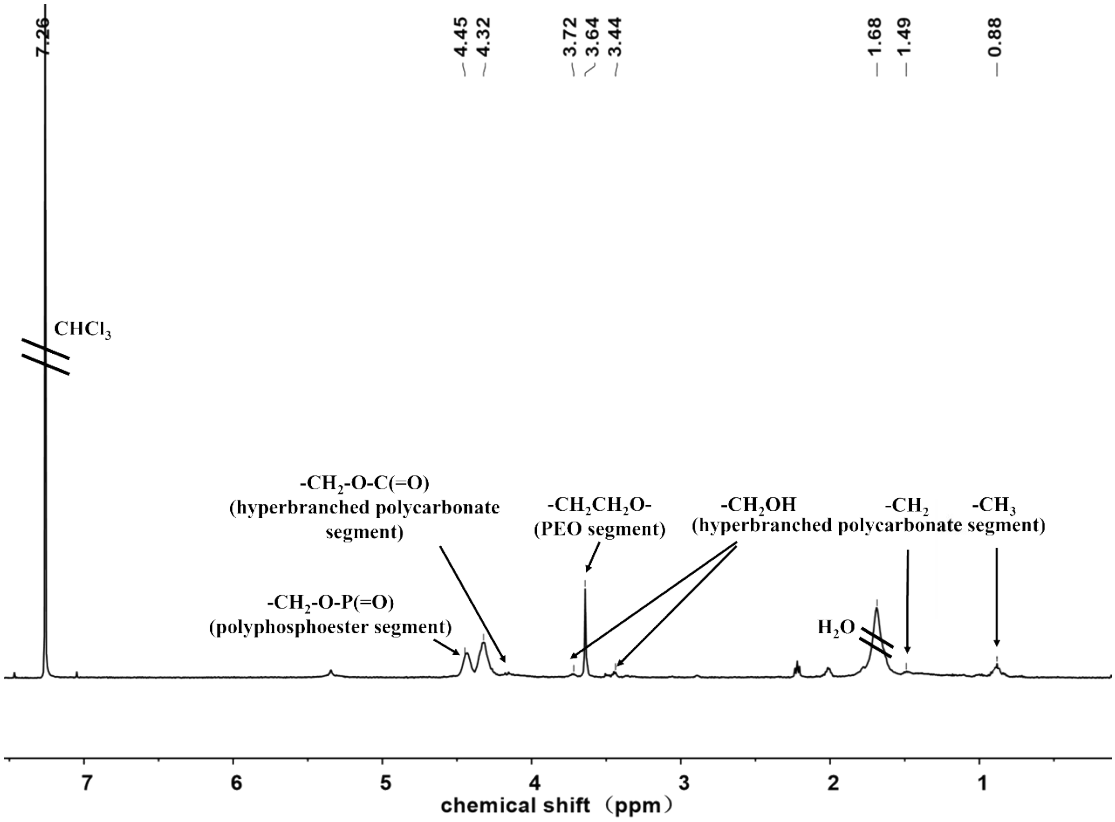

Figure S8 ^{1}H NMR spectrum of the extracted soluble fraction.

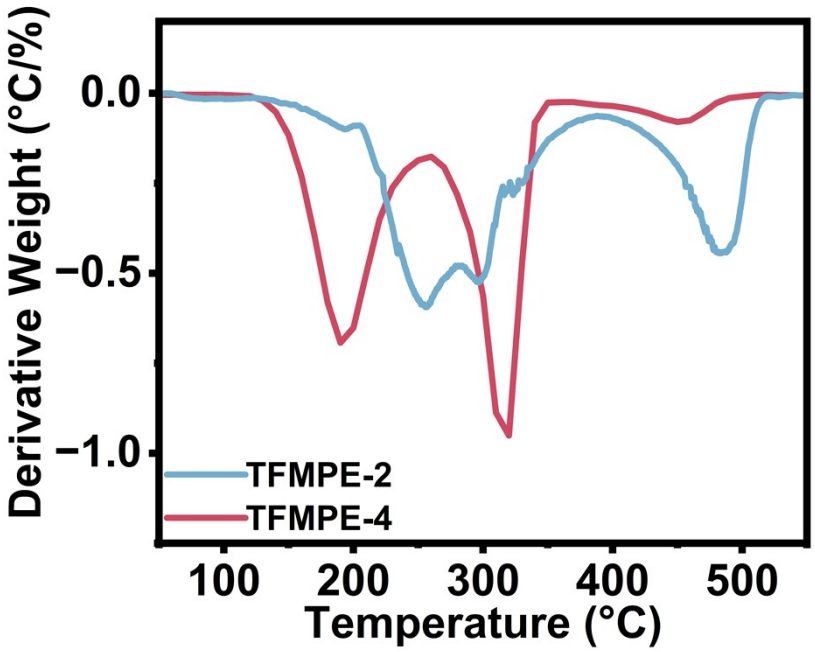

Figure S9 DTG of TFMPE-2 and 4.

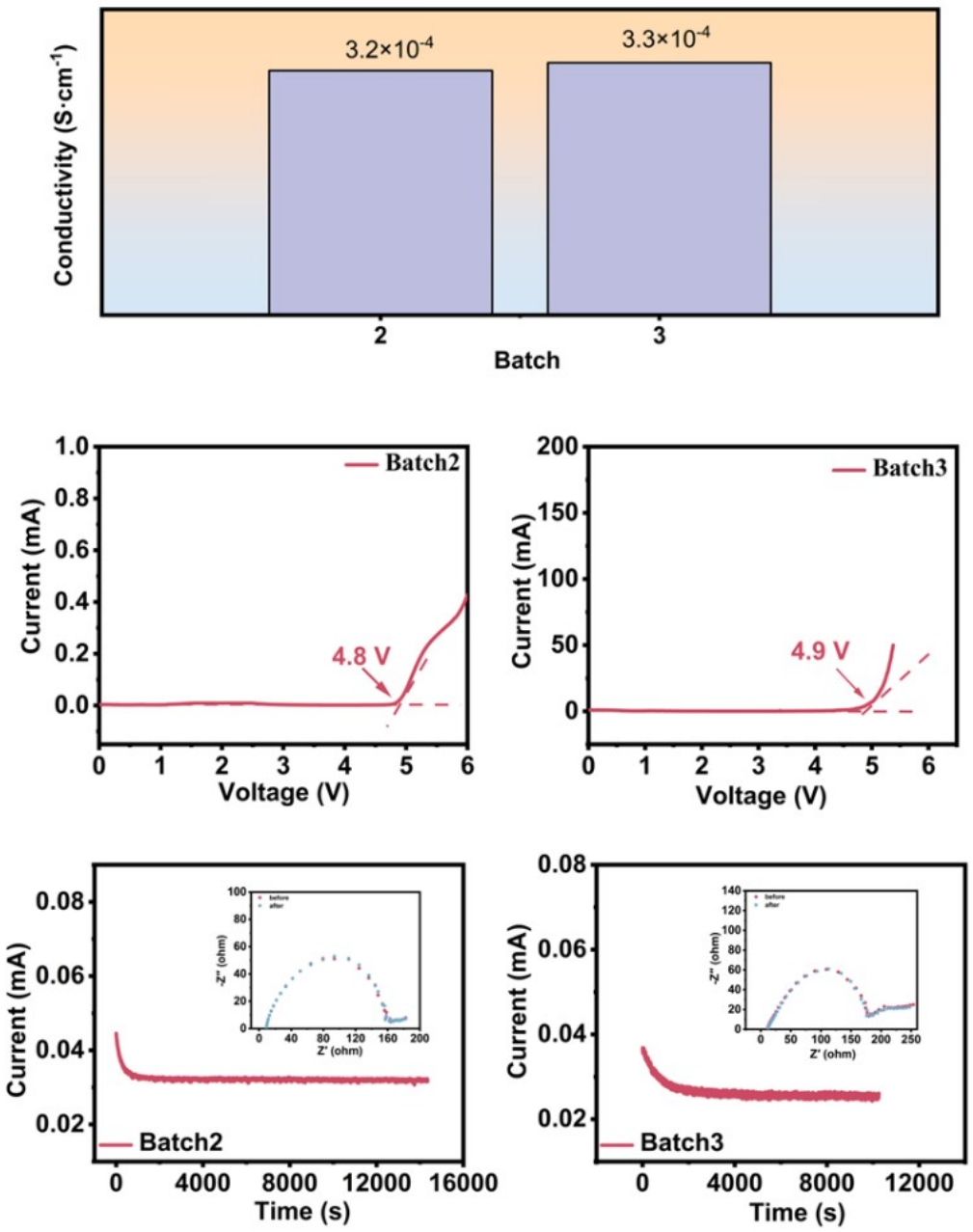

Figure S10 Ionic conductivity, ESW, and t_{Li^+} of the original batch, Batch 2, and Batch 3 of the optimized TFMPE-4 electrolyte at 30 ℃.

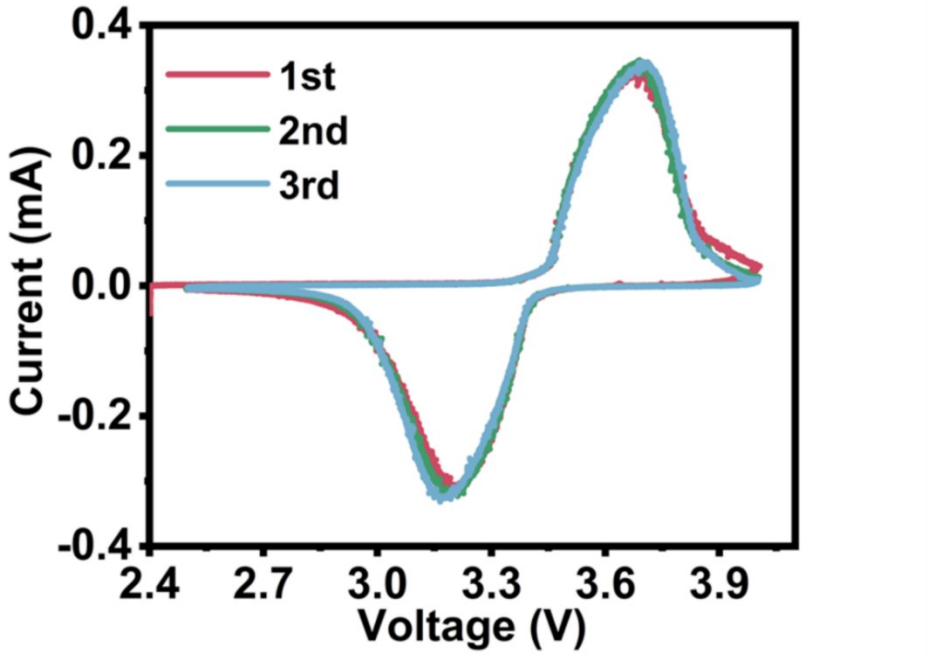

Figure S11 CV spectra of the in-situ Li|TFMPE|LFP cell at 0.1 mV s^{-1} and 25 ℃.

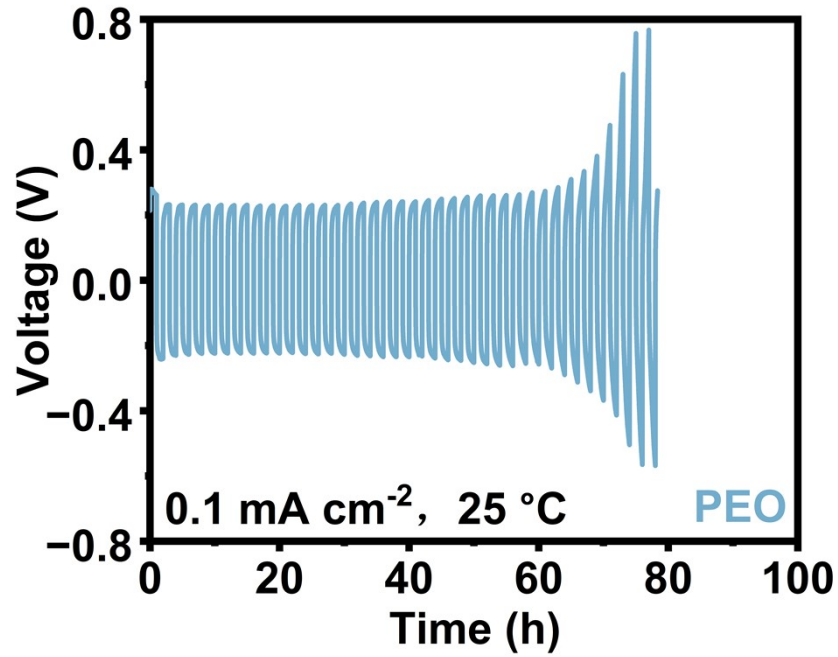

Figure S12 Cycling performance of the Li|PEO|Li symmetric cell at 0.1 mA cm^{-2} and 60 ℃.

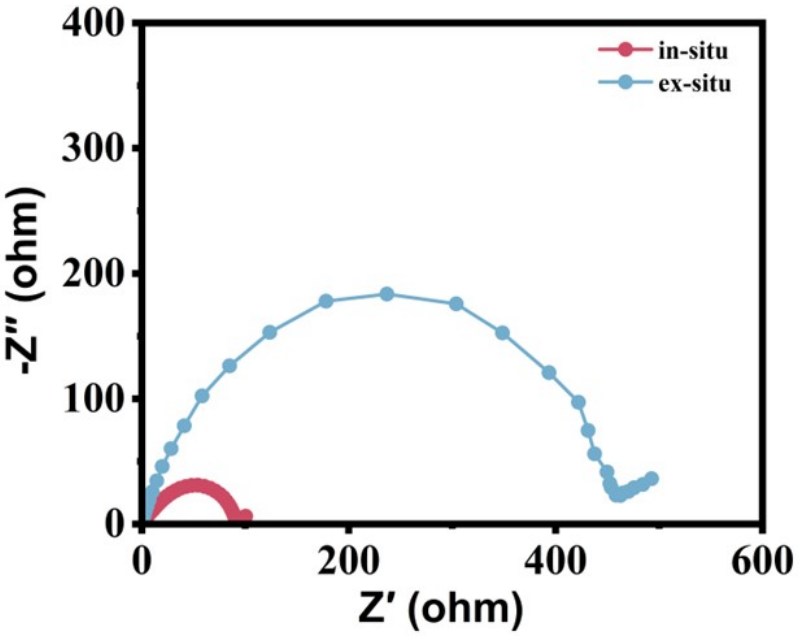

Figure S13 EIS of in-situ and ex-situ assembled cells before cycling.

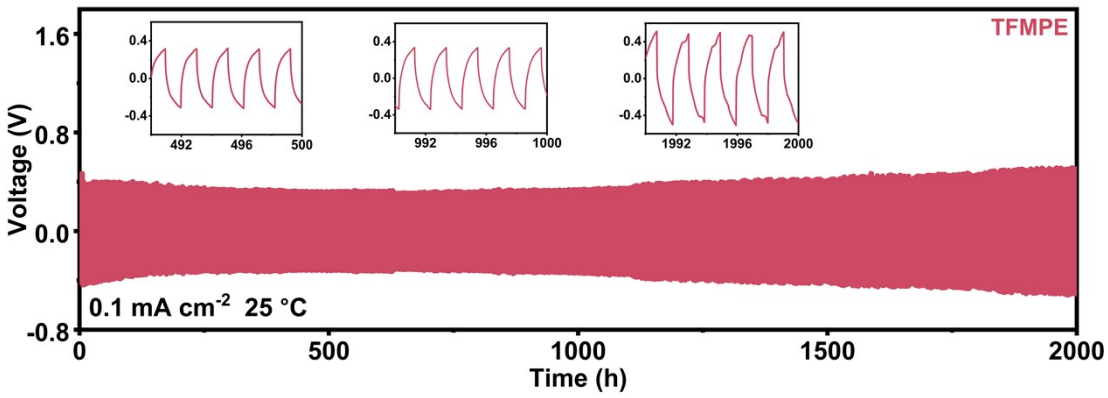

Figure S14 Cycling performance of the in-situ Li|TFMPE|Li symmetric cell at 0.1 mA cm^{-2} and 25 °C.

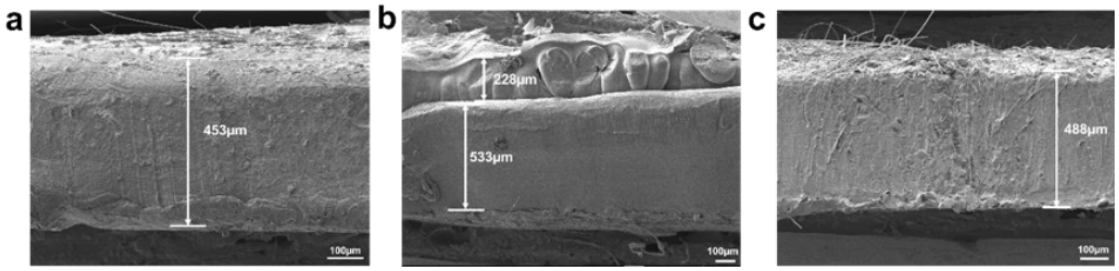

Figure S15 Cross-sectional morphologies of: (a) pristine Li foil, (b) an ex-situ assembled Li||Li symmetric cell, and (c) an in-situ assembled Li||Li symmetric cell after 2000 h of cycling.

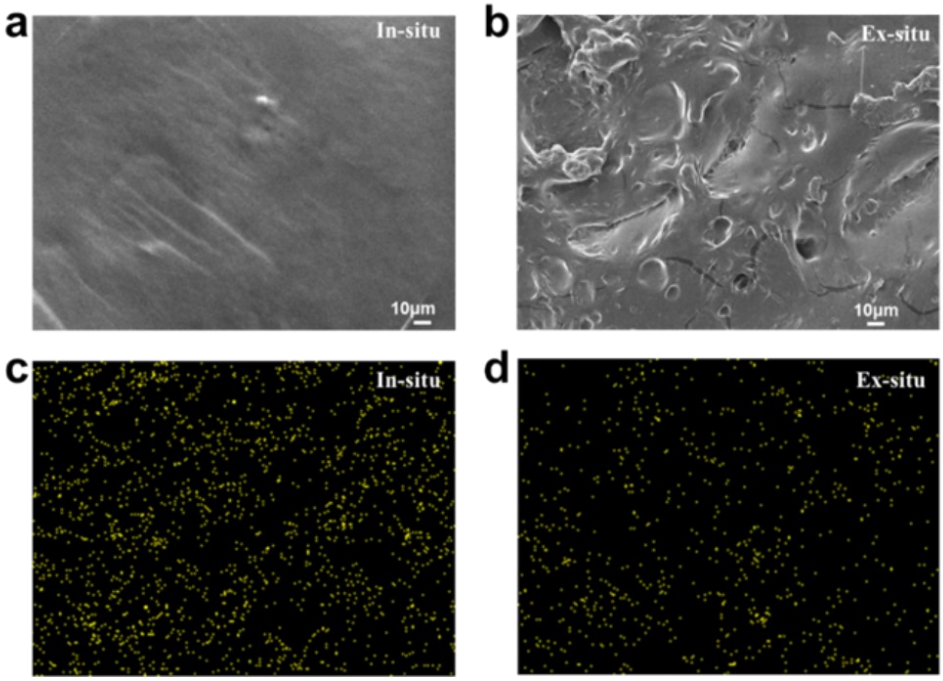

Figure S16 Surface SEM images of cycled lithium metal anodes from (a) in-situ and (b) ex-situ polymerized cells. (c, d) Corresponding EDS mapping of the F element for each electrode.

References

1. C.-C. Su, M. He, C. Peebles, L. Zeng, A. Tornheim, C. Liao, L. Zhang, J. Wang, Y. Wang and Z. Zhang, *ACS Appl. Mater. Interfaces*, 2017, **9**, 30686-30695.
2. H. Matsukizono and T. Endo, *Macromol. Chem. Phys.,* 2017, **218**, 1700043.