Phosphorus flame retardant-fixed in situ gel polymer electrolyte for safety-enhanced and superior electrochemical performance lithium metal battery

Hao Yu[†], Su Wang[†], Yan Zhang, Yanrui Pan, Zhaokun Wang, Chen Li, Yue Ma[*], Dawei Song, Hongzhou Zhang, Xixi Shi, Chunliang Li[*], Lianqi Zhang[*]

School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, China.

†These authors contribute equally to this work

[*]Corresponding author. *E-mail:* MY18002118645@163.com *(Y. Ma),* chunliang1123@163.com *(C. Li),* tianjinzhanglq@163.com *(L. Zhang).*

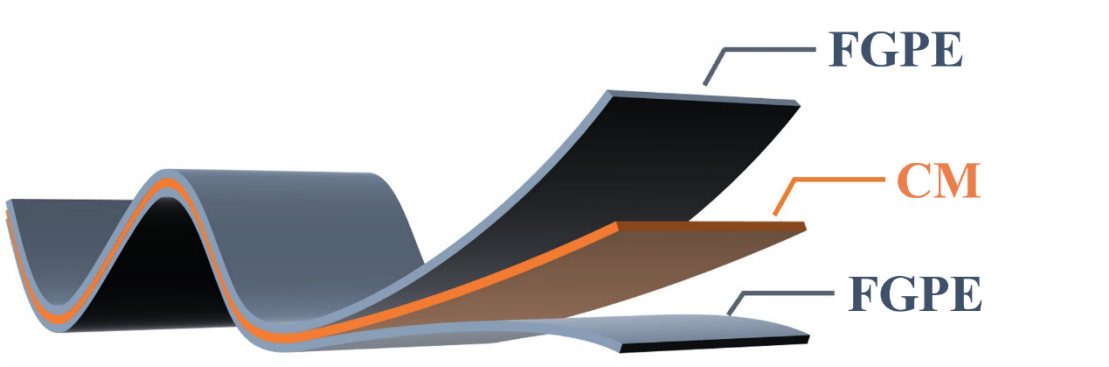

Fig. S1. Structure diagram of FGPE.

Fig. S2. Optical images comparison before and after FGPE polymerization.

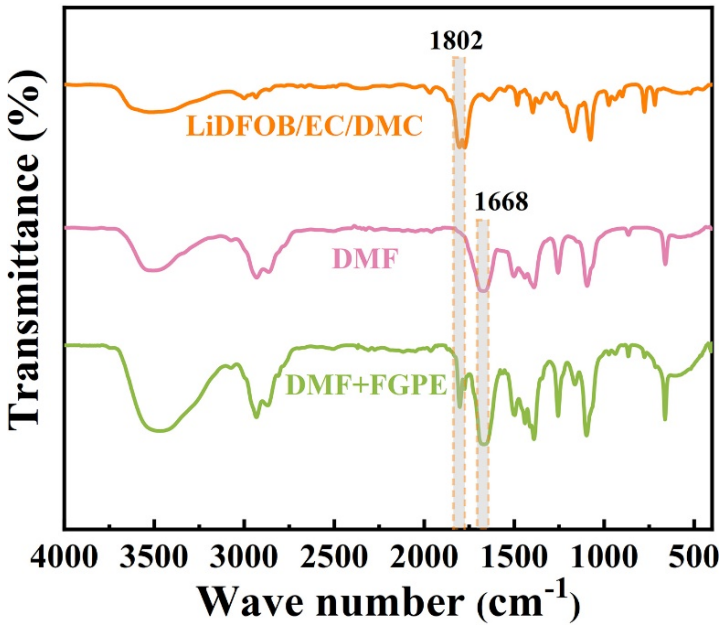

Fig. S3. FTIR spectra of LiDFOB/EC/DMC, DMF, and DMF+FGPE.

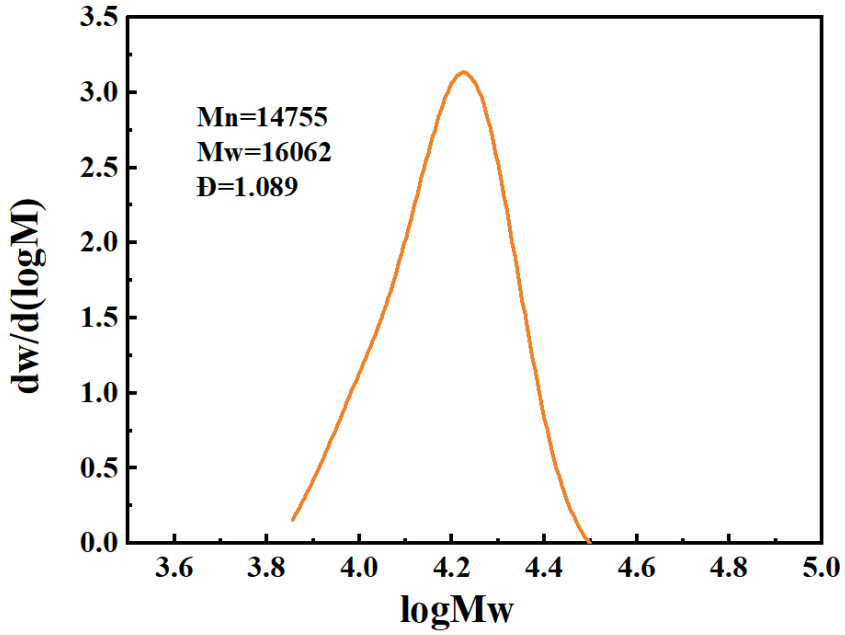

Fig. S4. GPC analysis of FGPE polymer.

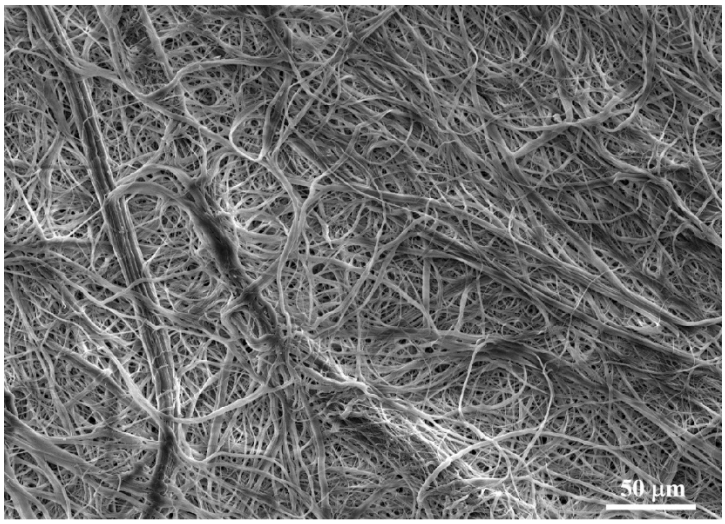

Fig. S5. Typical SEM image of cellulose film.

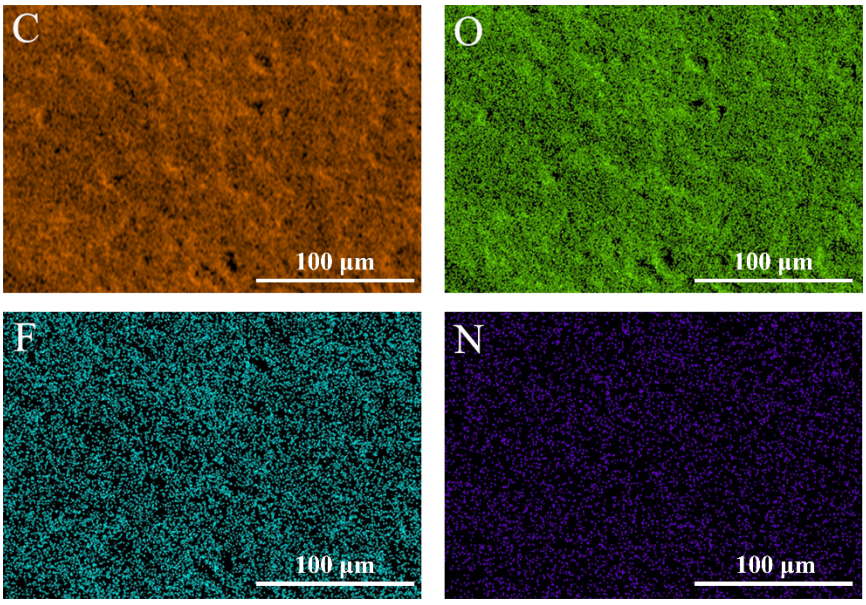

Fig. S6. C, O, F and N elements EDS mappings of FGPE.

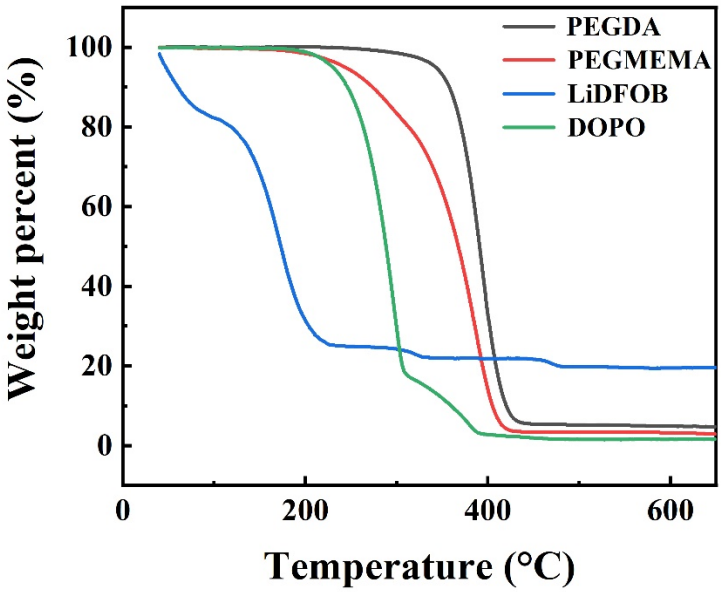

Fig. S7. TG curves of PEGDA, PEGMEMA, LiDFOB and DOPO.

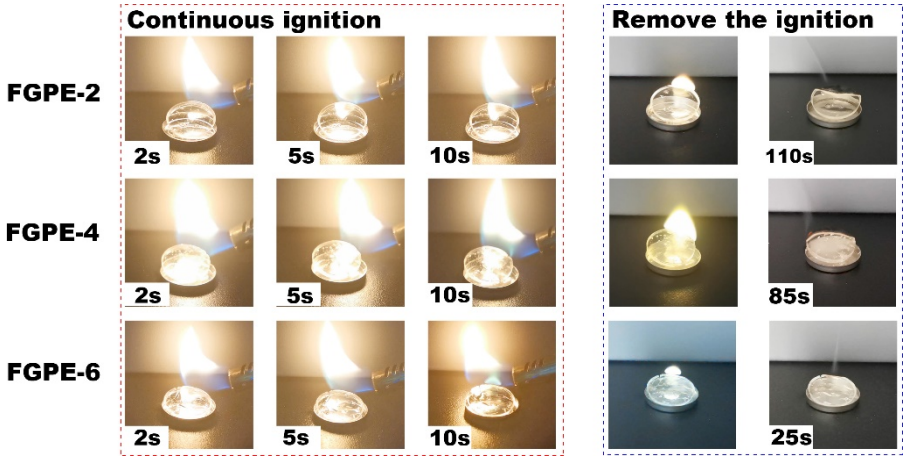

Fig. S8. Open combustion tests of FGPE-2, FGPE-4 and FGPE-6.

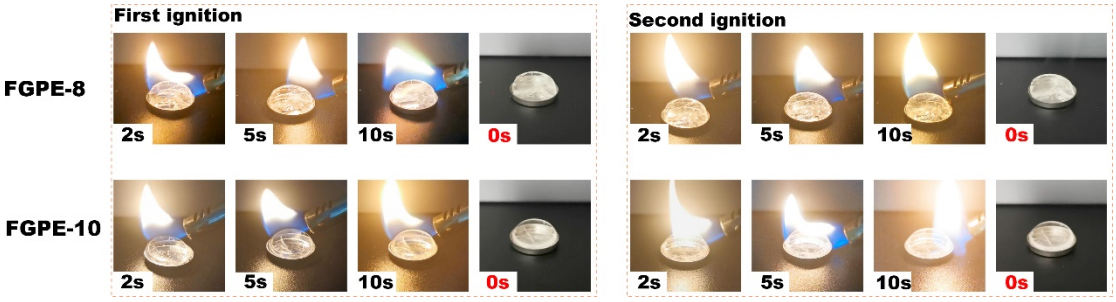

Fig. S9. Open combustion tests of FGPE-8 and FGPE-10.

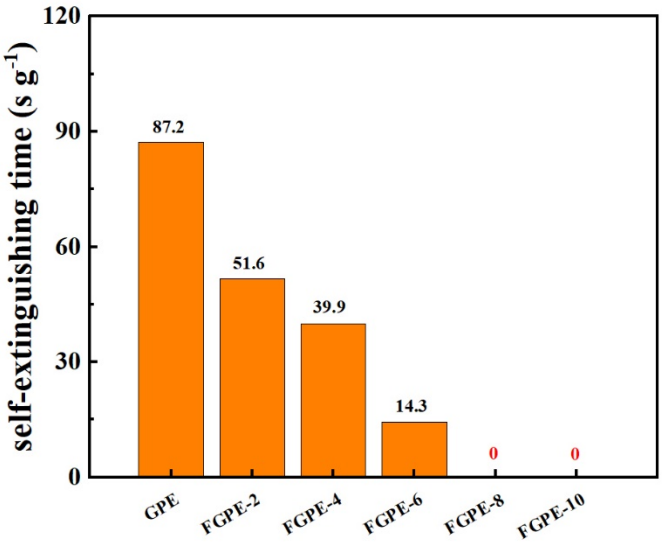

Fig. S10. The self-extinguishing time of GPE, FGPE-2, FGPE-4, FGPE-6, FGPE-8 and FGPE-10.

$$P_4+2O_2 \rightarrow 4PO\cdot$$

$$H_3PO_4 \rightarrow HPO_2+HPO+PO\cdot$$

$$H\cdot+PO\cdot \rightarrow HPO$$

$$H\cdot+HPO \rightarrow H_2+PO\cdot$$

$$2OH\cdot+PO\cdot \rightarrow HPO+H_2O$$

$$OH+H_2+PO\cdot \rightarrow HPO+H_2O$$

Fig. S11. Flame retardant principle of DOPO.

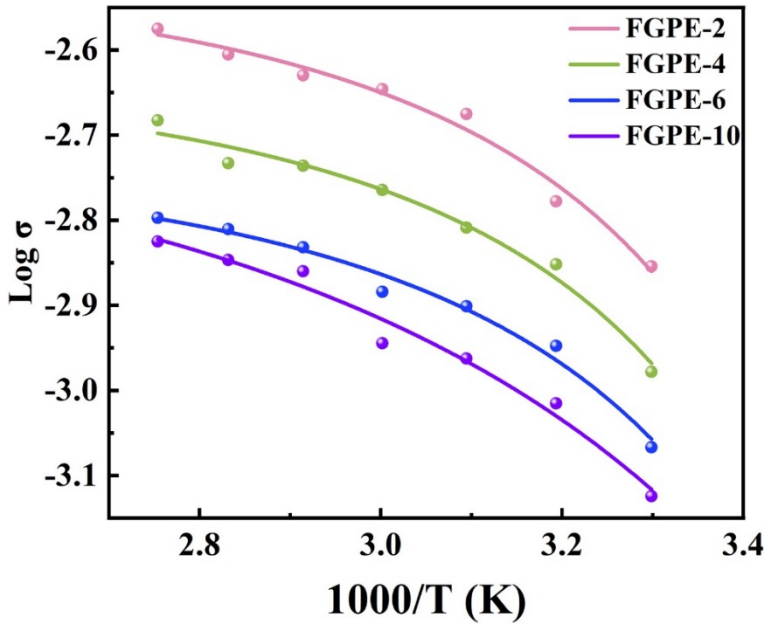

Fig. S12. The ion conductivity dependence of SS/FGPE/SS symmetrical cells with DOPO content of 2%, 4%, 6%, and 10% in the temperature range of 30-90°C.

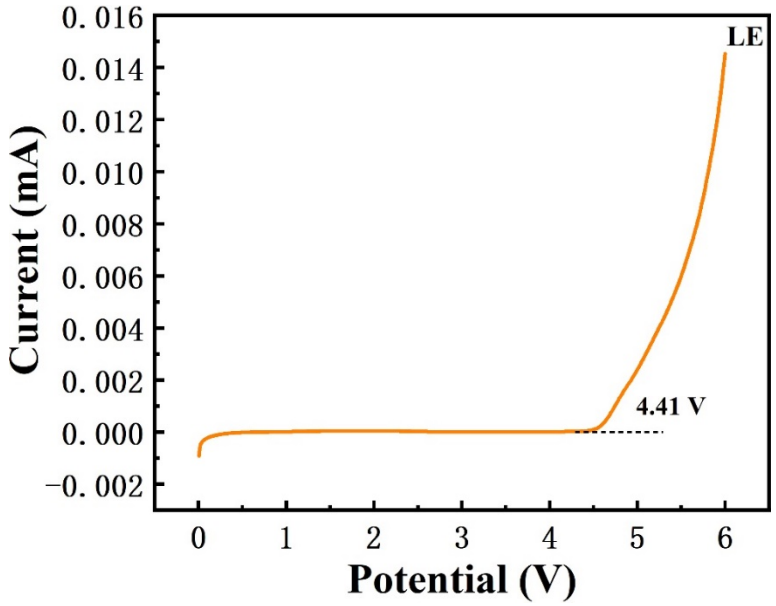

Fig. S13. LSV profile of SS/LE/SS symmetrical cell.

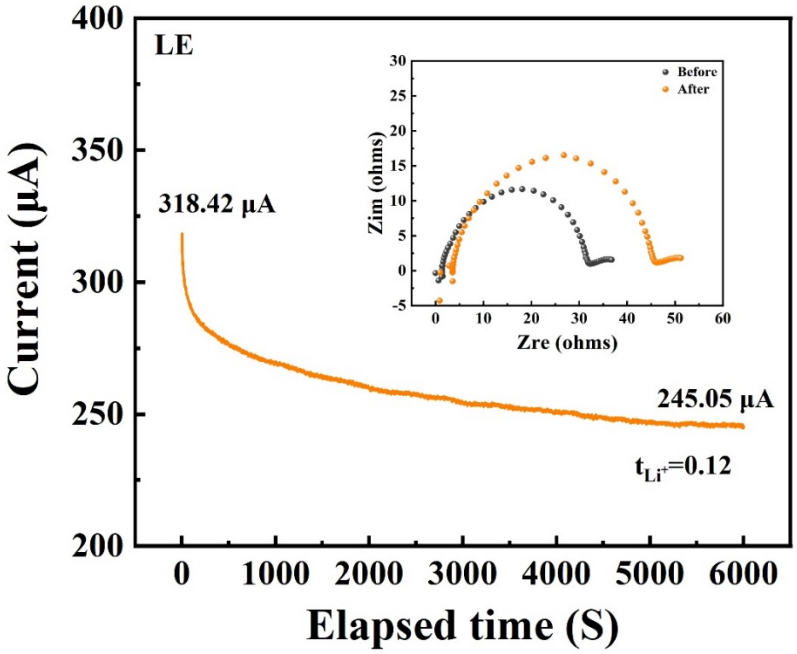

Fig. S14. Current-time profiles of Li/LE/Li symmetrical cell, the insert showing the EIS profiles before and after polarization.

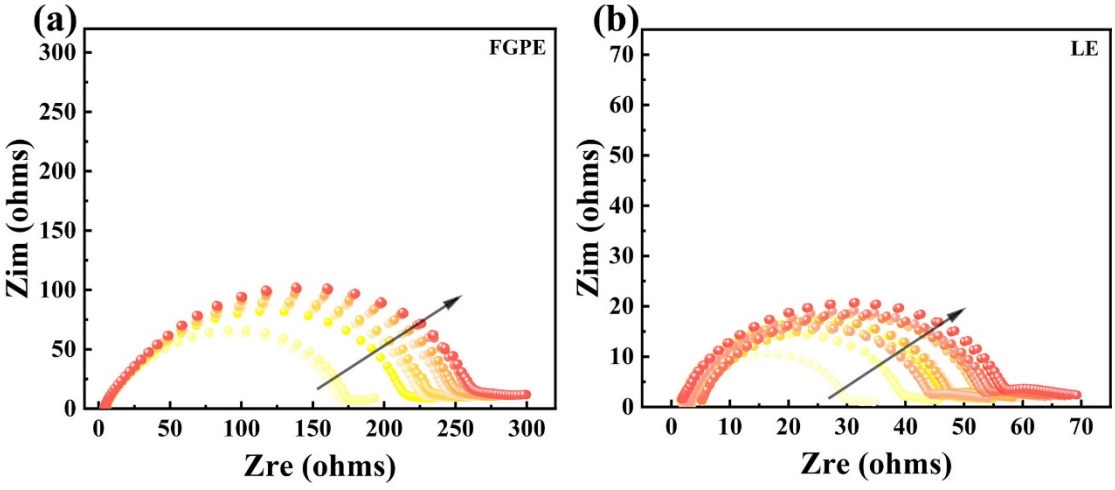

Fig. S15. Impedance changes of (a) Li/FGPE/Li and (b) Li/LE/Li symmetrical cells during different storage times.

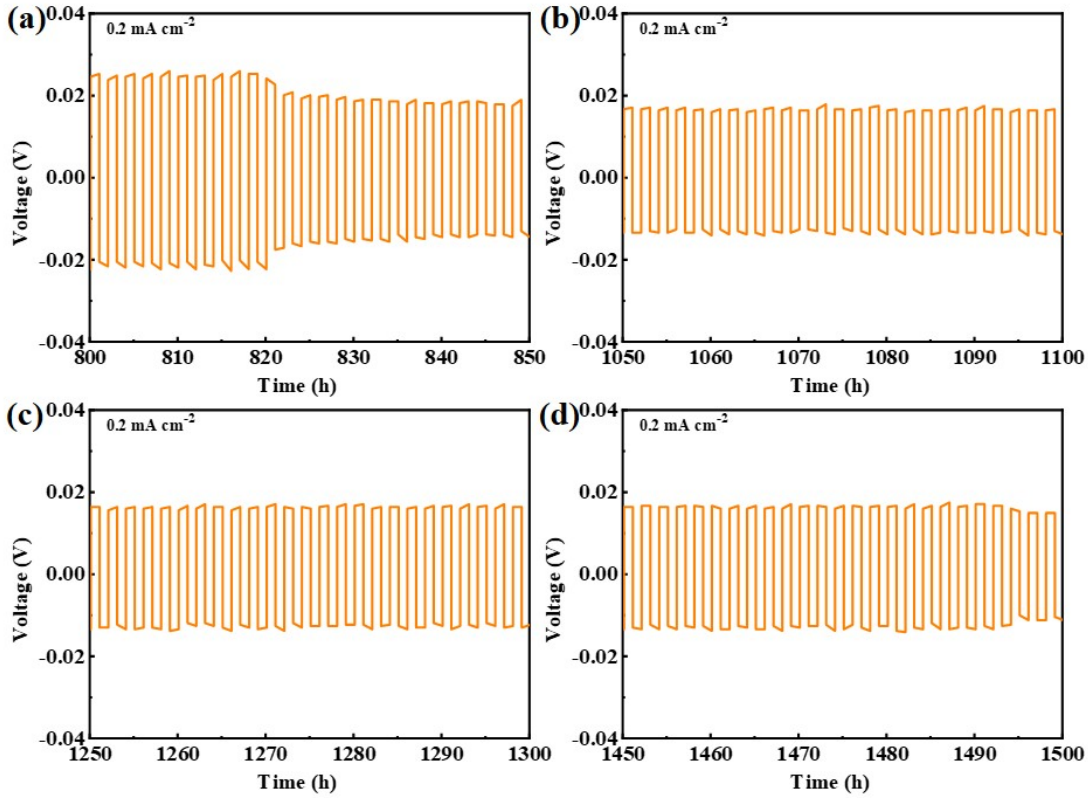

Fig. S16. Selected polarization voltage profiles of Li/FGPE/Li symmetric cell with a current density of 0.2 mA cm^{-2} at different testing times.

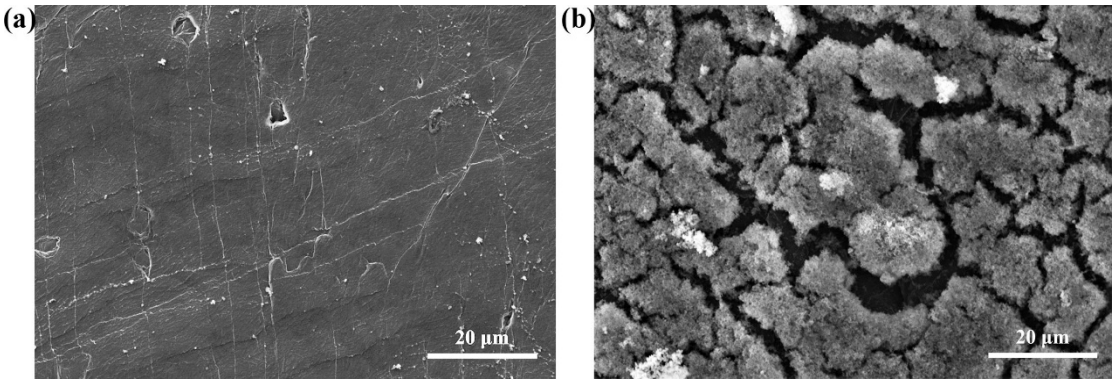

Fig. S17. SEM images of cycled Li anode in (a) Li/FGPE/Li and (b) Li/LE/Li symmetric cells after 600 h at the current density of 0.2 mA cm^{-2}.

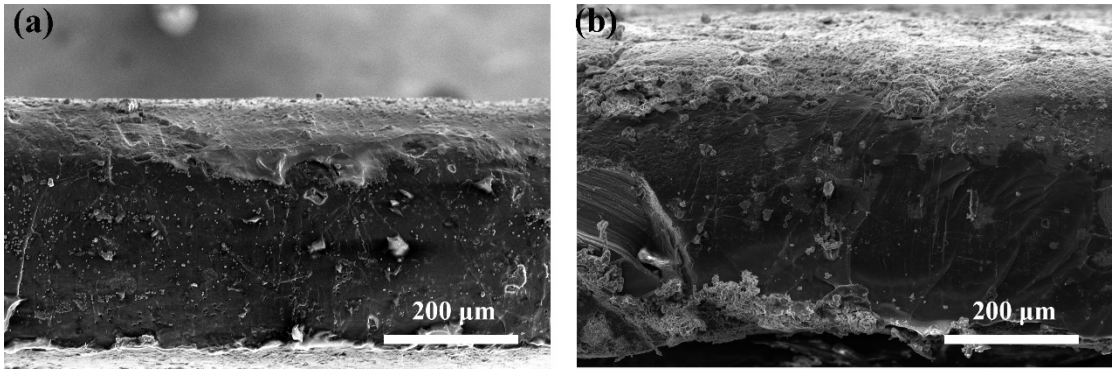

Fig. S18. Cross-sectional SEM images of cycled Li anode in (a) Li/FGPE/Li and (b) Li/LE/Li symmetric cells after cycling at the current density of 0.2 mA cm^{-2}.

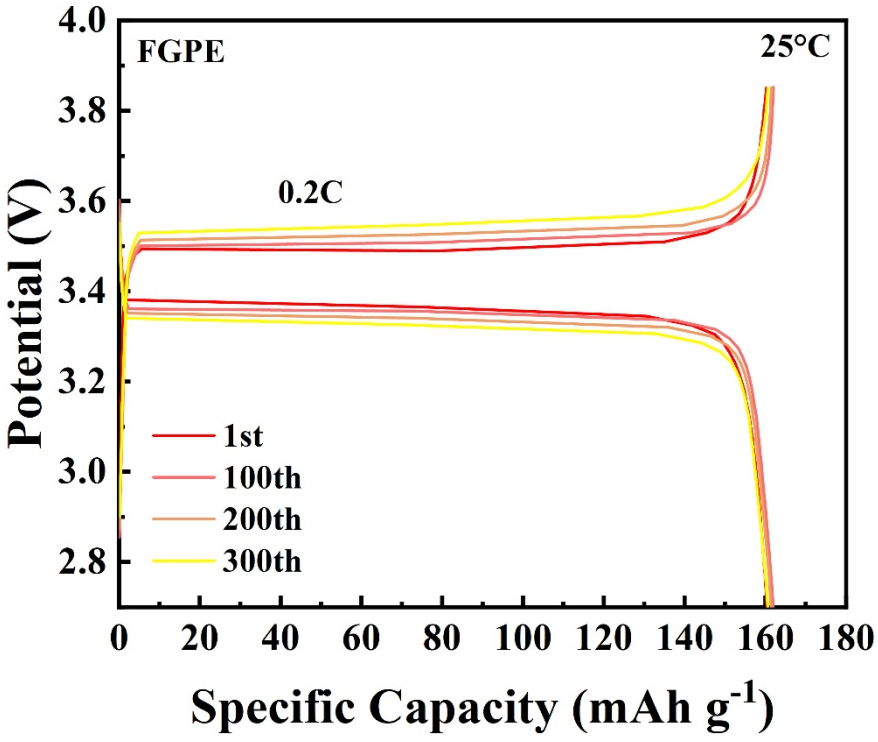

Fig. S19. Charge/discharge profiles of LFP/FGPE/Li battery at 0.2C.

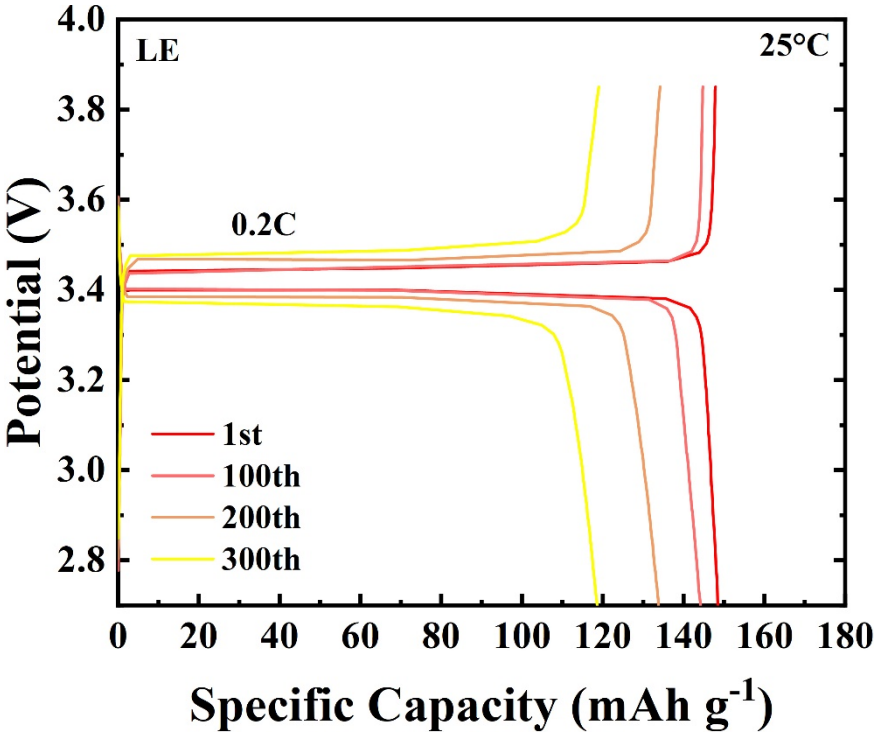

Fig. S20. Charge/discharge profiles of LFP/LE/Li battery at 0.2C.

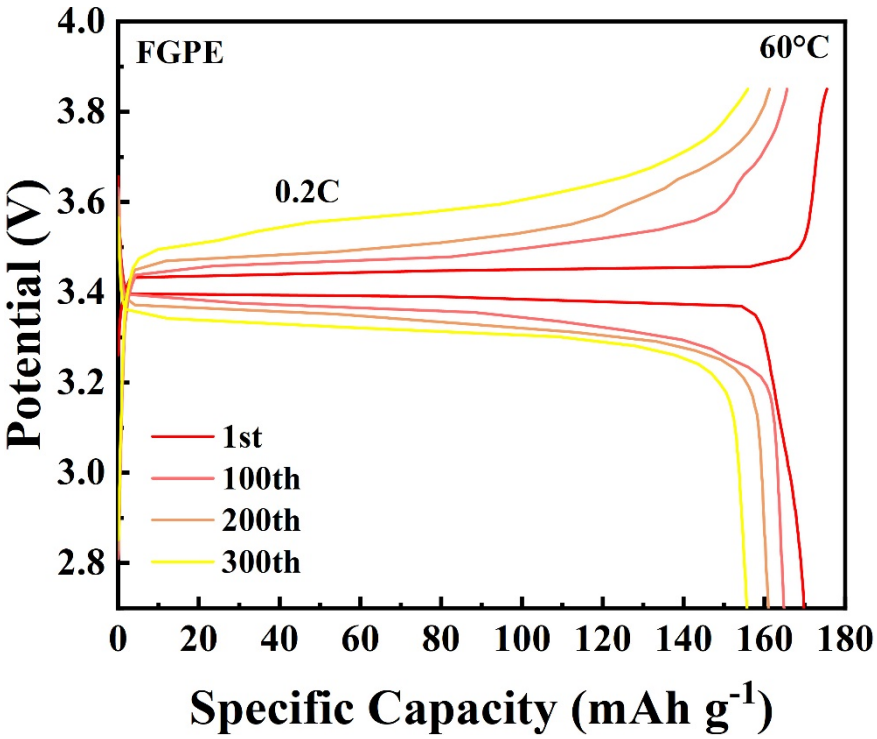

Fig. S21. Charge/discharge profiles of LFP/LE/Li battery at 0.2C.

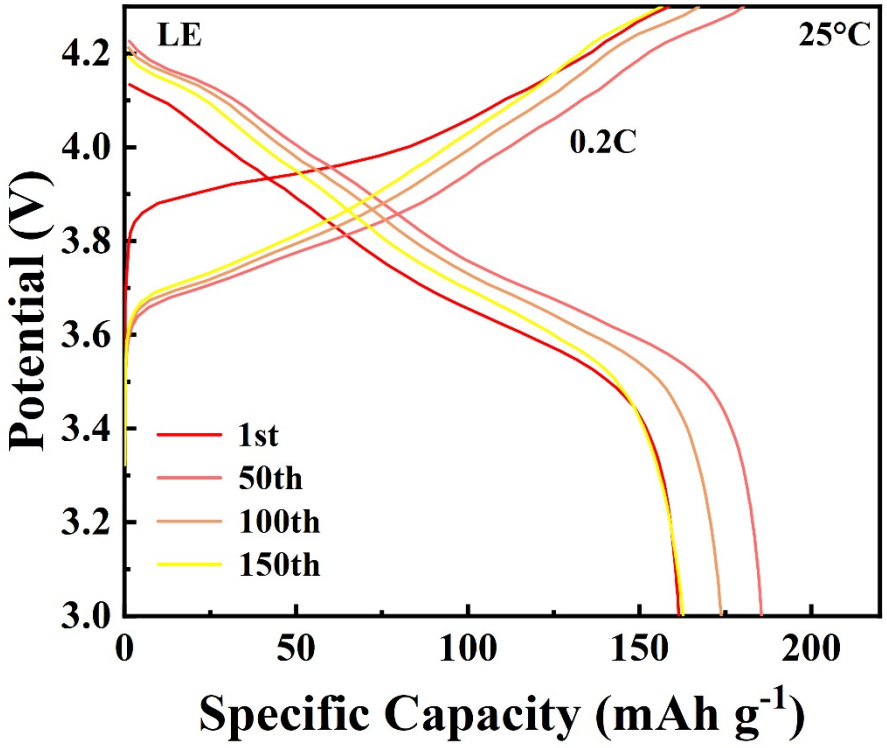

Fig. S22. Charge/discharge profiles of NCM811/LE/Li battery at 0.2C.

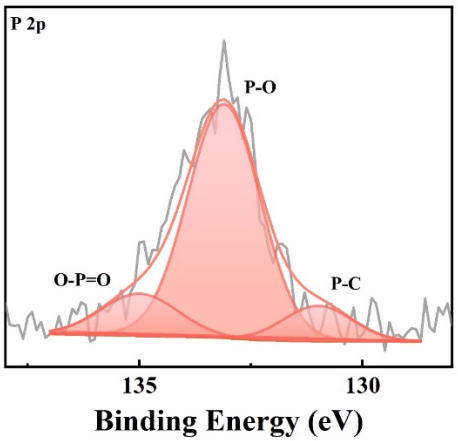

Fig. S23. XPS spectrum of P 2p for Li anode of cycled LFP/FGPE/Li battery.

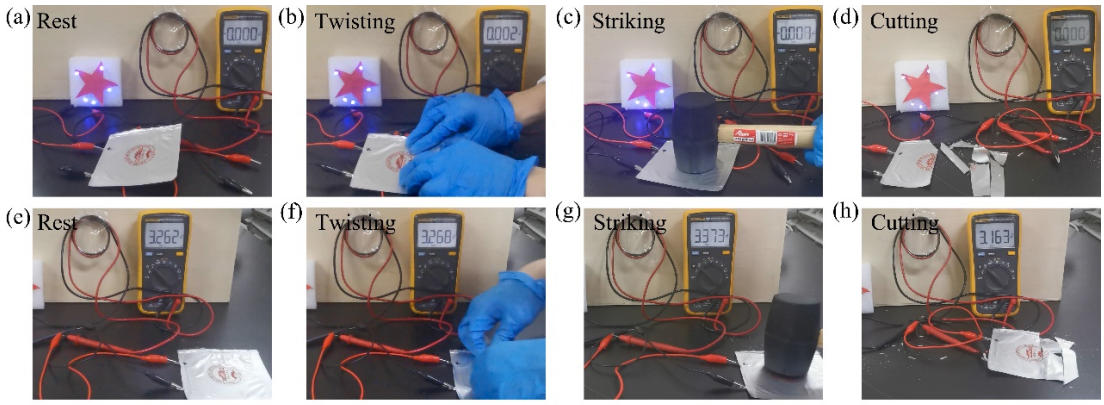

Fig. 24. (a-d) Powering LED lamps test and (e-h) voltage test of LFP/FGPE/graphite pouch cell under fully-charged rest state, twisting, hammer striking and cutting.

Table S1. Electrochemical performances of phosphorus flame retardant applied to gel polymer electrolytes in previous reports.

Polymerization strategy	Monomer	Ionic conductivity (mS cm^{-1})	Capacity (mAh g^{-1})	Capacity retention	Flame retardant ratio	Flame retardant effect	Ref.
Free radical polymerization	**PEGDA/ PEGMEMA/ DOPO**	**1.13 (RT)**	**LFP 165.7, 0.1C 160.4, 0.2C**	**99% (300 cycles) 99.7% (300 cycles)**	**8%**	**Flame contact for 190 s without ignition**	**This work**
UV curing	PUA/SN/ Al_2O_3/DOPO	0.266 (RT)	LFP 144.6, 0.2C	96.3% (100 cycles)	4%	Flame contact is ignited for 5 s and extinguished after 3 s	[ref.1]
---	TTE/DOPO in carbonate electrolyte	About 5.7 (RT)	LFP 152, 0.2C	99.7% (65 cycles)	5%	Flame contact without ignition	[ref.2]
Free radical polymerization	PEG/KH560/ DOPO	0.0298 (RT)	LFP 130.7, 0.2C, 60°C	About 99% (200 cycles)	13.67%	Flame contact without ignition	[ref.3]
Free radical polymerization	VC/TEP	4.4 (RT)	LFP 147, 0.5C	98.7% (300 cycles)	50%	Flame contact for 1 s without ignition	[ref.4]
Free radical polymerization	TAEP/ PEGDMA	0.51 (RT)	LFP 138, 0.5C	About 92% (300 cycles)	7.5%	Flame contact for 10 s without ignition	[ref.5]

Reference

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4. Energy Storage Mater. 39 (2021) 186–193.
5. Adv. Funct. Mater. 2022, 32, 2203006.