Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting information for

A multifunctional polymeric additive with synergistic effect for excellent performance of lithium-ion batteries

Yunfeng Zhang[a#], Yi Zhang[a#], Wei Bao[a#], Yaying Wang[a], Shikang Huo[a], Rui Wang[b], Zhenyuan Hu[a*], Weijie Chen[a], and Deli Wang[b*]

[a]Sustainable Energy Laboratory, Faculty of Material Science and Chemistry, China University of Geosciences (Wuhan), 388 Lumo RD, Wuhan 430074, China. E-mail: zhenyuan_hu@163.com (Z. Hu).

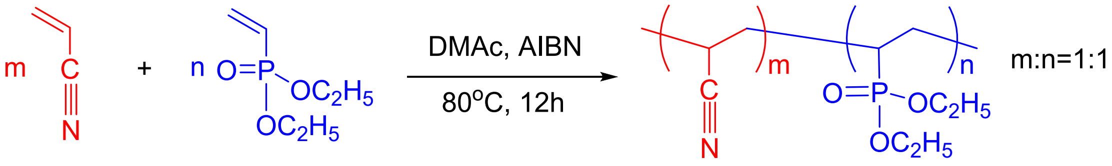
[b]Key Laboratory of Material Chemistry for Energy Conversion and Storage (Huazhong University of Science and Technology), Ministry of Education, Hubei Key Laboratory of Material Chemistry and Service Failure, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China. E-mail: wangdl81125@hust.edu.cn (D. Wang).

#These authors contributed equally to this work

Experimental section

Materials: Poly(vinylidene fluoride)-co-hexafluoropropylene (PVDF-HFP, Mw = 450 000 g mol-1), acrylonitrile (AN, 99.9%), diethyl vinylphosphonate (DEVP, 98%) were purchased from Sigma Aldrich Co., Ltd. N-methyl-2-pyrrolidone (NMP, 98%), N,N-Dimethylacetamide (DMAc, 99%), ethanol (99%), and 2,2'-azobis(2-methylpropionitrile) (AIBN, 99%) were purchased from Aladdin Biochemical Technology Co., Ltd. Acetylene black, lithium foils (thickness: ~450 μm) and LiFePO4 were purchased from Tianjin STL Energy Technology Co., Ltd. Polypropylene (PP) separators (Celgard 2400) were purchased from Celgard company. Liquid electrolyte (1M $LiPF_6$ in EC/DMC = 1:1, v/v) was purchased from Suzhou Dodochem Technology Co. All chemical materials were used without further purification.

Preparation of FRPA additive



Scheme. S1. Schematic diagram of synthesis of FRPA.

The FRPA co-polymers were prepared via free-radical copolymerization of AN and DEVP with a feed molar ratio of 1:1 using AIBN as the initiator (Scheme. S1). Briefly, AN (1.06 g, 20 mmol), DEVP (3.28 g, 20 mmol), AIBN (43.42 mg, 0.26 mmol), and DMAc (20 ml) were mixed in a 100 ml round-bottle flask, followed by stirring and bubbling using N_2 for 20 min. Then, the mixture was heated at 80 °C under stirring for 24 h to perform the polymerization. After that, the FRPA copolymers were obtained by precipitating the resultant reaction mixture in an excess amount of ethane, followed by thoroughly washing the precipitates with ethane. The products were dried in a vacuum oven at 80 °C for 12 h. The chemical structure of FRPA was successfully verified by the 1H NMR analysis (Fig. S1) and FT-IR spectroscopy (Fig. S2). The molecular weights (Mw) of the copolymer are measured to be 12248 g mol^{-1} with a narrow polydispersity index (PDI) of 1.21.

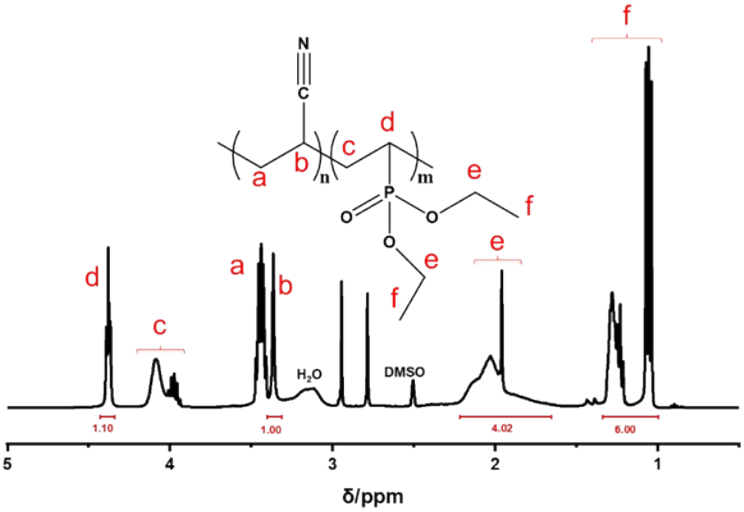


Fig. S1. ^{1}H NMR spectrum of FRPA.

The peaks that appeared at a (3.45-3.5 ppm) and b (3.4 ppm) are assigned to the -CH_2 and –CH of poly(AN), respectively. The peaks at d (4.4 ppm), e (1.5-2.2 ppm), and f (1-1.4 ppm) are ascribed to the –CH, -CH_2, and -CH_3 of poly(DEVP), respectively. Therefore, the measured molar ratio between AN and DEVP in the FRPA copolymer is calculated to be 1:1.1.

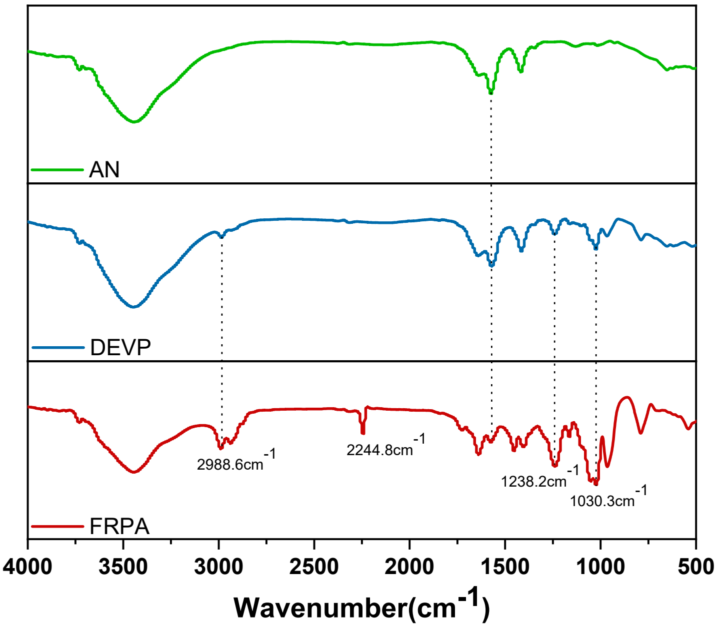


Fig. S2. FTIR spectrum of AN, DEVP, and FRPA.

The characteristic of C≡N is not present in the AN monomer due to the conjugate effects of C=C bond before reaction. Notably, a new characteristic peak at 2244.8 cm^{-1} corresponds to the stretching vibration of C≡N for the FRPA after polymerization, and the peaks located at 1030.3 and 1238.2 cm^{-1} ascribe to the stretching vibration of P-O-C and P=O bonds, respectively.

Preparation of FRPA electrolytes

The FRPA-containing electrolytes were separately made by adding different amounts of FRPA material into commercial electrolyte in the glove box (Fig. S3). The as-prepared FRPA electrolyte will be named FRPA-*X*%, where *X* of 5, 10, and 20 stand for the weight ratio to the blank liquid electrolyte. All electrolytes were stored in the glove box before use.

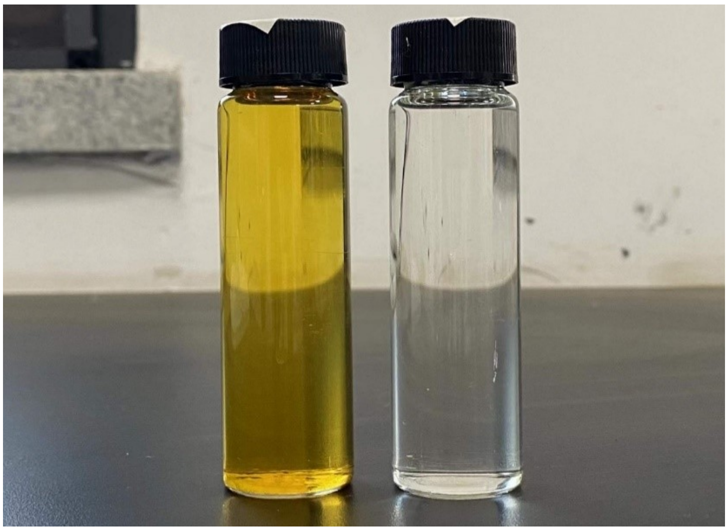


Fig. S3. Optical photograph of CE (right) and FRPA-5% (left) electrolytes.

Preparation of $LiFePO_4$ cathode

The $LiFePO_4$ cathode was made by uniformly mixing the $LiFePO_4$, acetylene black, and P(VDF-HFP) in NMP with a mass ratio of 7:2:1 to obtain a viscous slurry. Afterward, the slurry was pasted on an aluminum foil and dried in an oven at 70 °C for 36 h. Then, the obtained electrodes were cut into disks with diameters of 15 mm, and the loading of active material ($LiFePO_4$) was approximately 2.0 mg cm^{-2}.

Characterization

^1H NMR spectrum was performed on a 400 MHz instrument (AVANCE III HD 400 MHz, Swiss BRUKER). The Fourier transform infrared (FTIR) spectra were recorded on a FTIR-6700 (Nicolet iS50). The thermogravimetric analysis (TGA) was measured by a thermogravimetric analyzer (STA 409 PC, Germany NETZSCH) with a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. Differential scanning calorimetry (DSC) tests were tested on a TA instrument (METTLER TOLEDO DSC3) at the heating/cooling rate of 10 °C min^{-1} in a nitrogen atmosphere. The morphology of Li metal and cathode were analyzed by scanning electron microscopy (FE-SEM, SU8010, HITACHI). Molecular weights (M_w) of the copolymer were measured using gel permeation chromatography (GPC, Waters1515) with DMF as the mobile phase.

The self-extinguishing time (SET) test in this study was to place various electrolytes in a positive electrode shell, and then ignited them while recording the time from the start of combustion to the extinction of flame. Then, the SET can be calculated *via* the recorded time divided by the mass of the electrolyte. When the flame is close to the electrolyte for more than 60 s and still cannot ignite the electrolyte, it is judged as a non-flammable electrolyte.

The limiting oxygen index (LOI) of various electrolytes was tested on a Limiting Oxygen Index Chamber (COI, motis-tech) to determine the flammability of various samples. It is noted that the percentage of O_2 in the N_2 and O_2 mixture was only sufficient to make combustion, which is the value of LOI.

The ionic conductivity (σ) of electrolytes can be tested by sandwiching the electrolytes between two stainless plates of steel (SS) as electrodes and tested by AC impedance spectroscopy using the Zahner potentiostat-galvanostat electrochemical workstation model (PGSTAT) in the frequency range from 1MHz to 1Hz at different temperatures. The calculation of the formula of ionic conductivity (σ) is as follows:

$$\sigma = \frac{L}{R_b S}$$

where L is the thickness of PP separators, R_b is the total resistance of the electrolytes, and S is the surface area of the electrode.

The electrochemical stability of electrolytes was measured in a Li|electrolytes|SS cell with the use of linear sweep voltammetry (LSV) and cyclic voltammograms (CA) methods at a voltage scan rate of 1 mV s^{-1} from 1-6 V.

The coin cells (2025-type) constructed by different electrolytes were carried out by the Battery Measurement System (CT2001, Wuhan Land Electronic Co. Ltd., China) at 25 °C.

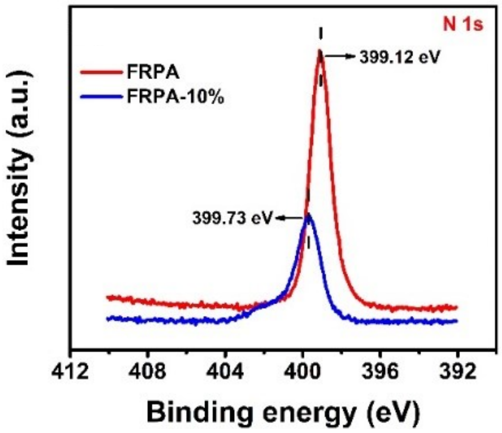


Fig. S4. N 1s core XPS spectrum of FRPA and FRPA-10%.

Fig. S5. The calculated electrostatic potential of the -C≡N group of FRPA and Li-ion with binding energy.

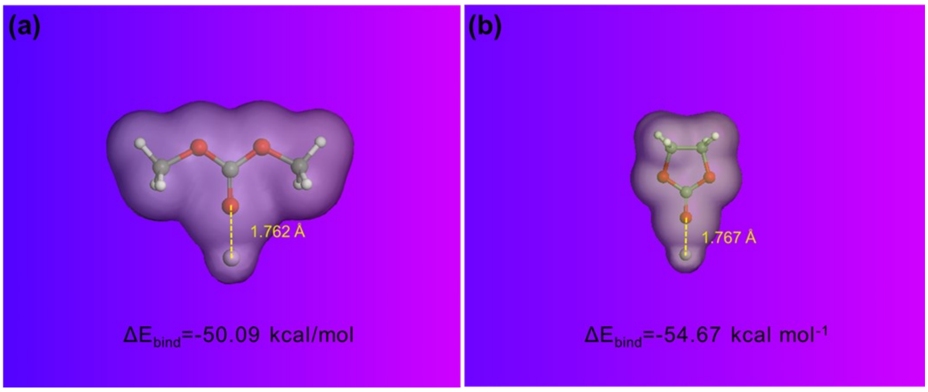


Fig. S6. The schematic illustration of DFT structure optimization for (a) DMC and (b) EC with Li^+, respectively.

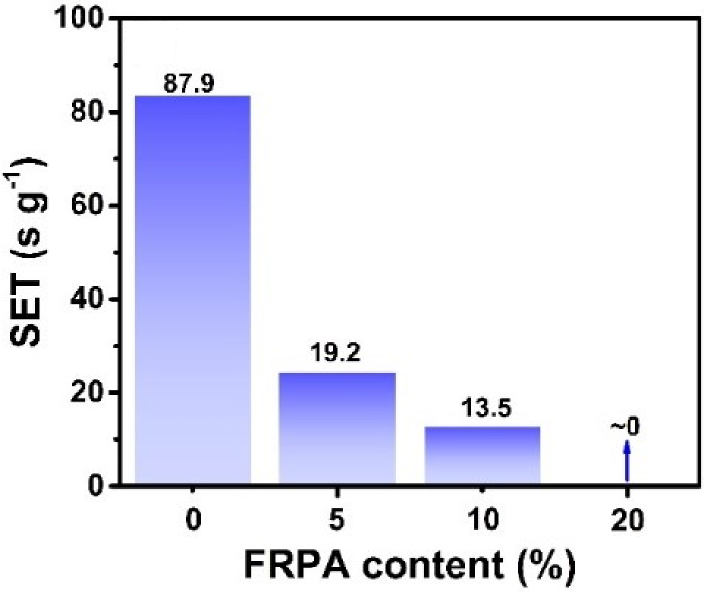


Fig. S7. Self-extinguishing time of commercial electrolytes and electrolytes with different contents of FRPA.

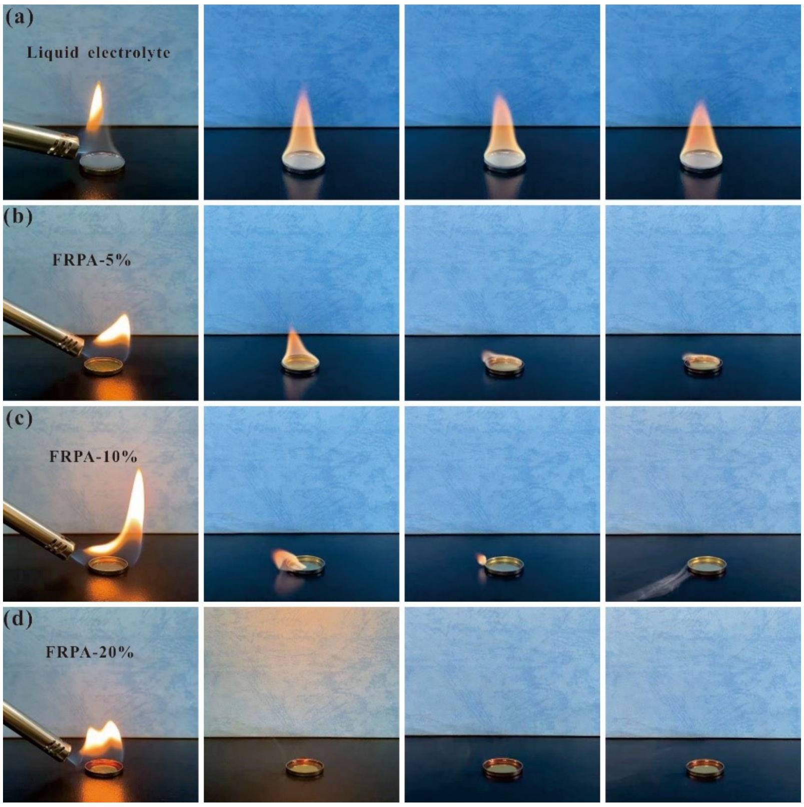


Fig. S8. Optical photograph of flame retardant tests for (a) CE, (b) FRPA-5% (c) FRPA-10%, and (d) FRPA-20%.

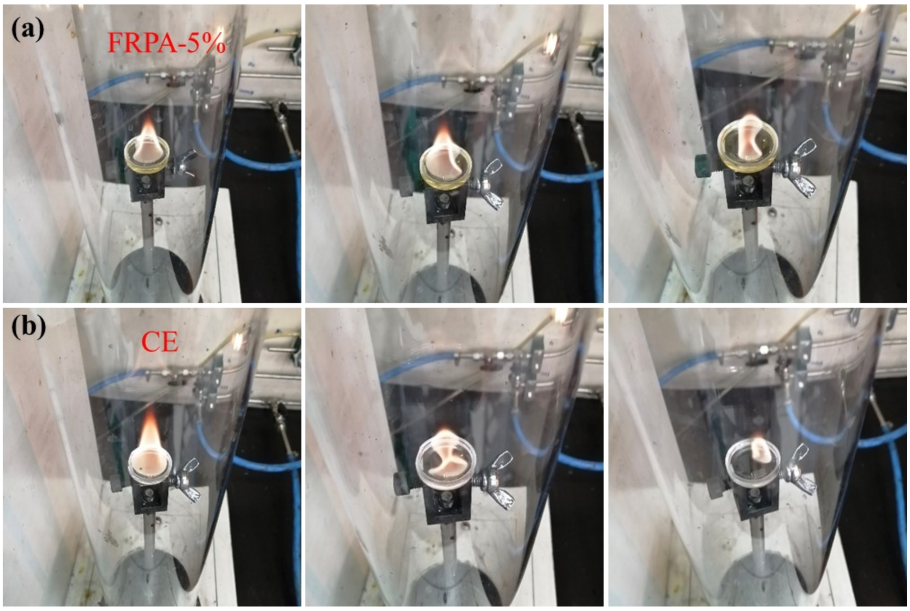


Fig. S9. Limit oxygen index test of (a) FRPA-5% and (b) commercial liquid electrolyte.

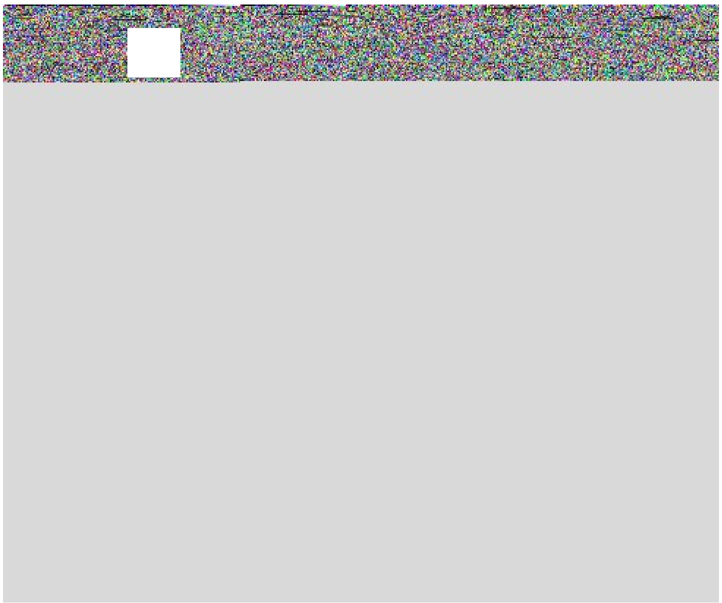


Fig. S10. The TGA curves of the electrolytes.

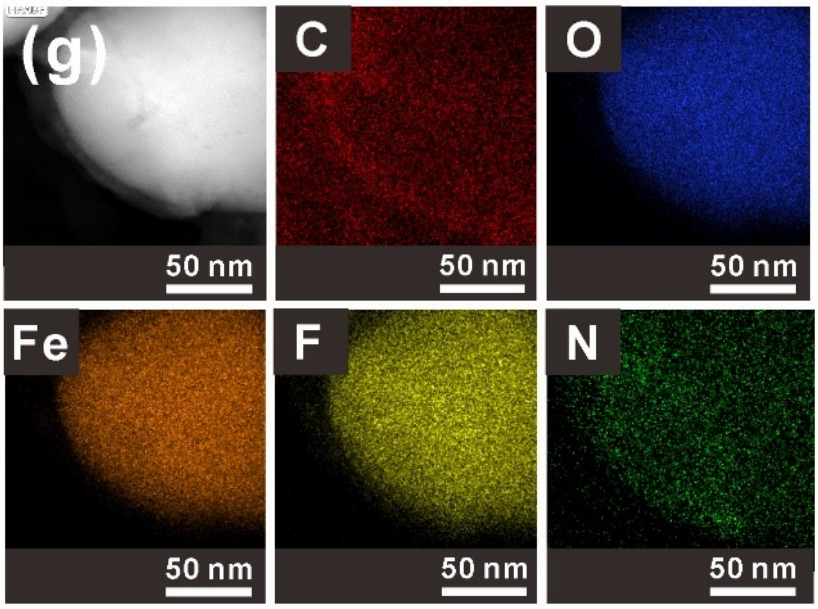


Fig. S11. The element distribution of the electrode materials in the FRPA-10% electrolyte.

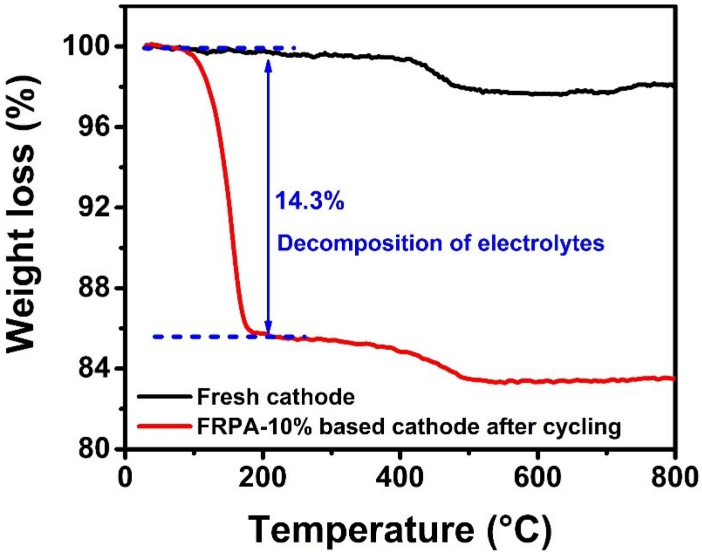


Fig. S12. The TGA tests of fresh cathode and FRPA-10% based cathode after 1500 cycles at 20 C. The weight loss of 14.3% from 105 to 210 °C is due to the decomposition of CEI deposited on the cathode surface after 1500 cycles.

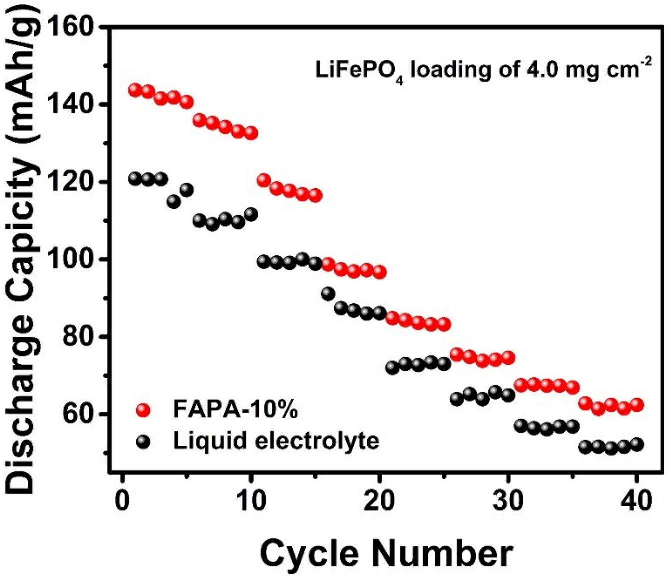


Fig. S13 The rate performances of high LiFePO4 loading (4.0 mg cm-2) of the battery with FRPA-10% and pure liquid electrolyte at 25 °C.

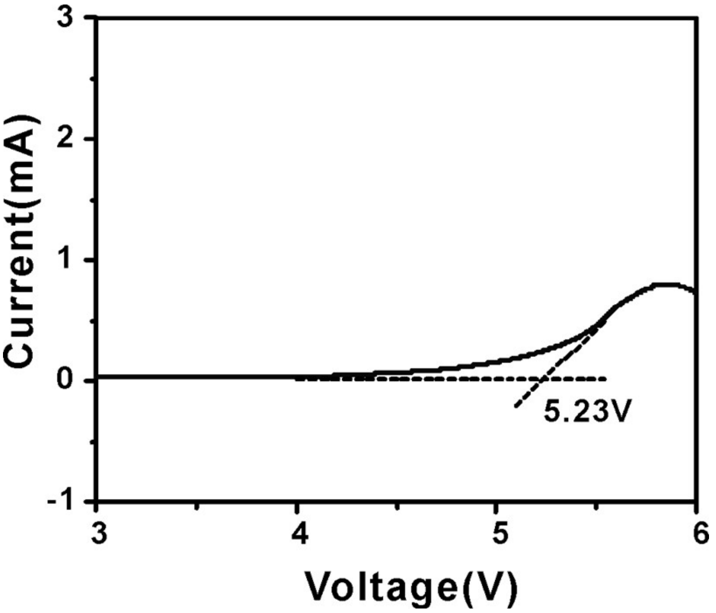


Fig. S14. Electrochemical stability of the FRPA-10% electrolyte.

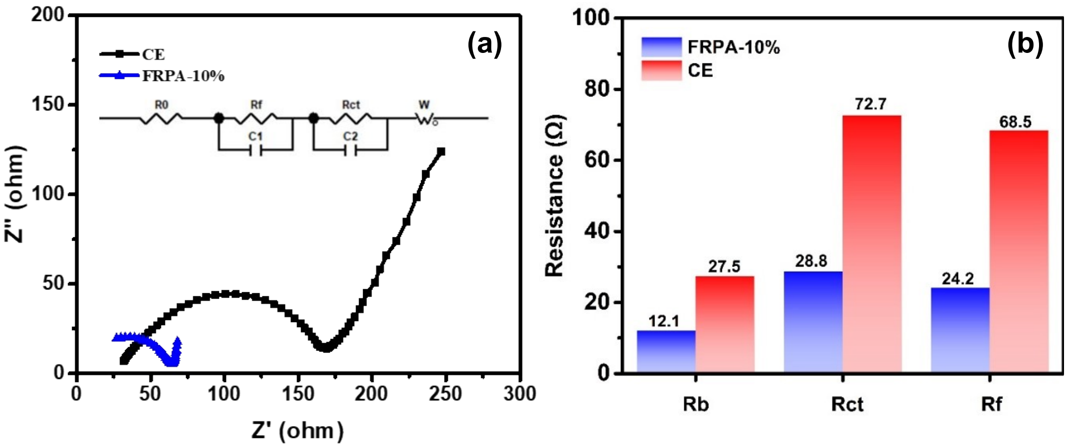


Fig. S15. (a) The EIS tests of $LiFePO_4$/Li battery before cycling at 25 °C and (b) the corresponding bulk resistance (Rb), charge transfer resistance (Rct), and interfacial resistance (Rf) values of the cells with FRPA-10% and CE.

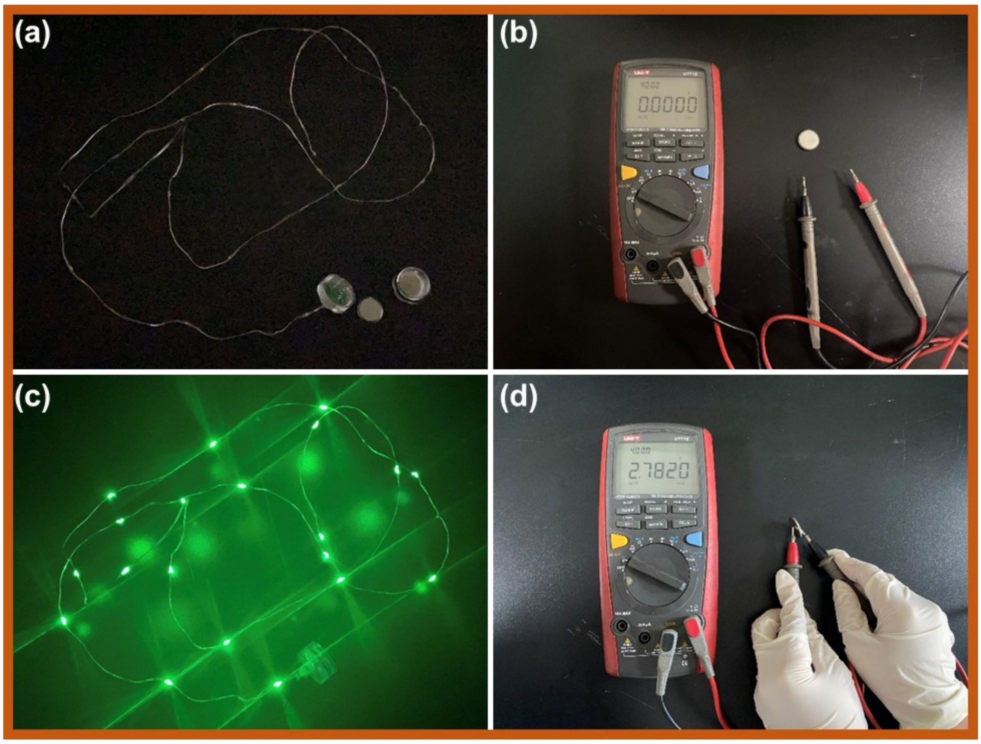


Fig. S16. Optical images of LED logo (a, b) before and (c, d) after lighting by the 2025coin cell assembled with the FRPA-10% electrolyte.

Table S1 *SET* and C_{SET} experimental data of FRPA series electrolytes

	CE	FRPA-5%	FRPA-10%	FRPA-20%
SET (s g^{-1})	83.52	24.31	12.73	0
C_{SET} (%)	-	29.11%	15.24	0