

## Supporting Information

# **A Fluorine-Rich and Flame-Retardant Gel Polymer Electrolyte Enables by Thermal Polymerization of Fluorinated Acrylates for Stable Quasi-Solid-State Na-ion Battery**

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### **Experimental Section**

#### **Synthesis of HP-GPE**

The NaPF<sub>6</sub> (1.0 M) was dissolved in a mixed solvent of ethylene carbonate (EC) and diethyl carbonate (DEC)(1:1 volume ratio) to form the liquid electrolyte (LE). The LE was mixed with pentaerythritol tetracrylate (PETEA, 100 mg mL<sup>-1</sup>) with hexafluorobutyl methacrylate (HFBMA, 100 mg mL<sup>-1</sup>) to form a precursor solution. After adding azodiisobutyronitrile (AIBN, 0.1 wt.%) as the polymerization initiator, this precursor solution was heated at 60 °C for 6 h to form HP-GPE without flowability.

#### **Synthesis of NFM cathode material**

The NFM cathode material was synthesized by ball milling a mixture of Na<sub>2</sub>CO<sub>3</sub>, NiO, Fe<sub>2</sub>O<sub>3</sub>, and Mn<sub>2</sub>O<sub>3</sub> in a molar ratio of 3.2 : 2 : 1 : 1 at 450 rpm for 4 h. The resulting powder was annealed at 850 °C for 18 h at a heating rate of 5 °C min<sup>-1</sup>, yielding the NFM cathode material.

#### **Material characterization**

X-ray diffraction (XRD, Bruker D8 Advance, Cu K $\alpha$ ), X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250), Fourier transform infrared spectrometer (FTIR, NicoletIS50), and Raman spectroscopy (Raman, Zhongke Kaili) were used to investigate the chemical composition of the samples. Thermogravimetric analysis (TGA, Mettler Toledo 8510e) was performed in N<sub>2</sub> atmosphere to assess the electrolyte properties.

### **Assembly and tests of half cells**

The half cells were conducted using CR2016 coin cells with Na metal foil as the counter and reference electrode. The working electrode consists of an NFM, carbon black (Super P) and polyvinylidene fluoride (PVDF) binder in a weight ratio of 9 : 0.5 : 0.5 on carbon-coated Al foil. The active mass loading is 11–12 mg cm<sup>-2</sup>. A glass fiber separator was used for cell assembly. The precursor solution of the HP-GPE was added to the cell and sealed, followed by heating at 60 °C for 6 h to obtain a quasi-solid-state half-cell. For comparison, the liquid-based half cells were assembled similarly except for using LE. All the cells were assembled in an Ar-filled glove box (H<sub>2</sub>O < 0.1 ppm, O<sub>2</sub> < 0.1 ppm). The cells were cycled in a voltage window of 2.0–4.0 V (vs. Na/Na<sup>+</sup>) at various current densities on LAND CT2001A battery testers.

### **Assembly and tests of quasi-solid-state full cells**

The quasi-solid-state full cells were assembled using the NFM cathode and CC anode. The N/P ratio was 1.1–1.2. A glass fiber separator was used for cell assembly. The precursor solution of the HP-GPE was added to the cell and sealed, followed by heating at 60 °C for 6 h to obtain a quasi-solid-state full cell. For comparison, the liquid-based full cells were assembled similarly except for using LE. All the cells were assembled in an Ar-filled glove box (H<sub>2</sub>O < 0.1 ppm, O<sub>2</sub> < 0.1 ppm). The cells were cycled in a voltage window of 1.0–4.0 V at various current densities on LAND CT2001A battery testers. For cycling stability tests, the full cell was first cycled at a current density of 12 mA g<sup>-1</sup> and then cycled at various current densities. All battery tests were conducted at 30 °C unless otherwise specified.

The quasi-solid-state pouch cells were assembled using the NFM cathode and CC anode, with the same N/P ratio for assembling coin full cell. The precursor solution of the HP-GPE was added to the cell and sealed with an aluminum-plastic shell, followed by heating at 60 °C for 6 h to obtain a quasi-solid-state full cell. All battery tests were conducted at 30 °C unless otherwise specified.

### **Electrochemical test of HP-GPE**

The ionic conductivity ( $\sigma$ ) of the electrolyte was measured by using a symmetric coin cell with stainless steel (SS) as the working electrode. The HP-GPE or LE serves as the electrolyte with a glass fiber separator. The  $\sigma$  was obtained from the impedance spectroscopy of the customized two-electrode cell by the following equation:

$$\sigma = \frac{L}{A \times R} \quad (1)$$

Where  $R$  is the ohmic resistance,  $A$  is the electrode area, and  $L$  is the space between two stainless steel electrodes, respectively. The data points from 30 to 80 °C were measured by CHI 760E electrochemical workstation in a frequency range of 1000 kHz to 0.1 Hz.

The  $\text{Na}^+$  transference number ( $t_{\text{Na}^+}$ ) of the electrolytes was determined by the potentiostatic polarization technique using a CHI 760E electrochemical workstation. A voltage of 10 mV was applied to a symmetric coin cell with Na metal as the working electrodes for 180 min to measure the initial current ( $I_0$ ), which is derived from both cation and anion transfer in the electrolyte. The steady-state current ( $I_{ss}$ ) is solely attributed to the transportation of  $\text{Na}^+$ . Electrochemical impedance spectroscopy (EIS) measurements were conducted before and after the polarization step to obtain the impedance of the cells. The transference number was calculated by the following equation:

$$t_{\text{Na}^+} = \frac{I_{ss}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{ss} R_{ss})} \quad (2)$$

where  $\Delta V$  is the applied bias voltage,  $R_0$  is the initial impedance, and  $R_{ss}$  is the steady-state impedance.

The electrochemical stability window (ESW) of the electrolytes was measured by linear sweep voltammetry (LSV) scan of an asymmetric coin cell at a scan rate of 5 mV  $\text{s}^{-1}$ . The stainless steel was used as the working electrode and Na metal acted as the countered and reference electrode. The HP-GPE or LE serves as the electrolyte with a glass fiber separator.

### ***In-situ* XRD tests**

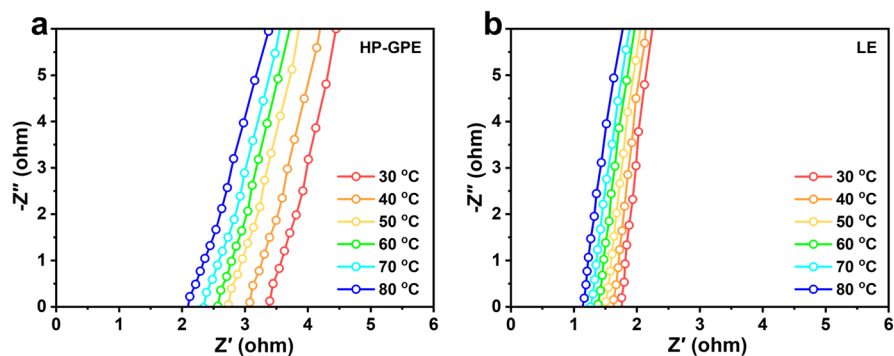
*In-situ* XRD analysis were performed on half cells using NFM as the working electrode and Na metal foil as the countered and reference electrode. *In-situ* XRD patterns were recorded using a X-ray diffractometer with a 2D detector (Bruker D8 DISCOVER) on a cell module with a Be window. The XRD patterns were collected per 600 s in a  $2\theta$  range of 10 to 40°. Meanwhile, the discharge-charge tests were conducted by using a LAND CT2001A battery tester between 2.0–4.0 V (vs. Na/Na<sup>+</sup>) at a current density of 12 mA  $\text{g}^{-1}$ .

### ***In-situ* Raman tests**

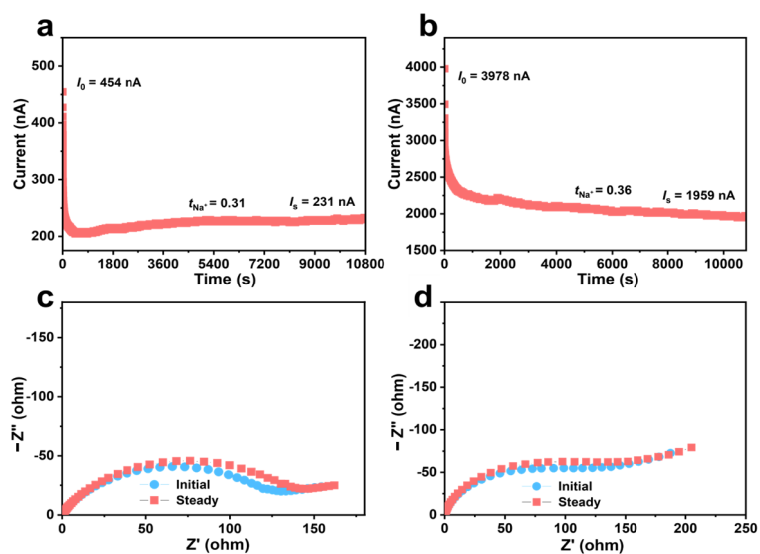
*In-situ* XRD analysis were performed on half cells using CC as the working electrode and Na metal foil as the counter and reference electrode. *In-situ* Raman spectra were collected using an electrochemical cell with a quartz window on a Raman spectrometer (Zhongke Kaili, China) with a laser wavelength of 532 nm per 20 min. Meanwhile, the discharge-charge tests were conducted by using a LAND CT2001A battery tester between 0.0–2.0 V (vs. Na/Na<sup>+</sup>).

### **Nail penetration test.**

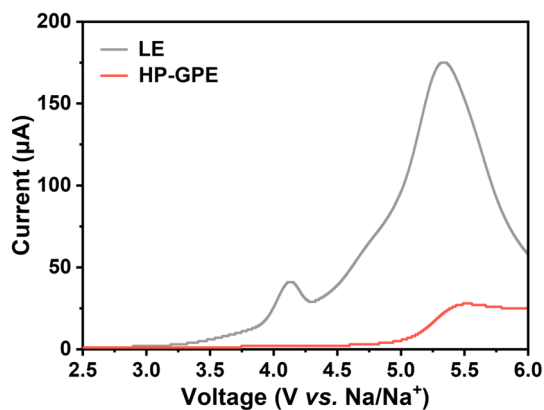
The nail penetration test was conducted on a commercial nail penetration tester (ASR-9016, Guangdong AISRY Ins. Tech. Co., Ltd) under ambient air conditions. During the test, a stainless-steel nail with a diameter of 5 mm was driven through the fully charged pouch cells at a speed of 20 mm s<sup>-1</sup>.



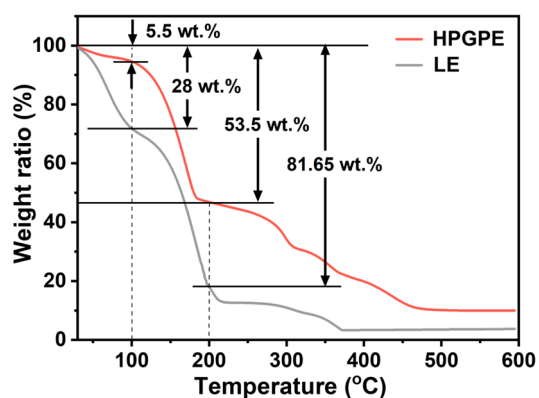
**Fig. S1** Nyquist plots of (a) HP-GPE and (b) LE at various temperatures.



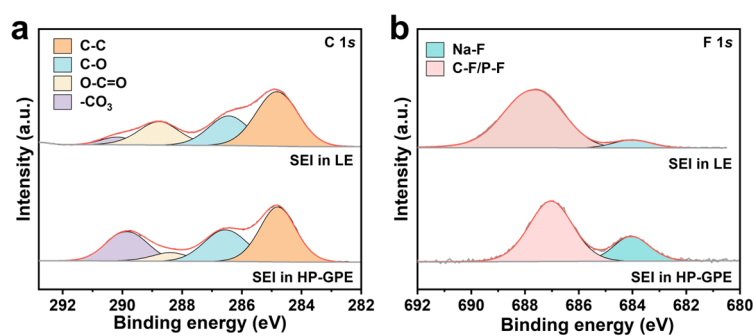
**Fig. S2** (a) Chronoamperometry profiles of (a) HP-GPE and (b) LE. Nyquist plots of (c) HP-GPE and (d) LE.



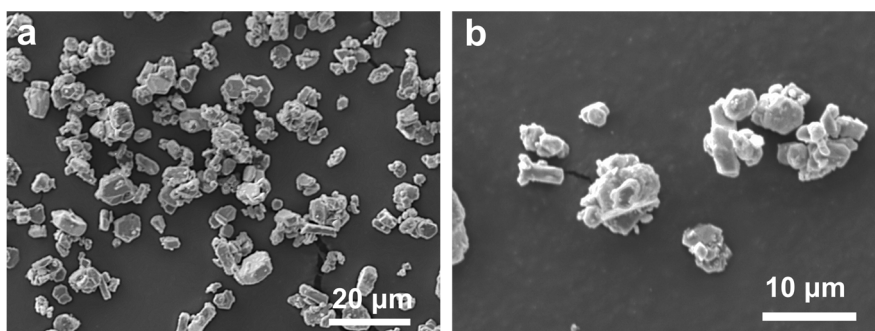
**Fig. S3** Linear sweep voltammetry curves of HP-GPE and LE at a scan rate of  $5 \text{ mV s}^{-1}$  in an asymmetric cell using stainless steel as the working electrode and Na metal as the counter and reference electrode.



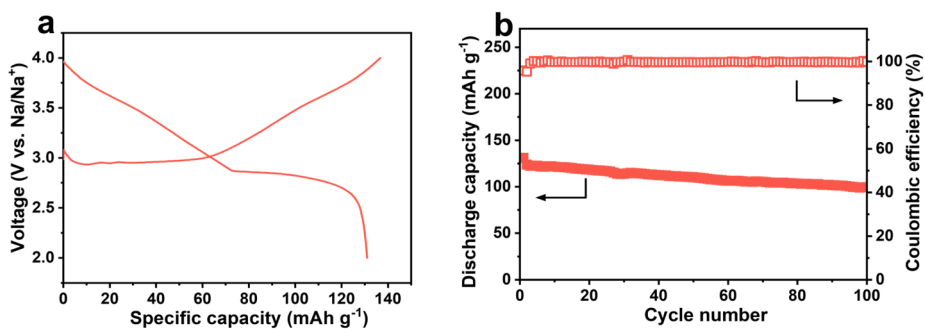
**Fig. S4** TGA curves of HP-GPE and LE in N<sub>2</sub> flow at a ramp rate of 10 °C min<sup>-1</sup>.



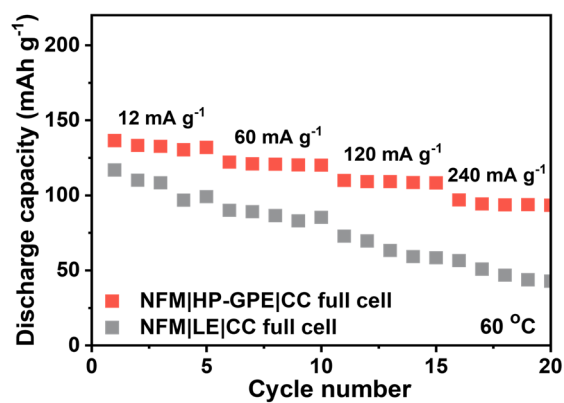
**Fig. S5** (a) C 1s and (b) F 1s XPS spectra of SEI formed on CC anode in HP-GPE or LE.



**Fig. S6** SEM images of NFM material synthesized via the solid-state method



**Fig. S7** (a) Charge-discharge voltage profiles and (b) cycling stability of NFM cathode in HP-GPE at a current density of 12 mA g<sup>-1</sup> between 2.0–4.0 V (vs. Na/Na<sup>+</sup>).



**Fig. S8** A comparison of rate capabilities of NFM|HP-GPE|CC and NFM|LE|CC full cells at 60 °C when cycling at various current densities.

**Table S1** A comparison between our work and recent studies in the performance of gel polymer electrolytes and quasi-solid-state Na-ion batteries.

<b>Gel polymer electrolytes</b>	<b>Ionic conductivity (mS cm<sup>-1</sup>)</b>	<b>Safety</b>	<b>Cycle life</b>	<b>Reference</b>
HP-GPE	<b>2.08</b>	<b>flame-retardant nonleaky</b>	<b>400 cycles</b>	<b>This work</b>
IL-UIOSNa	0.36	nonleaky	100 cycles	Ref. S1
TPDBD-CNa	0.13	nonleaky	160 cycles	Ref. S2
FNCPE	1.37	nonleaky	200 cycles	Ref. S3
SIL-GPE	1.1	nonleaky	50 cycles	Ref. S4
SIL-GPE	1.12	nonleaky	40 cycles	Ref. S5
DPEPA-GPE	1.97	nonleaky	300 cycles	Ref. S6

### References

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