A Sandwich Structure FPI-PEO/Celgard/FPI-PEO Separator with Polysulfide Shuttle Suppression and Dendrite Puncture Resistance for Room-Temperature Sodium-Sulfur Batteries

Xiaoguang Jiao[a], Chao Yang[a], Kaixuan Ma[a], Suyu Ge[a], Huanhuan Zhu[a], Caihong Feng[a], Qingze Jiao[a,b], and Yun Zhao[a,]*

a. Beijing Key Laboratory for Chemical Power Source and Green Catalysis, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, 5 South Zhongguancun Street, Haidian District, Beijing 100081, China

b. School of Materials and Environment, Beijing Institute of Technology, Jinfeng Road No. 6, Xiangzhou District, Zhuhai 519085, China

E-mail: zhaoyun@bit.edu.cn

Experimental section

Materials

4,4'-diaminodiphenyl ether (ODA): 98%, 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA): 98%, pyromellitic anhydride (PMDA): 99%, N, N'-Dimethylformamide (DMF): 99.5%, Poly (propylene glycol) bis (2-aminopropyl ether) (PEO) were purchased from Mackin Co., Ltd. Sublimed sulfur was purchased from Aladdin Scientific Co., Ltd. Carbon nanotubes was purchased from Anhui Senrise Technology Co., Ltd. Celgard 2500 was purchased from DoDo Chem Co., Ltd.

Synthesis of Fluorinated Polyamic Acid Copolymerized with Polyether (FPAA-PEO)

1.6 g of polyether diamine was added into a three-necked bottle with nitrogen protection and mechanical stirring, then 3.27 g of ODA and 15ml of DMF were added, and kept stirring for 30 minutes. Then the reaction temperature was reduced to 0 ℃, 3.12 g of PMDA and 4.58 g of 6FDA were added in batches, then kept solution at 0 ℃ for 12 hours. DMF was added during the reaction to adjust the viscosity of the solution.

Preparation of FPAA-PEO fiber membrane

As-prepared FPAA-PEO solution was poured into a syringe, and the modified polyamic acid fiber membrane was prepared by electrospinning. Set spinning parameters: voltage 20 KV, advancing amount 0.7 ml/h, receiving roller rotation speed 600 r/min, spinning time 8 h. Different thicknesses of films were obtained by changing the spinning time.

Preparation of FPI-PEO nanofiber membrane

As-prepared FPAA-PEO nanofiber membrane was placed in a muffle furnace, and thermally treated at 100 ℃, 150 ℃, and 200 ℃ for 1 hour respectively to obtain FPI-PEO nanofiber membrane (marked as: FPI-PEO). The synthesis and preparation process of FPI-PEO nanofiber membranes are shown in Scheme. S1 and Fig. S1.

Preparation of C/S cathode material

Sulfur (S) and carbon nanotubes (CNTs) were mixed together in a weight ratio of 7:3 through a mallet. The mixture product was then placed into a reaction kettle, and heated in an oven to 155

℃ for 12 hours to obtain the final CNTs/S composite material.

Preparation of sulfur cathode

S/CNTs, Ketjen black (KB) and polyvinylidene difluoride (PVDF) were mixed evenly at a mass ratio of 8:1:1, and fully ground. Then a certain amount of N-Methylpyrrolidone was added, and grinding was continued to make the slurry appear as an ink-like liquid without obvious particles. The ground slurry was evenly coated on the copper foil with a spatula. The electrode sheet was first placed in a blast drying oven for drying at 60 °C for 6 hours, and then transferred to a vacuum drying oven for 12 hours at 60 °C. Finally, the dried electrode sheet was cut into small round sheets with a diameter of 12 mm using a microtome. The active sulfur loading capacity in the individual electrode sheet was 1.2 mg/cm^2.

Battery assembly

FPI-PEO was placed on both sides of the Celgard separator to build a sandwich structure of composite separator for battery assembly (marked as: FPI-PEO/Celgard/FPI-PEO). Assemble the battery in the order of negative electrode, FPI-PEO, Celgard, FPI-PEO, electrolyte, positive electrode, gasket and spring plate. Among them, the electrolyte was 1M $NaCF_3SO_3$ in diethylene glycol dimethyl ether.

Characterizations

The structure and morphology of the separators were characterized by Fourier Transform Infrared Spectroscopy (Thermo Fisher Scientific Nicolet iS5) and Scanning Electron Microscopy. The thermal and mechanical properties of the separators were characterized by Thermal Gravimetric Analyzer (Rigaku TG/DTA 8122) and Universal Testing Machine (INSTRON 5982/ 8872/ CMT4104/ RGM-6300). The contact angles of the separators were characterized by a contact angle measuring instrument (Dataphysics OCA 20). The heat release rate (HRR) and total heat release (THR) were characterized by a micro combustion calorimeter (MCC, Gomak's instrument mcc_2).

Electrochemical measurements.

Galvanostatic charge-discharge (GCD) curves were obtained by a battery test system (LAND CT2001A, China). Cyclic voltammetry (CV), linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) were measured on a CHI 760D electrochemical workstation.

Ionic conductivity.

Ionic conductivity was measured by electrochemical AC impedance spectroscopy (EIS) in the frequency ranging from 1 kHz to 0.1 Hz with an AC amplitude of 100 mV via a CHI760E electrochemical workstation. The ionic conductivity was calculated using the following equation:

$$\sigma = \frac{L}{(R * A)}$$

where L is the measured thickness, S is the facing area of the two stainless steel foils, and R is the horizontal intercept obtained from electrochemical impedance spectroscopy.

Na ion transference number (t_{Na^+}).

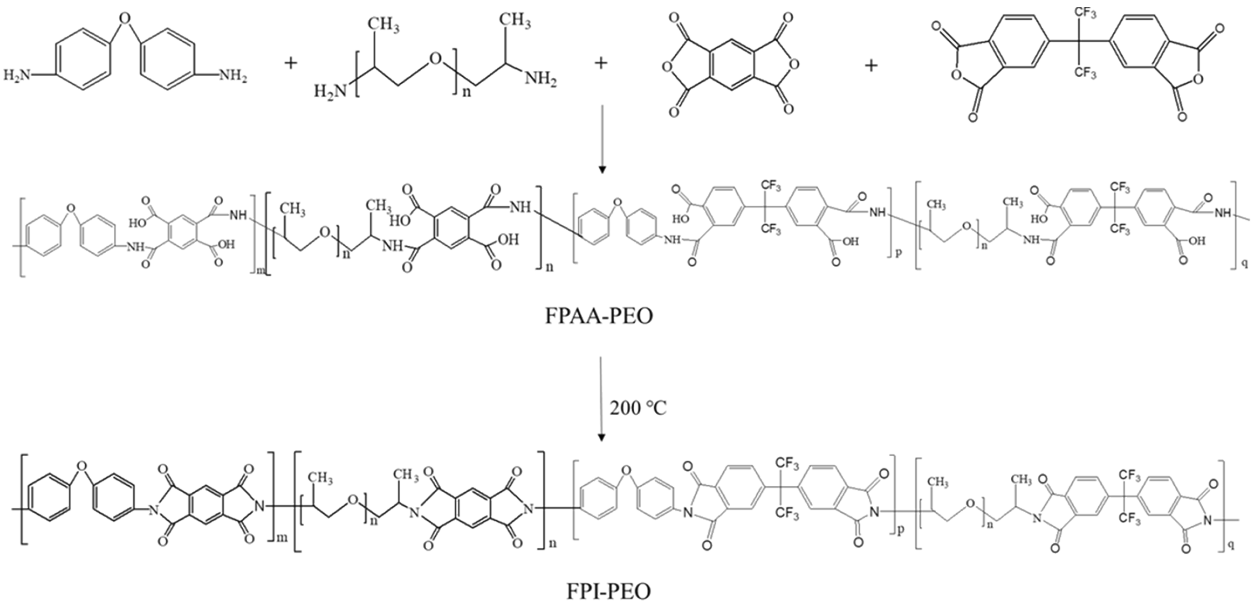
Na ion transference number was measured utilizing amperometric technique with an applied DC voltage of 10 mV and EIS measurement in a Na symmetric cell based on Celgard and FPI-PEO/Celgard/FPI-PEO. EIS was tested before and after the DC polarization conducted by amperometric technique. The t_{Na^+} value was calculated according to Bruce's equation:

$$t_{Na^+} = \frac{I_S(\Delta V - I_0 R_0)}{I_0(\Delta V - I_S R_S)}$$

where ΔV is the polarization voltage (10 mV), I_0 is the initial current, which is the steady state current, R_0 is the initial resistance, and R_s is the steady state total resistance.

Density functional theory (DFT) calculations

All density functional theory (DFT) calculations were performed using Gaussian 16 software. All calculations used the B3LYP function combined with D3BJ dispersion correction. For geometric optimization and frequency calculations, all atmospheres used the 6-31G (d, p) basis set. The single point calculations were under the level of M062x-D3/6-311G (d, p).



Scheme. S1 Synthesis of FPI-PEO.

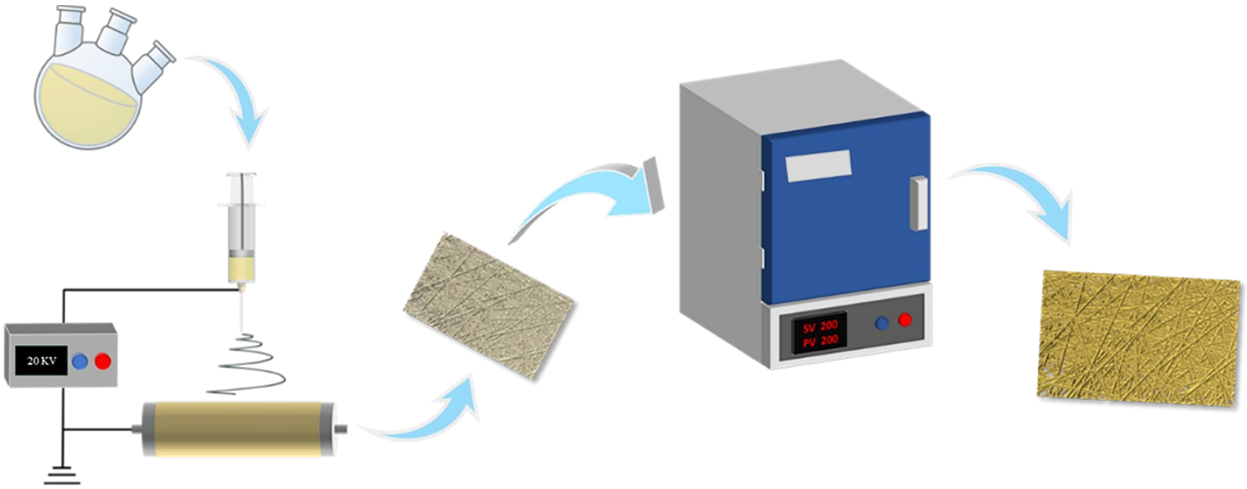


Fig. S1 Preparation process of FPI-PEO fiber membrane.

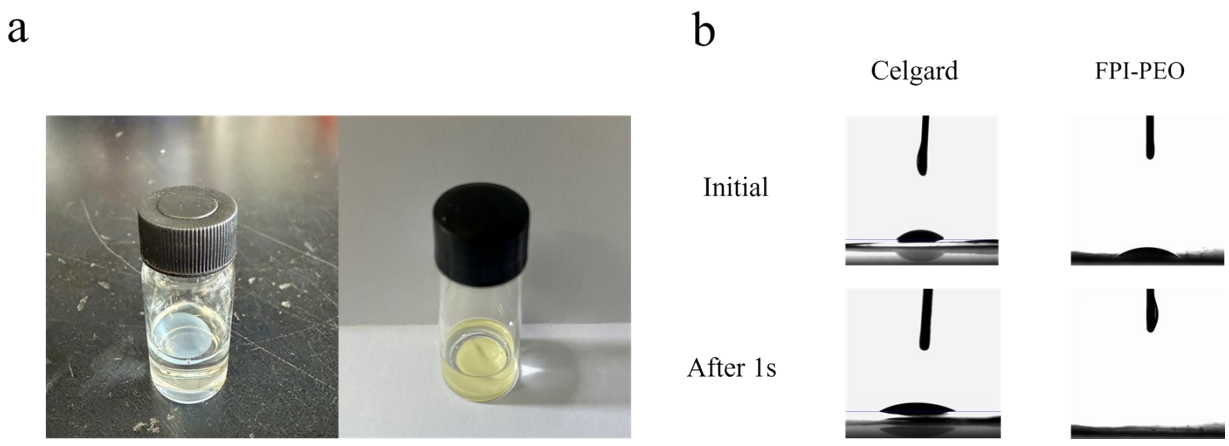


Fig. S2 (a) Photographs of Celgard and FPI-PEO immersed in the electrolyte for 24 hours; (b) Contact angle between electrolyte and separators.

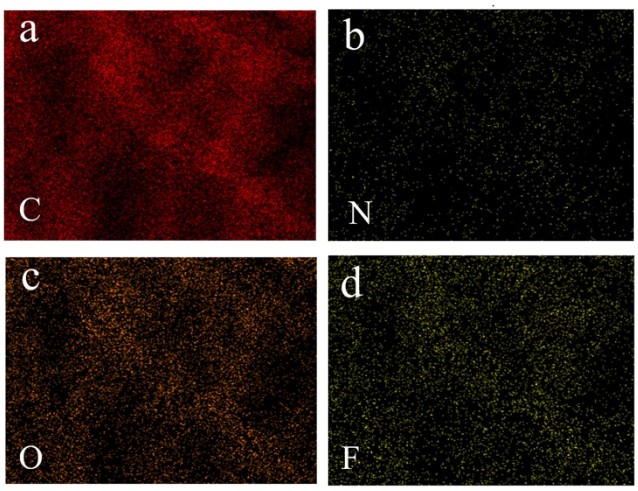


Fig. S3 EDX of carbon residue.

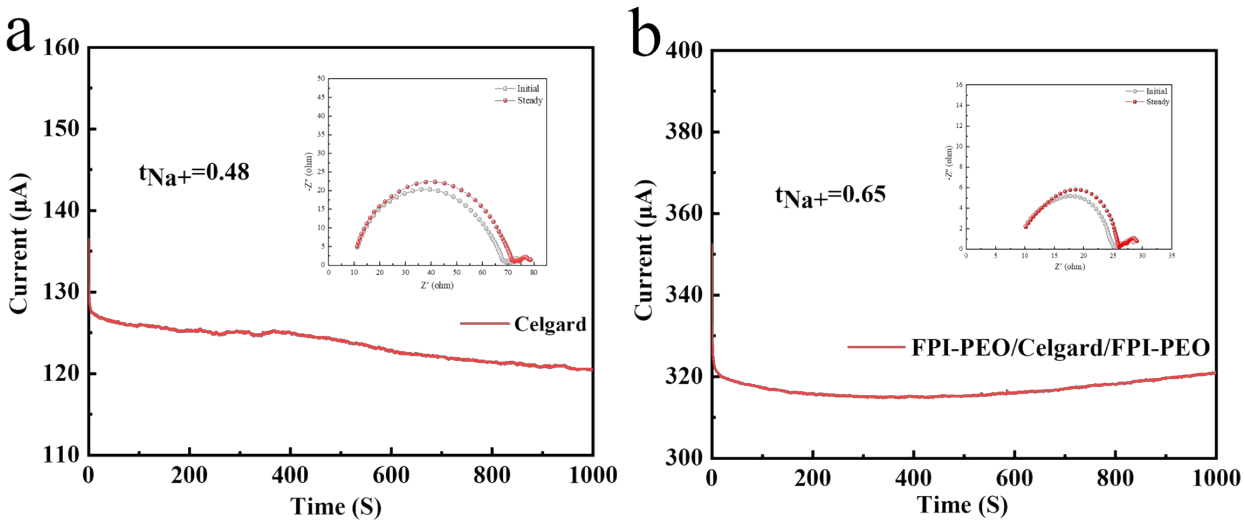


Fig. S4 Electrochemical impedance spectra and direct-current polarization curves of symmetric cells based on (a) Celgard (b) FPI-PEO/Celgard/FPI-PEO.

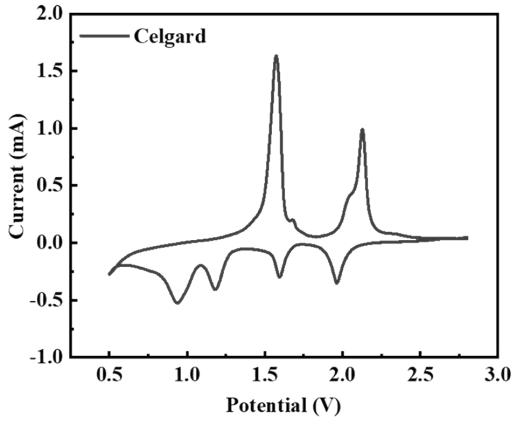


Fig. S5 CV curves of Na|Celgard|S at a scan rate of 0.1 mV s^{-1}.

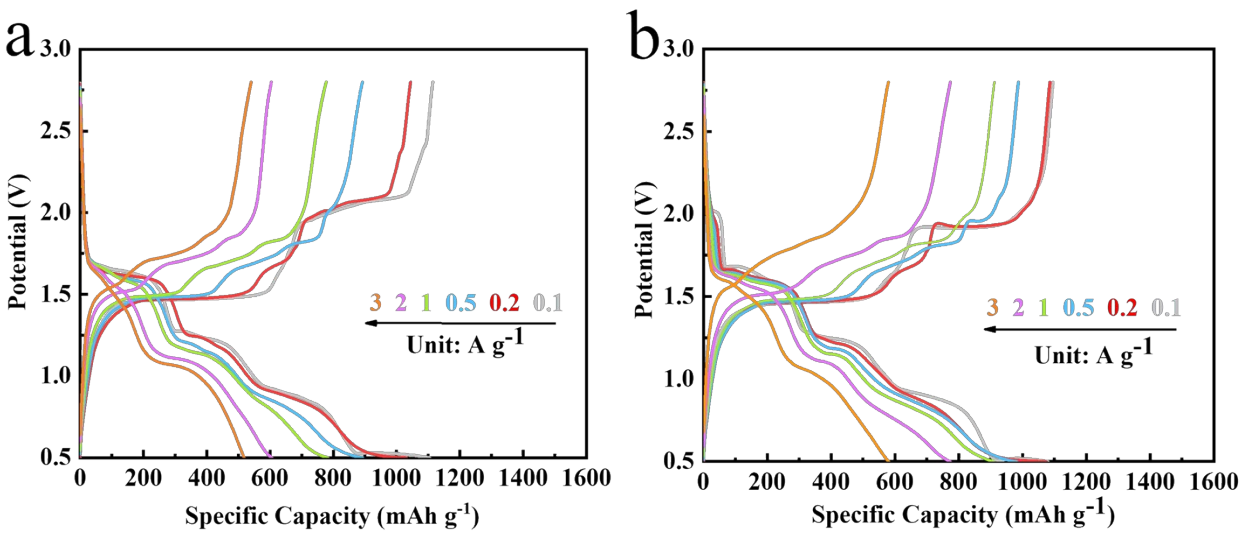


Fig. S6 Charge-discharge curves of the battery at 0.1-3 A g^{-1}: (a) Celgard; (b) FPI-PEO/Celgard/FPI-PEO.

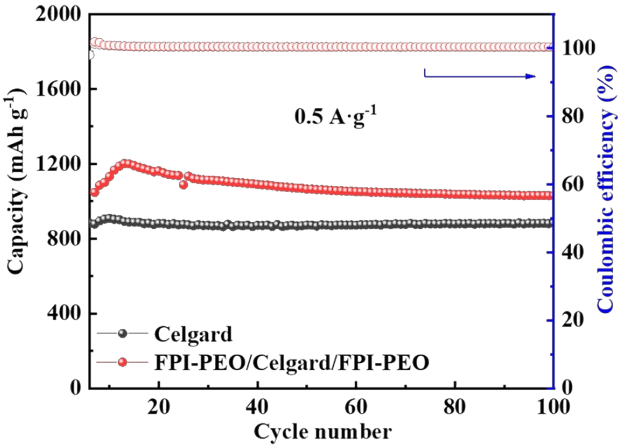


Fig.S7 Cycle stability of cells assembled with separators at 0.5 A g^{-1}.

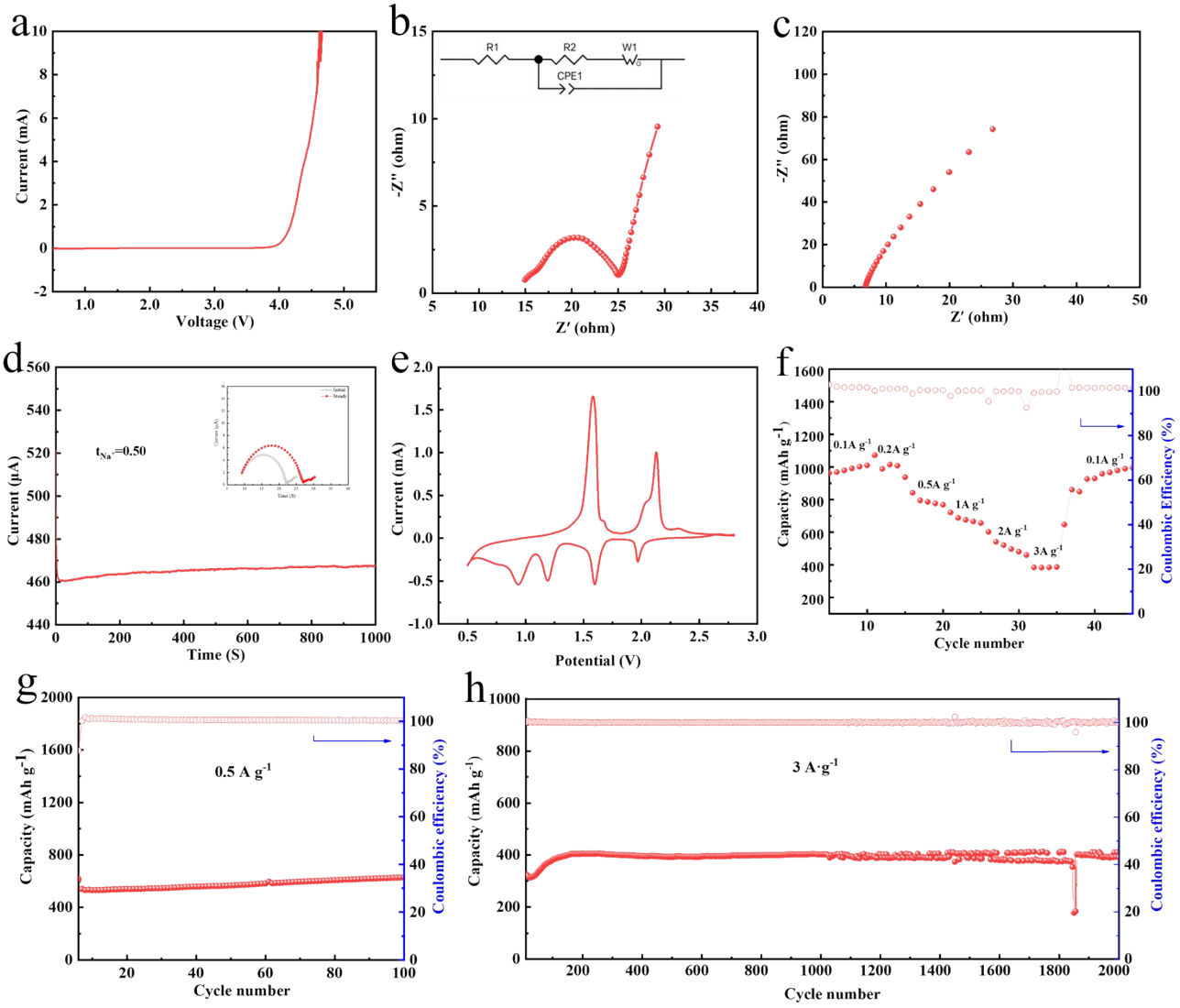


Fig. S8 Electrochemical properties of FPI-PEO/Celgard/FPI-PEO separator batteries with low fluorine content: (a) LSV curve. (b) EIS curve based on S|Separator|Na. (c) EIS curve based on SS|Separator|SS. (d) Na-ion transference numbers (e) CV curve. (f) Rate capabilities.

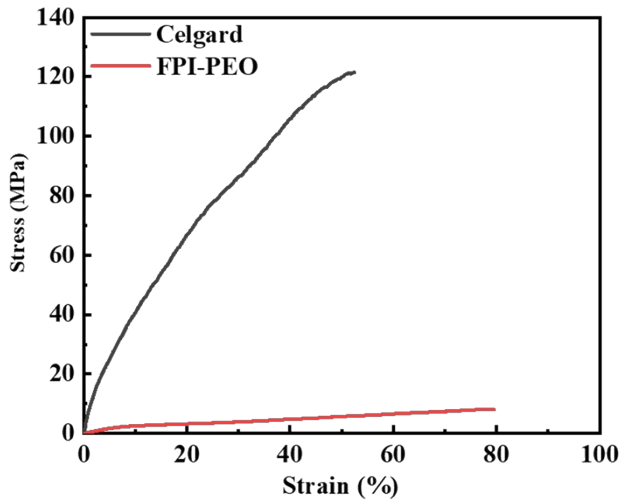


Fig. S9 Stress-strain curves of Celagrd and FPI-PEO.

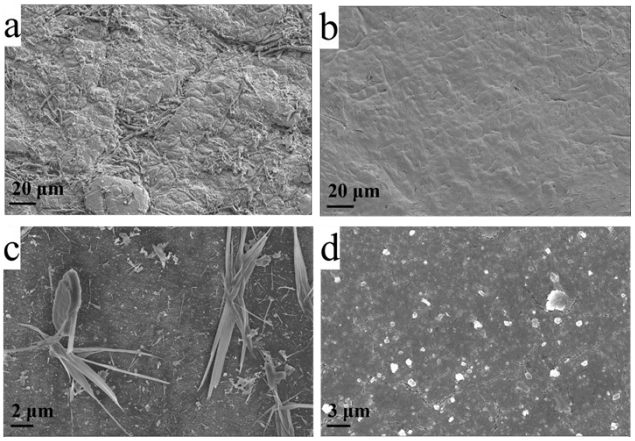


Fig.S10 SEM images of sodium negative electrodes and Celgard after plating stripping cycles of assembled (a, c) Celgard and (b, d) FPI-PEO/Celgard/FPI-PEO separator batteries.

Fig. S11 Polysulfur penetration testing of low fluorine content FPI-PEO/Celgard/FPI-PEO separator.

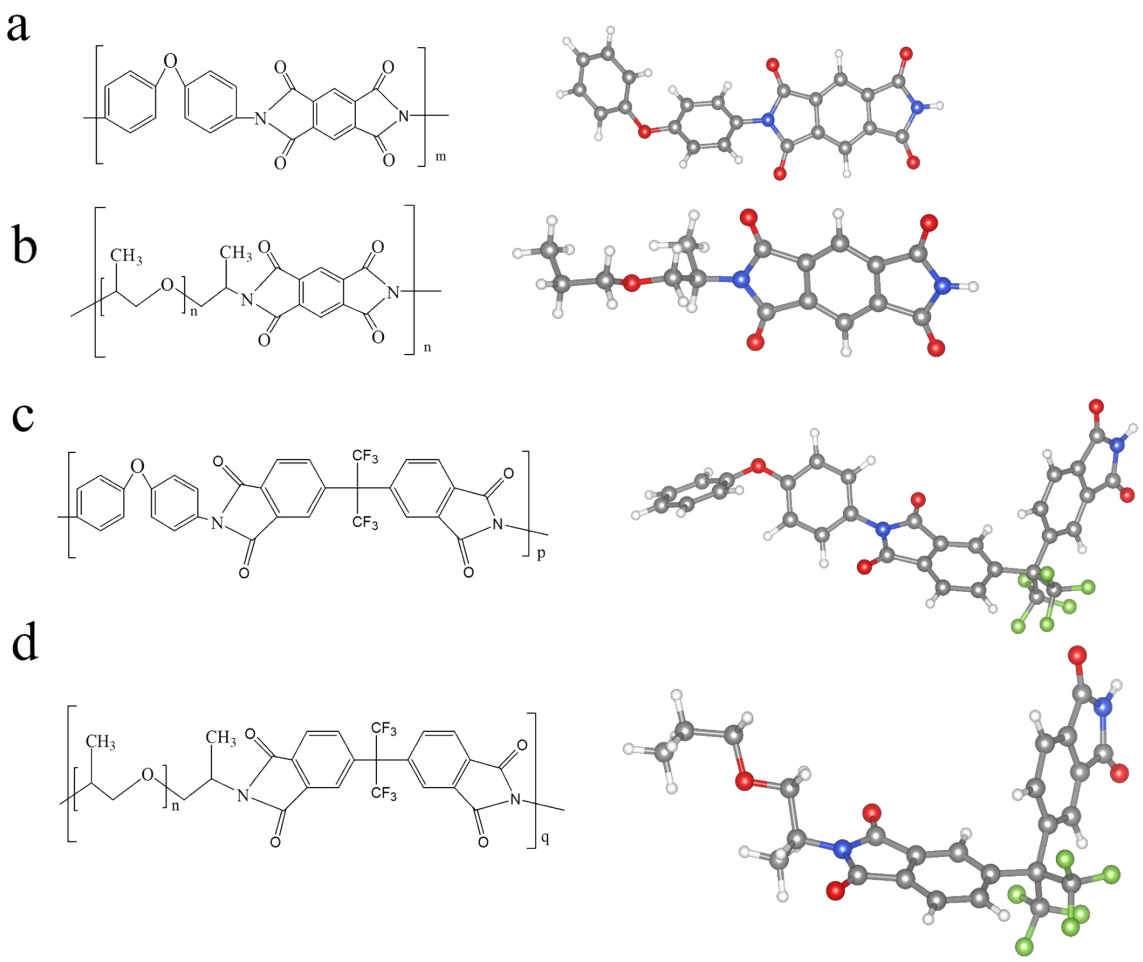


Fig. S12 Chemical structure and model of (a) segment E;(b) segment F;(c) segment G and (d) segment H. Color matching: carbon (gray); nitrogen (blue); oxygen (red); fluorine (green).

Table S1. Wettability of different separators to electrolytes

Sample	Thickness (μm)	Electrolyte uptake (%)	initial contact angle (°)	Contact angle after 1 s (°)
Celgard	25	120±5	38.2	21.2
FPI-PEO/Celgard/FPI-PEO	65	726±6	21.7	0

Table S2. Oxygen index of separators

Sample	LOI（%）	combustion characteristics
Celgard	17.27	dripping
FPI-PEO	23.68	/

Table S3. The fitting results based on equivalent circuit.

Sample	Rs (Ω)	Rct (Ω)
Celgard	12.68	5.6
FPI-PEO/Celgard/FPI-PEO	9.9	3.3

Table S4. Electronegativity of different chain segments

Segment	Electronegativity （eV）
Celgard	-
G	-4.70
H	-5.28