Supporting Information

Electropolymerization Growth of an Ultrathin, Compact, Conductive and Microporous (UCCM) Polycarbazole Membrane for High Energy Li-S Batteries

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Experimental Section

Materials: 1,3,5-Tris(N-carbazolyl) benzene (TCB), tetrabutylammonium hexafluorophosphate (TBAPF₆, 99%), anhydrous dichloromethane (DCM, 99.8%), acetonitrile (MeCN, 99.8%) and Indium tin oxide (ITO) slide were purchased from Sigma. TBAPF₆ was recrystallized twice in ethanol and vacuum dried for 24 h before use. Dichloromethane was purified by distillation with CaH₂ as the water removal agent. The single-wall carbon nanotube (CNT) was purchased from

XFNANO Materials Tech Co., Ltd. Polypropylene (PP) separator (Celgard 2500) and lithium metal chip were received from MTI Corporation.

Preparation of CNT/PP separator: The CNT was first treated with a thin layer of polydopamine to enhance its hydrophilicity and dispersion ability in aqueous solution according to the previous report. Then a certain amount of the as-prepared CNT aqueous solution (0.01 mg mL^{-1}) was filtrated onto the PP separator and washed with DI water. The obtained CNT/PP separator was vacuum dried at 60°C overnight, and the CNT layer on the PP separator was controlled to be around 0.08 mg cm^{-2} .

Preparation of the UCCM/PP separator: Electropolymerization was performed with a typical one-compartment, three-electrode electrochemical cell connected to a CHI 660C electrochemical workstation. An Ag/Ag⁺ non-aqueous electrode was used as the reference electrode, the CNT/PP separator or ITO was used as working electrode, and titanium plate acted as counter electrode. The electrolyte is TBAPF₆ (0.1 M) in anhydrous CH₃CN/CH₂Cl₂ (1:1 v/v) with the dissolved TCB (0.8 mg mL^{-1}) monomer, and the solution was filtrated through $0.45 \mu\text{m}$ PTFE filter before usage. The potential range was set between -0.8 and 1.03 V and scan rate is 50 mV s^{-1} . The thickness of the films was controlled by adjusting the number of CV cycles. After the electropolymerization completed, the resulting separators were washed with acetonitrile to remove unreacted monomers and supporting electrolytes followed by drying under vacuum. When replacing the ITO with the CNT/PP as the working electrode, the polymerized porous film could be deposited on ITO and peeled off as a freestanding membrane, which was collected for further characterization.

Sulfur cathode fabrication. The sulfur cathode was prepared by a typical slurry casting method. Typically, the sulfur was mixed with CNT (7:3, w/w), and the CNT-S composite was obtained after heating at 155 °C for 6 h in an argon atmosphere. Then the CNT-S was well mixed with PVDF (9:1, w/w) in NMP solution to form a slurry, which was uniformly casted on aluminum foil via a doctor blade system. After vacuum dried at 55 °C overnight, the electrode was punched into Ø12mm disk with a sulfur loading of around 2.1 mg cm⁻².

The high-loading MXene based self-assembled sulfur cathodes were also prepared based on our previous work^[1]. Specifically, the process involves the self-assembly of the positive charged CNT-PEI and negative charged MXene (Ti₃C₂T_x) nanosheets. The thickness of the composite film was controlled by the amount of assembled dispersion. After punched into Ø12mm disks, the S/CS₂ solution was dropped onto the film and slowly dried at RT. The sulfur contained films were further treated at 155 °C for 6 h in a sealed glass bottle filled with Ar. The obtained sulfur infused composite film was used directly as the self-standing cathode, and the areal sulfur loading was determined by weighing composite film before and after loading sulfur. For the anode in the full-cell, the mixture of graphite and PVDF (9:1 w/w) in NMP was tape cast on copper foil followed by drying overnight. The graphite was discharged to 0.01 V in Li || graphite cell and then disassembled carefully, the lithiated graphite electrode was subsequently washed and dried, and assembled as anode in lithium-ion sulfur cell. The amount of intercalated lithium is controlled at about 30 wt% higher than the theoretical one calculated based on the chemical equation of $\text{Li} + \text{S} \rightarrow \text{Li}_2\text{S}$.

Materials characterization. The samples morphology and structures were captured by scanning electron microscopy (FESEM, Nova nano) and STEM (FEI Titan), Energy dispersive X-ray

spectroscopy (EDS). The surface area and pore size distribution of samples were evaluated by Brunauer-Emmett-Teller (BET) measurements using an ASAP-2420 surface area analyzer. X-ray photoelectron spectroscopy was analyzed by XPS, Kratos Amicus spectrometer equipped with an Al Ka X-ray source. FTIR spectra was recorded on FT-IR is10 with baseline correction. Thermogravimetric analysis (TGA, SDT Q600) was obtained under N₂ atmosphere with temperature ramp of 5 °C min⁻¹. Electronic conductivity was measure by the four-point probe method. ¹³C NMR spectra is collected on 400M WBA Solid NMR (Advance III 400 MHz Wide Bore). The elementary porous structures of the CMPs were optimized by using a Gaussian 09 D.01 package under b3lyp/6-31g** level.

Electrochemical Measurements. CR2032 coin cells were assembled in an Argon-filled glovebox with CNT/S as the cathodes and Li metal as anodes. PP, CNT/PP and PTCB/PP were used as the separator. The electrolyte was 1 M lithium bis(trifluoromethane)sulfonimide (LiTFSI) in a mixture of 1,2-dimethoxyethane (DME) and 1, 3-dioxolane (DOL) (1:1, v/v) with 0.4 M LiNO₃. The ratio of electrolyte to sulfur was controlled to be approximately 50 μ L for regular sulfur loading electrode. The self-supporting cathode films with high sulfur loading require a higher amount of electrolyte to infiltrate the electrode compared with the regular blade-casted cathode, and the electrolyte was controlled to be around 10 μ L mg⁻¹. The electrochemical performance of the batteries were evaluated on Neware cell test system with a potential range of 1.8–2.8 V (vs Li/Li⁺). Cyclic voltammetry (CV) scans and the electrochemical impedance spectroscopy (EIS) were performed on potentiostat BioLogic VMP3a CHI 660D electrochemical workstation. Shuttle current was measured according to the previous method^[2]. The lithium ion conductivities for pristine separator and modified separators were investigated via EIS spectra^[1].

The separators saturated with electrolyte were sandwiched between two stainless steel electrodes in coin cell, and the Li⁺ conductivity could be determined according to the equation:

$$\sigma = l/(AR)$$

Where σ is the ionic conductivity, l represents the distance between two stainless steel electrodes (the separator thickness), A refers to geometric area of electrode and R is the bulk resistance measured in impedance Nyquist plot.

Supplementary Figures

Figure S1. Cross-section SEM images of the electropolymerized films at various number of CV cycles on the CNT layer, scale bar: 500 nm.

Figure S2. Optical microscope image of the electropolymerized film.

Figure S3. TEM images of the electropolymerized film and corresponding elemental mapping.

Figure S4. SEM image of the EP film before (left) and after (right) wetted with electrolyte.

Figure S5. N1s XPS spectra of the TCB monomer and EP film.

Figure S6. XRD profile for the electropolymerized film.

Figure S7. Polysulfide permeation tests. Photographs of H-type glass cells with LiPS (Li_2S_6) in DOL/DME solution and pure DOL/DME solvent in the left and right chambers, respectively, separated by (a) UCCM/PP, (b) CNT/PP and (c) PP separator.

Figure S8. Electrochemical impedance spectroscopy data (Nyquist plots) of a PTCB membrane. The membrane was soaked in the liquid electrolyte for 2 days.

Figure S9. DC polarization (V-I_e curves) of the PTCB membrane, and slope of DC voltage V vs. I_e plot represents the electronic resistance of the membrane. The electrical conductivity of the electrolyte soaked PTCB membrane is around 0.19 S m⁻¹

Figure S10. DC polarization (V-I_e curves) of the PTCB membrane in electrolyte of 0.5M (red curve) and 1.5 M (green curve) LiTFSI/(DOL/DME).

Figure S11. The thermogravimetric curve of the CNT/S composite.

Figure S12. CV curve of the cell with different separators. (a) UCCM/PP, (b) CNT/PP and (c) PP separator.

Figure S13. Charge/discharge curves of the cells with PP and CNT/PP separators at various rates.

Figure S14. Rate performances of the cells with the three different separators at 3 C.

Figure S15. Cycling performance for the cell with the thick electropolymerized film. (a) SEM images of the interlayer (2.8 μm), (b) Rate capability of the cell with the thick film, and (c) long-term cycling stability at 1 C for 200 cycles.

Figure S16. Coulombic efficiency of the batteries with different separators. The unstable and low Coulombic efficiency for the PP and CNT/PP based cell indicates the severe polysulfide shuttling without the UCCM layer.

Figure S17. SEM cross-section and surface images of the Li metal anode paired with different separators after 100 cycles test at 0.2 C. (a, e) fresh Li anode, (b, e) paired with PP, (c, g) paired with CNT/PP and (d, h) paired with UCCM/PP separator. Scale bar: (a-d) 50 μm , (e-f) 5 μm . Cells were disassembled in the glove box, and the Li-metal anodes were washed gently with DME solvent. After being dried in glove box at room temperature, the Li-metal anodes were transferred into a sealed container for SEM observation.

Figure S18. GCD curves and cycling performance at 0.2 C for the cell with the PVDF coated on the prepared CNT/PP separator via drop coating method.

Figure S19. Characterization of the MXene/CNT-PEI (T@CP) cathode. (a-c) Cross-sectional SEM images of the self-supporting T@CP cathode with sulfur loading of 4.3, 7.1 and 11.2 mg cm⁻², respectively. (d) Digital photograph of the self-supporting cathode. (e) Surface image of the T@CP cathode. (f) The sulfur elemental mapping of the cathode.

Figure S20. Cyclic performance of the Li-S cell based on the slurry casting cathode with Al current collector.

Figure S21. Charge–discharge profiles of the lithium-ion sulfur full-cell.

Figure S22. The UCCM layer prepared based on the other two monomers. Chemical structure, SEM images and CV curves of the polymerized film for (a) 1,3,5-tris(4-(N-carbazolyl)phenyl)benzene (TPBCz), and (b) spiro-(N-carbazolyl)phenyl)benzene (Spiro-CB).

Figure S23. Discharge/charge curves of the cells with UCCM layer based on the above TPBCz (a) and Spiro-CB (b) at 0.2 C.

Table S1. Performance comparison of Li–S batteries with functional separators/interlayers in recent representative publications.

Interlayer	Interlayer weight (mg cm ⁻²)	Interlayer thickness (μm)	Preparation method	Sulfur loading (mg cm ⁻²)	Rate	Capacity Retention	Ref.
UCCM layer	<0.01 _a	0.06	Electropolymerization	2.1	0.2 C	970 (600th)	This work
UCCM layer	<0.01	0.06	Electropolymerization	2.1	1 C	780 (300th)	This work
Super P	0.61	60	Slurry casting	0.7~1.0	1 C	721 (200th)	S[6]
Ce-MOF/CNT	/	3.5	Slurry casting	2.5	1 C	~350 (800th)	S[7]
Fe ₃ O ₄ NPs	0.478	15	Vacuum filtration	0.6–0.9	1 C	659 (497th)	S[8]
Black phosphorus	0.4	1.4	Vacuum filtration	1.5–2	0.2 C	~800 (100th)	S[9]
Co ₂ B@CNT	/	20.1	Vacuum filtration	3.6	0.2 C	1283 (200th)	S[10]
COF	/	28	Vacuum filtration	1.0–1.5	0.1 C	1169 (50th)	S[11]
CNT@TiO ₂	0.7	12	Slurry casting	1.7	0.1 C	803 (200th)	S[12]
HKUST-1/GO	0.3	10	Vacuum filtration	0.6–0.8	0.5 C	799 (500th)	S[13]
BaTiO ₃	2.4	5	Dip coating	3.0	0.5 C	929 (50th)	S[14]
Graphene/TiO ₂	0.15	3	Slurry casting	1.8	0.5 C	~600 (250th)	S[15]
MoS ₂ /Polymer	0.10	3	LBL	1.2	0.5 C	790 (100th)	S[16]
Graphene oxide	/	0.8	Slurry casting	1–1.2	1 C	~820 (200th)	S[17]
Nafion	0.25	1.25	drop coating	1.6	0.2 C	780 (30th)	S[18]

a. It is hard to determine the areal weight of the UCCM layer because it is ultrathin nature. Based on the typical porous polymers which density are below 0.3 mg cm⁻³, the areal mass of this UCCM layer should be below 0.01 mg cm⁻².

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