Supporting Information

Ion-selective aramid nanofibers-based Janus separators fabricated by dry-wet phase inversion approach for lithium-sulfur batteries

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*Preparation of ZIF-67/ANF-JS*_{30s}: The ANF-JS_{30s} membrane was immersed into 0.15 mol L⁻¹ cobaltous nitrate (Co(NO₃)₂·6H₂O, Sinopharm Chemical Reagent)/ethanol solution for 0.5 h, then followed by the same procedure with 0.5 mol L⁻¹ 2-methyl-imidazole (Alfa Aesar)/ethanol solution. The purple membrane was collected and washed with ethanol and n-hexane several times and then dried at 100 °C.

Preparation of MoS₂/ANF-JS_{30s}: 500 mg phosphomolybdic acid hydrate (H₃[P(Mo₃O₁₀)₄], Sinopharm Chemical Reagent) was dissolved in 60 mL of distilled water containing ANF-JS_{30s} membrane. After being kept for 0.5 h, 500 mg thiourea (NH₂CSNH₂, Alfa Aesar) was dissolved in the solution. The mixed solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and kept at 180 °C for 24 h. The black membrane was collected and washed with ethanol and n-hexane several times and then dried at 100 °C.

Preparation of Fe_2O_3/ANF **-** JS_{30s} : The ANF-JS_{30s} membrane was immersed into 0.5 mol L⁻¹ ferric chloride (FeCl₃, Sinopharm Chemical Reagent)/distilled water for 0.5 h, then followed by the same procedure with 0.5 mol L⁻¹ sodium hydroxide (NaOH, Sinopharm Chemical Reagent)/distilled water. The reddish-brown membrane was collected and washed with ethanol and n-hexane several times and then dried at 100 °C.

Preparation of Li_2S_6 **solution and sulfur cathode**: Li_2S_6 solution was prepared by mixing 0.1 g Li_2S and 0.5 g sulfur in 1,2-dimethoxyethane/1,3-dioxolane (DME/DOL) (V/V = 1:1). In a typical procedure for preparing the sulfur cathode, 4.8 g sulfur (Adamas, 60 wt%), 2.4 g carbon black (Azko Nobel, 30 wt%), 0.8 g poly(vinylidene difluoride) (Aladdin, 10 wt%) and 56 mL anhydrous N-methyl-2-pyrrolidone (NMP, Aladdin) were ground in a planetary mixer at 300

rpm for 5 h and then the mixture was coated on aluminum foil (15 μ m), followed by solvent evaporation at 60 °C and further dried at 60 °C under vacuum for 12 h. The sulfur loading in the cathode was ~1.4 mg cm⁻² for the regular tests and ~3.7 mg cm⁻² for high sulfur tests.

Electrochemical measurements: CR2032 type coin cells were used to test the electrochemical performance with Celgard 2325 separator, ANF-S and ANF-JSs separator. 1.0 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in DME/DOL (V/V = 1:1) with 1.0 wt% lithium nitrate (LiNO₃) was prepared as the electrolyte. The diameter of sulfur cathode, Lithium metal and separators were12 mm, 14 mm, and 16 mm, respectively. And same volume of 30 µL electrolytes were used in both Celgard assembled cells and ANF-JSs assembled cells for regular battery test, the electrolyte/sulfur (E/S) ratio was about 19 µL mg⁻¹. And 60 µL electrolytes were used for high sulfur tests, the electrolyte/sulfur (E/S) ratio was about 14 µL mg⁻¹. Linear sweep voltammetry (LSV) was carried out on an electrolyte-soaked separator sandwiched between Li metal and stainless steel with a scan rate of 10 mV s⁻¹ on an AUTOLAB impedance analyzer. The galvanostatic charge/discharge cycling was carried out with a voltage window of 1.7-2.6 V. The ionic conductivity was measured by electrochemical impedance spectroscopy (EIS) method and calculated by:

$$\sigma = L/R_b S \tag{S1}$$

where L and S are the thickness and area of the separators, respectively, and R_b is the bulk ohmic resistance of the electrolyte.

The porosity of Celgard 2325, ANF-S and ANF-JSs was estimated by the n-butyl alcohol immersion method and calculated using the following equation:

$$Porosity = \frac{W_{wet} - W_{dry}}{\rho_b V_P} \times 100\%$$
(S2)

where W_{dry} and W_{wet} are the mass of the sample before and after immersing in n-butyl alcohol for 1 h, ρ_b , V_p are respectively the density of n-butyl alcohol and the volume of dry sample.

The electrolyte uptake was evaluated by the weights of the sample before (W_{dry}) and after (W_{wet}) soaking in liquid electrolyte for 2 h and calculated according to the equation:

$$Electrolyte uptake = \frac{W_{wet} - W_{dry}}{W_{dry}}$$
(S3)

Tortuosity τ was calculated from equation (4)^[S1]:

$$\tau = \left(\frac{\sigma_0}{\sigma_{eff}}\varepsilon\right)^{1/2} \tag{S4}$$

where σ_0 is the conductivity of the liquid electrolyte, σ_{eff} is the conductivity of the separator + liquid electrolyte combination, and ε is the porosity.^[S1] The conductivity measurements were performed using the DOL/DME electrolyte with 1.0 M LiTFSI and 1.0 wt% LiNO₃, (σ_0 =12.14 mS cm⁻¹).^[S2] The results are provided in Table 1.

Characterization: The morphologies were characterized by scanning electron microscopy (SEM, Hitachi S-4700). Thermogravimetric analysis (TGA) was tested from 30 °C to 800 °C via a PerkinElmer Instruments TGA 4000 at a heating rate of 10 °C min⁻¹ under N₂ atmosphere. X-ray diffraction (XRD) patterns were recorded using a PAN analytical X'Pert PRO diffractometer equipped with a Cu-Ka radiation ($\lambda = 0.154$ nm). The melt of Celgard 2325 and ANF-JS_{30s} was tested by using differential scanning calorimeter (DSC, Q2000 TA).



Figure S1. Upper-layer SEM surface images of (a) ANF-JS_{60s} and (b) ANF-JS_{120s}.



Figure S2. Lower-layer SEM surface images of (a) ANF-S, (b) ANF-JS_{60s} and (c) ANF-JS_{120s}.



Figure S3. (a) Nitrogen adsorption-desorption isotherm of ANF-JS_{30s}. (b) Pore size distribution of ANF-JS_{30s}.



Figure S4. (a, b) Cross-sectional images of a thinner (~8 μ m) free-standing ANF-JS_{30s} obtained by facile dry-wet phase inversion approach.



Figure S5. Middle cross-section of (a) ANF-S, (b) ANF-JS_{60s}, (c) ANF-JS_{120s}. Lower-side cross-section of (d) ANF-S, (e) ANF-JS_{60s}, (f) ANF-JS_{120s}.



Figure S6. (a) Cross-sectional SEM images of ANF-S. (b), (c) Cross-sectional SEM images of ANF-JS_{120s} after a mechanical failure show ANFs protruding from the edges of the upper layer, indicative of more efficient stress transfer in dense structures.



Figure S7. LSV curves of Celgard and ANF-JS_{30s}.



Figure S8. (a) Photographs of glass cells with left chambers containing Li_2S_6 in DOL/DME solution and right chambers containing pure DOL/DME solvent, respectively, separated by Celgard, ANF-S, ANF-JS_{30s}, ANF-JS_{60s}. (b) The absorbance of electrolyte in right chambers after 30 h.



Figure S9. Magnified the voltage trace for 120-122 h and 150-152 h corresponding to Figure 5d.



Figure S10. The SEM top surface images of the Li metals obtained from (a, d) Celgard, (b, e) ANF-S, (c, f) ANF-JS_{30s} assembled Li/Li cells after 100 cycles. The current density was fixed at 1 mA cm⁻² with a capacity of 1 mAh cm⁻².



Figure S11. The Young's modulus mapping of the upper-layer surface for (a) ANF-S and (b) ANF-JS_{30s}. Young's modulus distribution of the upper-layer surface for (c) ANF-S and (d) ANF-JS_{30s}.



Figure S12. The superficial morphology of (a) Celgard, (b)ANF-S, (c) ANF-JS_{30s}, (d) ANF-JS_{60s} facing Li-metal in the Li-S cell. (These separators were obtained from 100^{th} cycled Li-S cells.)



Figure S13. The superficial morphology and responding EDX spectra of Li anode obtained from (a,e) Celgard, (b,f)ANF-S, (c, g) ANF-JS_{30s}, (d, h) ANF-JS_{60s} assembled Li-S cells after 100 cycles.



Figure S14. EIS curves of Li-S cells assembled with Celgard, ANF-S, ANF-JSs before cycling.



Figure S15. The SEM top surface images of the Li metals obtained from (a, d) Celgard assembled Li-S cells, (b, e) control group, (c, f) ANF-JS_{30s} assembled Li-S cells after 100 cycles. (Control group was assembled with the upper layer facing the Li metal, ANF-JS_{30s} assembled Li-S cells was assembled with the upper layer facing the S-cathode.)



Figure S16. CVs at various scan rates and the linear fitting of the peak currents with the square root of the scan rates for the Li-S cell assembled with (a, b) Celgard and (c, d) ANF-JS_{30s}.



Figure S17. Charge-discharge curves of the Li-S cells with Celgard at various current densities of 0.2-3 C.



Figure S18. (a) Cycling performance and (b) rate performance of Celgard, ANF-JS_{30s} assembled Li-S cells with an increased sulfur loading of 3.7 mg cm⁻².



Figure S19. Voltage-time profiles of Celgard and ANF-JS_{30s} assembled Li symmetric cells at 1 mA cm⁻² with a capacity of 1 mAh cm⁻² and LiNO₃-free electrolyte (DME:DOL (V:V = 1:1) with 1 M LiTFSI).



Figure S20. Cycling performances of the (a) Celgard and (b) ANF-JS_{30s} assembled Li-S cells with LiNO₃-free electrolyte (DME:DOL (V:V = 1:1) with 1 M LiTFSI). The SEM top surface

images of the Li metals obtained from (c, d) Celgard, (e, f) ANF- JS_{30s} assembled Li-S cells after 100 cycles.



Figure S21. XRD curves of (a) ZIF-67/ANF-JS_{30s}, (b) MoS₂/ANF-JS_{30s}, (c) Fe₂O₃/ANF-JS_{30s}.



Figure S22. The coulombic efficiency of Celgard and ANF separators assembled Li-S cells.

Abbreviation	Description	Citation
PBO-NM	PBO: poly(p-phenylene benzobisoxazole)	[83]
	NM: nanoporous membranes	
vacuum filtered ANF	ANF: Aramid Nanofiber	[S4]
(PEO/ANF) ₂₀₀	ANF: Aramid Nanofiber	[85]
L@K/C	L: LbL assembly	[S6]
	K: Kevlar layer	

Table S1. Abbreviations for Figure 5e

	C: COF layer	
CmPEEK/PMMA/CmPEEK	Cm: chloromethylated	[\$7]
	PEEK: poly(ether ether ketone)	
	PMMA: polymethyl methacrylate	
fiberglass-PVDF	PVDF: polyvinylidene fluoride	[S8]
SiO ₂ @PI/m-PE/SiO ₂ @PI	PI: polyimide	[89]
Cellu/PVDF-HFP	Cellu: cellulose	[S10]
РР	PVDF-HFP: poly(vinylidene fluoride-co	
	hexafluoropropylene)	
ANF/PPS	PPS: polyphenylene sulfide	[S11]
PVDF-HFP/Al ₂ O ₃	PVDF-HFP: poly(vinylidene fluoride-co-	[812]
	hexafluoropropylene)	
ANF/PEO-LiTFSI (SPE)	LiTFSI: Lithium	[813]
	bis(trifluoromethanesulfonyl)imide	
ANF/PEO-DF (SPE)	DF: dripping film	[S14]
	1	1

Table S2. The areal density of Celgard, ANF-JS_{30s}, functionalized ANF-JS_{30s}

	Celgard	ANF-	ZIF-67/ANF-	MoS ₂ /ANF-	Fe ₂ O ₃ /ANF-
		JS _{30s}	JS_{30s}	JS_{30s}	JS_{30s}
areal density	1.4	0.7	1.2	1	1.4
$(mg cm^{-2})$					

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