Supplementary Information

Ion-Sieving Separator Modified by Sulfonate Functionalized Carbon Nitride towards

Highly Stable Zinc Metal Anode

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Experiment Section

Preparation of carbon nitride (CN): Carbon nitride was synthesized by using urea as a precursor. 10 g of precursor was ground, placed in a covered 30 mL alumina crucible, and thermally treated in a muffle furnace. The sample was heated to 550 °C at 5 °C min⁻¹ under ambient conditions and held for 4 h. Following the thermal treatment, the product was allowed to undergo natural cooling to ambient temperature, yielding a light-yellow carbon nitride powder as the final product.

Preparation of sulfonated carbon nitride (SCNx): The synthesis of SCNx was carried out following a previously established protocol¹. In a typical procedure, 300 mg of CN was combined with a specified quantity of aminosulfonic acid and transferred into a covered 30 mL alumina crucible. The mixture was heated in a muffle furnace at 5 °C min⁻¹ to 250 °C, held for 2 h, further heated to 400 °C for 1 h. Since

aminosulfonic acid decomposes at 400 °C, the unreacted residual aminosulfonic acid can be removed after holding at 400 °C for 1 h. The reaction product is recorded as SCNx based on the mass of aminosulfonic acid used (x is 100, 200, 300 or 400 mg).

Fabrication of modified separators: SCNx@GF and CN@GF modified separators were prepared by vacuum filtration. A homogeneous dispersion was prepared by ultrasonically treating 6 mg of SCNx or CN powders combined with 1 mg of polyvinylidene fluoride (PVDF) in 10 mL of N-methyl pyrrolidone (NMP) solvent for 3 hours. This mixture was subsequently vacuum-filtered through a glass fiber substrate (GF/D) to achieve uniform coating. The composite separators were then thermally treated to ensure complete solvent (NMP) removal, ultimately producing modified separators (SCNx@GF or CN@GF) with precisely controlled active material loading at 0.3 mg cm⁻². The separators were cut into 19 mm discs.

*Construction of NH*₄*V*₄*O*₁₀ *(NHVO) cathode:* The NHVO cathode material was fabricated through a controlled solvothermal synthesis process. Initially, 1.17 g NH₄VO₃ and 1.89 g C₂H₂O₄·2H₂O underwent dissolution in separate 70 mL deionized water under vigorous agitation. The resultant solutions were combined in a Teflon-lined reaction vessel and thermally processed at 140 °C for 48 h under autogenous pressure. Post-synthesis purification involved multiple washing with deionized water, and drying overnight to yield the final NHVO product exhibiting characteristic dark green coloration. For electrode assembly, a composite slurry was formulated by precisely weighing NHVO active material, Super-P carbon additive, and PVDF binder in a 7:2:1 mass proportion. The components were dispersed in NMP solvent at a controlled concentration (70 mg active material per 500 µL solvent) through continuous mechanical mixing over 12 h. The slurry was then coated onto carbon fiber current collectors, and dried at 60 °C overnight to achieve uniform electrodes with controlled mass loading about 2.0 mg cm⁻². Final electrode fabrication involved precision punching of the composite-coated substrates into 12 mm disks for subsequent electrochemical characterization.

Material Characterizations: The synthesized powders and electrode surfaces were characterized using Xray diffraction (XRD) with a Rigaku SmartLab 9kW instrument to determine their crystal structure. Functional groups were examined through Fourier transform infrared spectroscopy (FT-IR, Thermo Fisher Scientific Nicolet iS20) and chemical composition were examined by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB Xi+). Surface morphology and the powders of CN and SCNx

were investigated by field emission scanning electron microscopy (SEM, FEI NOVA NanoSEM 450). Zinc deposition process were monitored in real-time using an optical microscope (Yuescope YM710TR), while separator wettability was assessed with a contact angle analyzer (KRUSS DSA30S).

Electrochemical measurements: Electrochemical characterizations including impedance spectroscopy (EIS), cyclic voltammetry (CV), chronoamperometry (CA), Tafel plots, and linear sweep voltammetry (LSV) were conducted using a Princeton multichannel workstation (PARSTAT MC) and a CHI760e system (Shanghai Chenhua). For LSV testing, Zn//Cu asymmetric cells with 1 M Na₂SO₄ electrolyte were scanned at 5 mV s⁻¹ across a potential range of -0.1 to -0.7 V. Tafel curves were generated from Zn//Zn symmetric cells under identical scan rates (5 mV s⁻¹) within a voltage window of ± 0.15 V. Battery performance metrics (galvanostatic charge-discharge (GCD), coulombic efficiency (CE), and full cell evaluation) were assessed on a LAND CT3002A test platform.

The ionic conductivity was calculated by the equation:

$$\sigma = \underline{\qquad \qquad } \\ R \times A$$

L: the thickness of the separator; A: the area of the separator; R: the impedance derived from EIS measurements.

The Zn²⁺ transference number
$$(t_{Zn}^{2+})$$
 was calculated by the equation:
 $I_S(V - I_0R_0)$
 $t_{Zn2+} = \overline{I_0(V - I_SR_S)}$

 I_0 : the initial state current; R_0 : the initial state interfacial resistance; I_s : the final state current; R_s : the

The activation energy (E_a) of the zinc deposition was calculated by the equation:

$$1 E_a = Aexp_{Rct} = RT$$

 R_{ct} : the charge-transfer resistance at different temperatures.

Theoretical computation: Density functional theory (DFT)^{2, 3} calculations using VASP were performed to quantify the binding interactions of Zn²⁺ and H₂O with CN and SCN substrates. This package employs plane-wave pseudopotentials within the projector augmented-wave (PAW) method.^{4, 5} Generalized gradient approximation (GGA) was applied to model electronic exchange-correlation effects, specifically using the Perdew-Burke-Ernzerhof (PBE) functional.⁶ Additionally, van der Waals interactions were accounted for by incorporating Grimme's DFT-D3 dispersion correction.⁷ Periodic boundary artifacts were mitigated through a 15 Å vacuum buffer layer between system replicas. Computational parameters included a 450 eV kinetic energy cutoff for plane-wave expansion and Γ -point sampling for Brillouin zone integration. Structural relaxation procedures maintained rigorous convergence thresholds, requiring maximum atomic forces below 0.02 eV Å⁻¹ and total energy variations within 1×10⁻⁵ eV across successive self-consistent field iterations. The adsorption energy (E_{ads}) was calculated by the equation:

Eads = Etotal - EM1 - EM2

 E_{total} : the energy of the systems of Zn atoms or H₂O molecules on CN or SCN; E_{Ml} : the energy of surface of CN or SCN; E_{M2} : the energy of Zn atoms or H₂O molecules under vacuum.



Fig. S1. Schematic diagram of the molecular structure of SCN.



Fig. S2. Zeta potential of CN and SCNx powders.



Fig. S3. SEM images of (a) CN, (b) SCN100, (c) SCN200, (d) SCN300, and (e) SCN400 powders.



Fig. S4. EDX mapping and elemental distribution of CN.



Fig. S5. EDX mapping and elemental distribution of SCN200.



Fig. S6. N₂ adsorption-desorption isotherms of CN and SCNx powders (the inserts shows the pore size distribution of CN and SCNx powders.



Fig. S7. Content of -SO₃⁻ and specific surface area of CN and SCNx powders.



Fig. S8. XRD patterns of the bare GF, CN@GF, and SCNx@GF separators.



Fig. S9. SEM images of (a) bare GF, (b) CN@GF, (c) SCN100@GF, (d) SCN300@GF, and (e) SCN400@GF separators.



Fig. S10. SEM images and related EDS mappings of CN@GF separator (a) surface view, (b) side view.



Fig. S11. The water contact angles of the (a) bare GF, (b) CN@GF, (c) and SCN200@GF separators.



Fig. S12. CE curves of Zn//Cu asymmetric cells with SCNx@GF separators at 2 mA cm⁻² and 1 mAh cm⁻

2.



Fig. S13. Cycling performance of Zn//Zn symmetric cells with SCNx@GF separators at 2 mA cm⁻² and 1 mAh cm⁻².



Fig. S14. Cycling performance of Zn//Zn symmetric cells with SCNx@GF separators at 5 mA cm⁻² and 1 mAh cm⁻².



Fig. S15. Simulated structure models of absorption energies of Zn^{2+} and H_2O with CN and SCN.



Fig. S16. (a) Zn 2p spectra of SCN200 and CN after being immersed in the electrolyte.



Fig. S17. (a) S 2p, (b) O 1s, (c) S 2p spectra of SCN200 before and after being immersed in the electrolyte.



Fig. S18. N 1s spectra of CN before and after being immersed in the electrolyte.



Fig. S19. (a) FT-IR spectra of SCN200 before and after being immersed in the electrolyte. (b) The enlarged of parts of sulfonate group.



Fig. S20. FT-IR spectra of CN before and after being immersed in the electrolyte.



Fig. S21. EIS curves of Zn//Zn symmetric cells with (a) bare GF, (b) CN@GF, and (c) SCN200@GF separators under various temperatures.



Fig. S22. Surface morphologies of anode surface after 100 cycles at 2 mA cm⁻² and 1 mAh cm⁻² in Zn//Zn symmetric cells with (a, b) bare GF, (c, d) CN@GF, and (e, f) SCN200@GF separators.



Fig. S23. Surface morphologies of anode surface after depositing at 5 mA cm⁻² for 30 min with (a, b) bare GF, (c, d) CN@GF, and (e, f) SCN200@GF separators.



Fig. S24. (a) XRD pattern and (b) SEM image of $NH_4V_4O_{10}$.



Fig. S25. Galvanostatic charge-discharge profiles of Zn//NHVO full cells with (a) bare GF, (b) CN@GF, and (c) SCN200@GF separators at different current densities.



Fig. S26. Surface morphologies of Zn surface in Zn//NHVO full cells with (a, b) bare GF, (c, d) CN@GF, and (e, f) SCN200@GF separators after 500 cycles at 5 A g⁻¹.



Fig. S27. Capacities retention of the Zn//NHVO full cells with (a) bare GF, (b) CN@GF, and (c) SCN200@GF separators.

 Table S1. Comparison of the Zn//Zn symmetric batteries performance with SCN200@GF and other separators in previous reports.

Separators	Current density (mA cm ⁻¹)	Areal capacity (mAh cm ⁻²)	Lifespan (h)	Cumulative plating capacity (mAh cm ⁻ ²)	Refs
BCM	2	1	400	400	[8]
CS-GF	4	1	500	1000	[9]
g-C ₃ N ₄ coated	3	1	590	885	[10]
separator	5	1	320	800	[10]
PANI-GF	2	1	560	560	[11]
	2	1	200	200	
PVDF@PDA	1	1	1200	600	[12]
FP-CQDs-14	5	1	240	600	[13]
CS-filter paper	5	1	450	1125	[14]
TTA-DHTPA- COF@GF@Gr	5	1	600	1500	[15]
PSO-30	5	1	520	1300	[16]
CS-CP	4	1	600	1200	[17]
	1	1	700	350	
MCE-200	1	0.5	1000	500	[18]
CNF + LMS separators	1	0.5	500	250	[19]
ZIF-8-GF	0.5	0.5	800	200	[20]
CRC	2	1	500	500	[21]
KL-GF	3	1.5	1000	1500	[22]
CA@DF	1	1	500	250	[23]

5C11200@GI	5	1	800	2000	work
SCN200@GF	2	1	820	820	This
WRPF	2	1	700	700	[25]
	1	1	300		
	0.5	0.5	1200		
SR-P-GF				150	[24]
				300	[24]

Raw material input							
Material	Price (\$ g ⁻¹)	Cost (\$ g ⁻¹)					
Urea	0.0024	0.051					
Aminosulfonic acid	0.0045						
Energy consumption							
Heat treatment time (h)	Electricity charge (\$ kW ⁻¹ h ⁻¹)	Cost (\$ g ⁻¹)					
5.77+4.27	0.1	7.53/2.4					
Waste gas treatment							
Waste gas	Processing cost (\$ t ⁻¹)	Cost (\$ g ⁻¹)					
CO ₂	40.9						
NH ₃	42.7	8.22×10^-4					
SOx	50.8						
Tot	3.19						

Table S2. The techno-economic assessment of SCN200.

Note:

[1] Urea (AR, Damao), Aminosulfonic acid (99.5%, Aladdin).

- [2] For the energy consumption cost calculation, since each synthesis yields 2.4 g of SCN200, the cost in this part is divided by 2.4 to determine the cost per gram.
- [3] Data Sources: Electricity charge (Sep. Purif. Technol., 2024, 349, 127821), Processing cost of CO₂ (Environ. Impact Assess. Rev., 2025, 114, 107933), Processing cost of NH₃ (ACS Sustainable Chem. Eng., 2021, 9, 312–325), Processing cost of SO_x (J. Cleaner Prod., 2018, 202, 934e945).

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