# **Supporting Information**

# A Si<sub>3</sub>N<sub>4</sub>-modified cellulose/glass fiber hybrid separator inhibiting

## zinc dendrites and cathode dissolution for aqueous zinc-ion batteries

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#### **Experimental section**

### Materials

Zinc sulfate heptahydrate (ZnSO<sub>4</sub>·7H<sub>2</sub>O), ammonium metavanadate (NH<sub>4</sub>VO<sub>3</sub>), oxalic acid dihydrate (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O) and N-Methylpyrrolidone (NMP) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Commercial zinc foil (50  $\mu$ m) and commercial copper foil (50  $\mu$ m) were purchased from Shenghang Metal Materials Co., Ltd. Glass fiber (GF) was purchased from Tianjin EVS Chemical Technology Co., Ltd. Cellulose nanofiber (CNF) was purchased from Zhongshan Nanofc Biomaterials Co., Ltd. Si<sub>3</sub>N<sub>4</sub> was purchased from Nangong Bole Metal Materials Co., Ltd.

#### Fabrication of GC (GC-SN) separator

A dispersion of 40 g of CNF with a concentration of 2.5 wt% was added into 160 mL of deionized water and stirred for 1 h. Subsequently, the dispersion underwent ultrasonic treatment in an ice-water bath for 10 min to achieve uniform dilution to a concentration of 0.5 wt%. The acrylic substrate with  $15 \times 15$  cm was injected with a 70 mL dispersion at 50 °C, following by drying for a duration of 12 h to obtain a translucent and uniform CNF film. CNF-Si<sub>3</sub>N<sub>4</sub> (CNF-SN) film were prepared by the strategy except for adding Si<sub>3</sub>N<sub>4</sub> with 0.025 g, 0.05 g, 0.08 g, 0.11 g. GF and CNF (CNF-SN) membranes were incorporated into GC (GC-SN-2.5, GC-SN-5.0, and GC-SN-7.5) separators following a sandwich structure.

### Preparation of NH<sub>4</sub>V<sub>4</sub>O<sub>10</sub> cathodes

 $NH_4V_4O_{10}$  cathode material was synthesized according to the previous report <sup>[1]</sup>. Firstly, 1.17 g  $NH_4VO_3$  was dissolved into 50 mL of deionized water at 80 °C in a water bath and stirred for approximately 10 min to form light yellow transparent solution. Subsequently, 1.891 g  $H_2C_2O_4 \cdot 2H_2O$  was added and stirred until the solution turned dark blue. The resulting mixture was then transferred into an 80 mL PTFElined hydrothermal reactor, sealed, and reacted at 140 °C for 48 h in an oven. After natural cooling to room temperature, the product was collected and washed several times with deionized water via centrifugation. After drying treatment at 80 °C for 12 h, the final  $NH_4V_4O_{10}$  was obtained. The  $NH_4V_4O_{10}$  was mixed with super-P acetylene black and PVDF at a mass ratio of 7:2:1, followed by dry grinding for 15 min. Subsequently, NMP was added for wet grinding until a homogeneous oily slurry was obtained. The slurry was evenly applied onto a 12 mm stainless steel mesh and subjected to vacuum at 80°C for 10h. The mass of the active substance is approximately 3 mg cm<sup>-2</sup>.

#### Characterizations

The static contact angles of the electrolyte on various separators were measured through the contact angle meter (SDC-350KS). X-ray diffraction (XRD, PANalytical/Empyrean 2) tests were carried out with a scanning range of 5~90°. Raman spectra were collected to analyze the structure and composition of chemical substances, using the laser confocal raman spectrometer (Renishaw/inVia Reflex) with a wavelength of 785 nm. X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi) was conducted to characterize the elemental composition, chemical state, and charge state of the samples. The morphologies of different separators and zinc anodes before and after cycling were characterized by scanning electron microscopy (SEM, JEOL/JSM- 7610FPlus). The surface morphologies and roughness of the zinc anodes after cycling were collected using the laser confocal microscopy (LCM, LSM700). Mechanical properties of GF and CNF membranes in a dry state with dimension (20 mm  $\times$  100 mm, 5 mm min<sup>-1</sup>) were measured using a universal testing machine (Instron 5944) at room temperature. The pore size distributions of GF and CNF membranes were collected by the BJH model, using the accelerated surface area and porosimetry system (BET, ASAP 2460).

#### **Electrochemical measurements**

All electrochemical tests were carried out by assembling into the coin cells (CR2025). 2025-type coin cells were assembled to measure the electrochemical performances with 2 M ZnSO<sub>4</sub> aqueous solution as the electrolyte and zinc foil as the

anode. Commercial copper foil was served as work electrodes to assemble asymmetric cells with different separators. The coin cells were assembled to measure the electrochemical performances with 2 M ZnSO<sub>4</sub> aqueous solution as the electrolyte and zinc foils as the anode. Two identical commercial zinc foils were used as work and counter to assemble the symmetric cells with different separators. Full cells using NH<sub>4</sub>V<sub>4</sub>O<sub>10</sub> as cathode were assembled to evaluate the cycling performances of the GC-SN separators. The galvanostatic charging/discharging tests were recorded using a Neware MIHW-200-160CH battery testing system at 30 °C. Electrochemical impedance spectroscopy (EIS) measurements for symmetric cells were carried out at the frequency range of 0.01~100000 Hz. CA curves of symmetric cells were conducted at a constant overpotential of -200 mV for 600 s. Tafel curves for the symmetric cells were measured at a potential scanning rate of 1 mV s<sup>-1</sup>. EIS, CA, and Tafel curves were carried out on an electrochemical workstation (CHI660E) at room temperature.

#### **Calculation of electrolyte uptake**

The GF, CNF, and CNF-SN membranes were immersed in a 2 M ZnSO<sub>4</sub> electrolyte to obtain the mass of the membranes before and after immersion. The liquid absorption and retention rates were calculated using the following equation:

$$Sa = \frac{W_1 - W_0}{W_0} \#(1)$$
$$Sr = \frac{W_1 - W_0}{W_1} \#(2)$$

 $W_0$  and  $W_1$  denote the mass of the membranes before and after immersion, respectively.

#### **Calculation of ionic conductivity**

The ionic conductivities of the GF, CNF, and CNF-SN separators was obtained by measuring the resistance of a symmetric cell with two stainless steel sheets as the electrode, which was calculated according to the following equation:

$$\sigma = \frac{L}{AR} \#(3)$$

where L is the thickness of the separator, A is the contact area between the separator and stainless steel sheet, and R is the resistance.

#### **Theoretical calculations**

The CASTEP code in Materials Studio was adopted to perform density functional theory (DFT) calculations. The generalized gradient approximation (GGA) and Perdew-Burke-Ernzerhof (PBE) were employed to demonstrate exchange and correlation potentials<sup>[2]</sup>. The k-point grid will be generated according to the specified k-point separation with 0.07 Å<sup>-1</sup>. The plane-wave energy cutoff was set to 517.0 eV. A  $5 \times 1 \times 1$  supercell was used to model a five-layered SN (200) and (210) surface, while a  $5 \times 1 \times 1$  supercell was used for the CNF (110) and (200) surface. Vacuum layers with thickness of 20 Å were added above the top layer of slabs in all cases. During the structural optimization process of the SN (200) and (210) surface, the atoms in the bottom three layers were fixed while the atoms in other layers were relaxed. The construction of the amorphous silica structure was realized through the geometry optimization and annealing steps of crystalline silica. Firstly, the crystalline silica was modified to right angle unit cell and then supersized to an appropriate size. Subsequently, the annealing process in molecular dynamics (MD) simulation consisted of heating up to 1996 K, and calculating 1000 ps, then cooling down to 298K. A NVT MD was run with a time interval of 1 fs. The binding energy was calculated by the following equation:

 $E_b = E(total) - E(substrate) - E(Zn)$ 

Where E(total), E(substrate) and E(Zn) represent the total energy of substrate with Zn, the energy of substrate and zinc atom, respectively.

 $E_b'=E(total)-E(substrate)-E(VO_2^+)$ 

Where E(total), E(substrate) and E(VO<sub>2</sub><sup>+</sup>) represent the total energy of substrate with  $VO_2^+$ , the energy of substrate and  $VO_2^+$ , respectively.



Figure S1. The flexibility test of CNF membrane.

Since the machinability of the separator is crucial in battery assembly, it is imperative for the as-prepared CNF membrane to possess excellent flexibility.



Figure S2. Optical photos of CNF (or CNF-SN) membranes.

Incorporation of SN into the film fabrication process can decrease the effects of particle agglomeration or binder failure compared to the introduction of inorganic nanoparticles coated directly onto the surface of a separator with an organic binder. The color of the prepared membranes gradually became darker after the addition of SN. And the membranes can maintain a flat surface when the concentration of SN was low. However, when the solid content of SN continued to increase, the membrane appeared to be wrinkled. This may be due to the agglomeration of SN leading to the uneven distribution of SN in the CNF dispersion.



Figure S3. The thickness of (a) GF, (b) CNF and (c) CNF-SN-5.0 membranes.

As for GF, the thickness was up to 543  $\mu$ m, while that of the CNF (CNF-SN) membrane was only 20-40  $\mu$ m. This composite membrane with a certain thickness can effectively improve its mechanical strength, thus reducing the risk of zinc dendrites penetrating the separator.



Figure S4. Electrolyte contact angle measurement of (a) CNF-SN-2.5 and (b) CNF-SN-7.5 membranes.

Tuble 51. The electrolyte absorption and recention face of various memoranes.					
me	embrane	$W_0(mg)$	$W_1(mg)$	Sa (%)	Sr (%)
	GF	37.8	470.2	1144	92
	CNF	8.5	37.6	342	77
CN	F-SN-2.5	8.0	36.4	355	78
CN	F-SN-5.0	10.0	67.1	571	85
CN	F-SN-7.5	8.2	32.9	301	75

Table S1. The electrolyte absorption and retention rate of various membranes.



Figure S5. The ionic conductivity of various membranes.



Figure S6. Tensile curves of GF and CNF membranes.



Figure S7. SEM image of  $Si_3N_4$  whiskers.



Figure S8. SEM images at the (a) low magnification and (b) high magnification, and (c, d) corresponding EDS mapping of GC-SN-2.5 membrane.



Figure S9. SEM images at the (a) low magnification and (b) high magnification, and (c, d) corresponding EDS mapping of GC-SN-5.0 membrane.



Figure S10. SEM images at the (a) low magnification and (b) high magnification, and (c, d) corresponding EDS mapping of GC-SN-7.5 membrane.



Figure S11. Pore size distributions of GF and CNF membranes.



Figure S12. Raman spectroscopy of  $Si_3N_4$  whiskers.



Figure S13. The cycling performance of Zn $\|$ Zn symmetric cells with (a) GF and (b) CNF separators at 1 mA cm<sup>-2</sup> and 1 mAh cm<sup>-2</sup>.



Figure S14 The cycling performance of Zn||Zn symmetric cells with GF separator at 5  $mA~cm^{-2}$  and 2 mAh cm<sup>-2</sup>.



Figure S15. The rate performance of Zn||Zn symmetric cells with (a) GC-SN-2.5 and (b) GC-SN-7.5 separators.



Figure S16. SEM image of commercial zinc foil.



Figure S17. SEM images of the zinc anodes post stripping with (a) GF, (b) GC, (c) GC-SN-2.5, (d) GC-SN-5.0 and (e) GC-SN-7.5 separators in zinc symmetric cell at 5 mA cm<sup>-2</sup> with 2 mAh cm<sup>-2</sup>.



Figure S18. SEM images of the zinc anodes deposition under (a) GF, (b) GC, (c) GC-SN-2.5 and (d) GC-SN-7.5 separators in zinc symmetric cell at 5 mA cm<sup>-2</sup> with 2 mAh cm<sup>-2</sup>.



Figure S19. SEM images of GF separators and corresponding EDS mapping in the (a) GF, (b) GC and (c) GC-SN-5.0 symmetrical cells after 50 cycles at 5 mA cm<sup>-2</sup> and 2 mAh cm<sup>-2</sup>.

The GF separator maintains its structural integrity with no discernible zinc deposition under the effect of the CNF-SN-5.0 membrane. On the contrary, partial rupture of the GF separators were observed in both GF and GC cells.



Figure S20. Cross-sectional SEM images of zinc deposition assembled with (a) GF, (b) GC, (c) GC-SN-2.5 and (d) GC-SN-7.5 separators after 50 cycles at 5 mA cm<sup>-2</sup> and 2 mAh cm<sup>-2</sup>.



Figure S21. The laser confocal microscopy images of zinc foils under (a) GF, (b) GC, (c) GC-SN-2.5, and (d) GC-SN-7.5 separators after 50 cycles at 5 mA cm<sup>-2</sup> and 2

mAh cm<sup>-2</sup>.



Figure S22. Binding energies of a zinc atom with various crystalline surfaces of CNF

and SN.



SN (200) and (d) SN (210).



Figure S24. XRD patterns of the zinc anodes after 50 cycles at 5 mA cm $^{-2}$  and 2 mAh





Figure S25. Tafel curves in various symmetrical cells at the scan rate of 1 mV s<sup>-1</sup>.



Figure S26. EIS measurement of Zn symmetric cells assembled with three separators

before cycling.



Figure S27. The voltage profiles of Zn||Cu asymmetric cells with (a) GF separator, (b) GC separator, and (c) GC-SN-5.0 separator.

The increased polarization voltage in the modified half cell may be attributed to the enhanced charge transfer resistance and interfacial impedance induced by the introduction of the CNF membrane.



Figure S28. XRD pattern of  $NH_4V_4O_{10}$  cathode material.



Figure S29. SEM images at the (a) low magnification and (b) high magnification, and (c-e) corresponding EDS mapping of  $NH_4V_4O_{10}$  cathode material.



Figure S30. Voltage-capacity profiles of (a) GF and (b) GC full cell recorded at various cycle numbers.



Figure S31. In-situ Raman spectroscopy of (a) GC and (b) GC-SN-5.0 separators within 10 min of initial Zn deposition.



Figure S32. XPS full spectrum of zinc anodes in  $Zn||NH_4V_4O_{10}$  cells after 50 cycles with (a) GF, (b) GC and (c) GC-SN-5.0 separators.



Figure S33. Optical photos of (a) pure zinc foil, and zinc anodes in (b) GF, (c) GC, and (d) GC-SN-5.0 full cells after 50 cycles.



Figure S34. SEM images and EDS of zinc anodes facing various separators in full cells after 50 cycles.



Figure S35. Calculation models of  $VO_2^+$  absorbed on (a) SiO<sub>2</sub>, (b) CNF (110), (c) CNF (200), (d) SN (200) and (e) SN (210).

## References

- [1] Zhang K, Zhang G, Liu X, et al. Large scale hydrothermal synthesis and electrochemistry of ammonium vanadium bronze nanobelts[J]. Journal of Power Sources, 2006, 157(1): 528-532.
- Perdew J P, Burke K, Ernzerhof M. Generalized gradient approximation made simple[J].
  Physical Review Letters, 1996, 77(18): 3865.