# Deposition Behavior Regulated by SPSF@PMIA nanofiber Separator for High-Performance Zinc Ion Batteries

### **1.Expermient Section**

#### 1.1 Preparation of SPSF@PMIA nanofibers

The SPSF@PMIA (SP) nanofiber separators were prepared by electrospinning method. SPSF nanoparticles (Sigma-Aldrich, 3.58 g) were dissolved in 18.62 g of N, N-dimethylformamide (DMF) and then stirred at 40 °C for 6 h until SPSF was fully dissolved. Meanwhile, 10 g of PMIA resin was dissolved in 6.8 g of N, N-dimethylformamide (DMAc), and then stirred at 30 °C for 3 h until PMIA was fully dissolved. The obtained homogeneous spinning solutions were respectively transferred to separate pipettes and then connected to a high-voltage power supply for spinning, wherein the spinning voltage was 30 kV; the extrusion rates of SPSF and PMIA solutions were 1 mL h<sup>-1</sup> and 0.8 mL h<sup>-1</sup> with a receiving distance of 20 cm. Finally, the SP nanofiber separators obtained at the collector was placed under vacuum at 50 °C for 12 h, to completely remove the residual solvent. As a comparison, pure SPSF and pure PMIA nanofiber separators were obtained by the same method and under the same conditions.

#### **1.2 Preparation of electrodes**

Zinc foil was cut into  $\Phi 15$  mm discs and used directly as anode, the 20  $\mu$ m thickness zinc foil was used for the symmetric cell and half-cell test, and the 100  $\mu$ m thickness zinc foil was used for the full-cell test. The cathode active materials MnO<sub>2</sub> (purity >99.0%, Aladdin.) and V<sub>2</sub>O<sub>5</sub> (purity >99.0%, Macklin), both of which are used

in current commercial materials, mixed with conductive agent carbon and binder polyvinylidene fluoride (PVDF) in a ratio of 7:2:1 by ball milling. The N-Methyl pyrrolidone (NMP) as the solvent and sired with the above mixtures to prepare cathode slurry. Subsequently, the cathode slurry was uniformly coated to a stainless-steel and dried at 80°C for 24 h. The mass loading of both cathodes was controlled as 1.0-1.2 mg cm<sup>-2</sup>.

#### **1.3.** Cell assembling

The above components were assembled to CR2025-type coin cell (room temperature) to evaluate the electrochemical performance. The symmetric batteries were assembled via two pieces of commercial Zn foil, and the 2 M Zn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> solution was served as electrolyte. The Zn-Ti half batteries were assembled by the zinc foil and Ti foil in the coin cells with different separators, 2 M Zn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> was served as electrolyte. The full batteries were assembled by the zinc anode and cathode materials (V<sub>2</sub>O<sub>5</sub> and MnO<sub>2</sub>) in the coin cells with different separators, and 2 M ZnSO<sub>4</sub> + 0.5 M MnSO<sub>4</sub> or 2 M Zn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> was served as electrolyte.

#### **1.4 Materials characterization**

The surface morphologies of the nanofiber membrane and the electrolytes were examined by the field emission scanning electron microscope (FE-SEM; S-4800, Japan), and elements distribution was analyzed by the energy-dispersive X-ray spectroscopy (EDS). FT-IR spectra was conducted on the Nicolet iS50 machine. X-ray diffraction (XRD) measurements were conducted on the Bruker AXS D8 Discover machine with an Ni-filtered Cu K $\alpha$  radiation (1.5418 A) to characterize the crystal structure, and the 2 $\theta$  range was changed from 10° to 80°.

#### 1.5 Electrochemical performance characterization

Electrochemical impedance spectroscopy (EIS) plots, Linear sweep voltammetry

(LSV) test, cyclic voltammetry (CV) profiles and the Tafel plots was recorded via CHI660E workstation (Chenhua, China). Cycling performance and the galvanostatic charge/discharge (GCD) profiles were obtained via a battery test system (LAND CT2001A battery, China).

**Calculation of porosity.** The different separators were immersing into n-butyl alcohol for 2 h, and the porosity was calculated by the following equation (1):

$$Porosity = \frac{W_t - W_0}{\rho V} \times 100\%$$
(1)

where  $W_0$  (g) and  $W_t$  (g) represented the weight before and after immersion,  $\rho$  (g/cm<sup>-3</sup>) and V (cm<sup>-3</sup>) represent density of n-butyl alcohol and the volume of the separators, respectively.

**Calculation of electrolyte uptake**. The electrolyte uptake was performed by soaking into the electrolyte for 0.5 h, and the uptake was obtained via the following equation (2):

$$Uptake = \frac{W_a - W_b}{W_b} \times 100\%$$
(2)

where  $W_{b}(g)$  and  $W_{a}(g)$  represent the weights of before and after immersing.

**Calculation of mechanical strength**. The tensile testing machine (YG005E, Wenzhou Fang yuan Instrument Co., Ltd., China) was utilized to test the mechanical strength of the electrolyte with the speed of 10 mm min<sup>-1</sup>, and the mechanical strength was obtained via the following equation (3):

$$\sigma = \frac{P}{b \times d} \tag{3}$$

where P (N) is the breaking strength, d ( $\mu$ m) is the thickness, and b (cm) is the width.

**Calculation of ionic conductivity**. The ionic conductivity ( $\sigma$ ) was measured by a CHI

660D (Chenhua, Shanghai) electrochemistry workstation. The separator was soaked in electrolyte solution with two stainless steel electrode clips to test the resistance ranging from 0.01 Hz to 100 kHz, and the ionic conductivity ( $\sigma$ ) was calculated by the following equations (4):

$$\sigma = \frac{L}{R \times A} \tag{4}$$

where R ( $\Omega$ ), A (cm<sup>2</sup>) and L(cm) represent the resistance, area and thickness of the separator, respectively.

**Calculation of ion transfer number**. The DC polarization and AC impedance methods were applied to evaluate the zinc ion transfer number  $\binom{t}{Zn^{2}+}$  of the Zn/Zn symmetric cell, while the voltage of 10 mV was applied until the current of the battery reached a stable value. The specific  $\binom{t}{Zn^{2}+}$  value was obtained from the Bruce-Vincent-Evans equation (5) as follows:

$$t_{Zn^{2}+} = \frac{I_{S}(\Delta V - I_{0}R_{0})}{I_{0}(\Delta V - I_{S}R_{S})}$$
(5)

where  $\Delta V$  (mV) was the applied polarization potential amplitude, I<sub>0</sub> (mA) and Is (mA) were the initial and steady-state current, respectively, and R<sub>0</sub> ( $\Omega$ ) and Rs ( $\Omega$ ) were the initial and steady-state interfacial resistance, respectively.

**Calculation of Coulombic efficiency (CE) and depth of discharge (DOD)**. The Coulombic efficiency (CE) in Fig. 3d was defined as below<sup>1</sup>:

$$CE = \frac{Discharge\ capacity}{Charge\ capacity} \times 100\%$$
(6)

The depth of discharge (DOD) in Fig. S9 was calculated as below:

$$DOD = \frac{Capacity of plate zinc}{Capacity of total zinc anode} \times 100\%$$
(7)

Calculation of energy density. The energy density was obtained by the following

equations (8):

$$E = \frac{UIt}{m} = \int U(c)dc \tag{8}$$

where E (Wh/kg) is the energy density, where U, I, t, m, C and V stand for discharge voltage, current, time, the active mass of cathode, specific capacity, and the voltage platform. respectively. We took the result of 15<sup>th</sup> cycle in rate performance test in Figure 4a and 4d. The results of the energy densities of Mn-SP/GF and V-SP/GF cells are 287.9, 224.5, 255.2 and 233.6 Wh kg<sup>-1</sup>.

**Calculation of capacitance contribution**. The CV curves of cells with different separator at different scan rates are used to identify whether the electrochemical behavior is controlled by the surface or diffusion. And the relationship between current and scan rate is measured by equations (9) and  $(10)^{2, 3}$ 

$$i = av^{b}$$
(9)  
$$\lg i = \lg a + \lg v$$
(10)

where i, a and v are the peak current, constant and sweep rate, respectively. And the value of b is equaled to the slope of the lg(v) versus lg(i) plot. For the surfacecapacitive process, b value is closed to 1, whereas the diffusion process is determined by b approached to  $0.5.^{2, 4}$  The total capacitance contribution can be quantified at a certain scan rate. According to equations (11) and (12),<sup>5, 6</sup> the total capacitive contribution is identified quantitatively at a certain scan sweep.

$$i(v) = k_1 v + k_2 v^{1/2} \tag{11}$$

$$i(v)/v^{1/2} = k_1 v^{1/2} + k_2 \tag{12}$$

where i(v),  $k_1v$  and  $k_2v^{1/2}$  represent the current at a certain voltage, surface capacitive-controlled current and diffusion-controlled current, respectively.  $k_{1}$  is equaled to the slope of the  $i(v)/v^{1/2} v^{1/2}$  plot.

# **Supporting Figures**



Fig. S1 Schematic diagram of electrospinning



Fig. S2 SEM images of a) PMIA, b) SPSF and c) GF separator.



Fig. S3 FT-IR spectra of SPSF, PMIA and SP separator.



Fig. S4 Contact angles (CA) of GF, SPSF, PMIA and SP separators.



Fig. S5 SEM (a) and diameter distribution (b) of SP separator after adsorption.



Fig. S6 Thermal shrinkage of different separators.



Fig. S7 The flexibility of SP separator.



Fig. S8 The thickness of SP separator.



Fig. S9 The equivalent circuit used for fitting the experimental EIS date.



Fig. S10 Cycling performance of Zn/SP/Zn symmetric cell at 20 mA cm<sup>-2</sup> and 10 mAh cm<sup>-2</sup>.



Fig. S11 Cycling stability of zinc symmetric cells at a) 1 and b) 5 mA cm<sup>-2</sup>.



Fig. S12 The overpotential of zinc symmetric cells at various current densities.



Fig. S13 Cycling performance of zinc symmetric cells with GF separators under various current densities.



Fig. S14 The voltage profiles of GF separator Zn-Ti cell at the different cycles.



Fig. S15 CV curves of Zn-Ti cells with a) GF, b) SP separator.



**Fig. S16** Optical pictures of the battery based on GF separator exhibit an apparent volume expansion after cycling.



Fig. S17 Linear polarization curves presenting the corrosion for GF and SP separator.



Fig. S18 The true color confocal microscope images of a) GF separator, b) SP separator.



Fig. S19 Schematic diagram of the coin cell.



Fig. S20 a) Capacity retention of the  $Zn/MnO_2$  full cells with different separators. b) Capacity retention of the  $Zn/V_2O_5$  full cells with different separators.



Fig. S21 The voltage-capacity curves for a)  $Zn/SP/MnO_2$  cell, b)  $Zn/SP/V_2O_5$  cell.



Fig. S22 SEM image of  $MnO_2$  cathode (a) before and (b) after cycling.



Fig. S23 XPS spectra of SP separator and SP separator after adsorption.



Fig. S24 XPS spectra of Zn 2p spectrum after adsorption for pure Zn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> salt.



Fig. S25 a) The CV curves scanned from 0.1 to  $1.0 \text{ mV s}^{-1}$ , b) log(i) versus log(scan rate) curves and (c) ratio of diffusion and capacitance contributions of  $\text{Zn/V}_2\text{O}_5$  cell.



Fig. S26 LSV curves of the different separators.

## **Supplementary Table**

	Porosity (%)	Electrolyte uptake	Tensile strength	
Separator		(%)	(MPa)	
GF	83.3	697	0.5	
SPSF	89.5	754	1.3	
PMIA	92.7	866	2.9	
SP	91.4	813	3.2	

**Table S1.** Experimental confirmation results for the thickness, porosity, and electrolyte

 uptake.

Table S2. The EIS fitting results corresponding to Fig.2a.

	Rsf			
	Pristine (Ω)	Fit (Ω)		
GF	1.07	1.02		
SPSF	0.72	0.70		
PMIA	0.81	0.63		
SP	0.56	0.51		

 Table S3. Calculation of transference numbers from analysis of polarization

 experiments.

Separator	ΔV(mV)	$R_0(\Omega)$	Rs(Ω)	I <sub>0</sub> (μA)	Is(µA)	$t_{Zn^2+}$
GF	10	1596	1714	2.4	1.2	0.385
SPSF	10	1112	1426	4.6	3.1	0.589
PMIA	10	1054	1619	2.2	1.4	0.632
SP	10	871	1058	9.2	7.4	0.736

Strategy	Current density (mAcm <sup>-2</sup> )	Areal capacity (mAh cm <sup>-2</sup> )	Lifespan (h)	Cumulative capacity (mAh cm <sup>-2</sup> )	Refences
Zn@NGO	1	1	1200	1200	Adv. Mater. 2021, 33, 2101649
Zn@rGO	1	1	300	300	Appl. Surf. Sci. 2019, 481, 852–859
Zn@PVDF	1.5	0.3	100	30	Chem. Eng. J. 2021, 411, 128584
Zn@PAN	1	1	1100	1100	Adv. Sci. 2021, 8, 2100309
Zn@In	1	1	300	300	Chem. Eng. J. 2020, 396,125363
Zn@TiO <sub>2</sub>	1	1	140	140	Adv. Mater. Interfaces 2018, 1800848
$Zn@ZnF_2$	1	1	800	800	Adv. Mater. 2021, 33, 2007388
Zn@MCHSs	1	1	500	500	Energy Storage Mater.2020, 25, 858- 865
Zn@Kaolin	4.4	1.1	800	880	Adv. Funct. Mater. 2020, 30, 2000599
Zn@502	2	1	400	400	Energy Storage Mater. 2021, 36, 132–138
Zn@DIP D	1	1	400	400	Adv. Mater. 2021, 33, 2101726
Zn@3D Cu	0.5	0.5	350	175	ACS Sustain. Chem. Eng. 2019,7,17737–17746
Zn@GF	1	1	700	700	Adv. Mater. 2020, 2003425
Zn@CNT	2	1	200	400	Adv. Energy Mater. 2019, 1901469
Zn@ZIF-8	10	10	200	2000	Joule 2019, 3, 1289– 1300
ZnP/CF	8	8	700	5600	J. Power Sources 2020, 479, 228808
Zn@HsGDY	1	1	2400	2400	Adv. Mater. 2020, 32, 2001755

**Table S4**. Comparison of cumulative capacities for zinc symmetrical cells between this

 work and previous reports with various strategies.

SP	5	2.5	500	1250	This work
SP	1	1	1100	1100	This work
PAN	0.283	0.283	800	226.4	Adv. Funct. Mater. 2021, 2109671
CG	2	1	1750	1750	Adv. Energy Mater. 2021, 11, 2101299
rGO/MOF	0.5	0.25	350	87.5	Appl. Surf. Sci. 2019, 481,852–859
Ligin@Nafion	0.6	0.6	380	228	ChemSusChem 2019, 12, 1–13
Zn@Nafion	5	0.5	550	275	J. Mater. Chem. A, 2021, 9, 4734–4743
GF/GO	2	1	500	500	J. Mater. Chem. A 2020, 8, 9331-9344
VG/GF	0.5	0.5	300	150	Adv. Mater. 2020, 2003425
MXene-GF	1	1	1180	1180	Adv. Funct. Mater. 2022, 2204306

Table S5. The cost of raw material, dates from Taobao.

		SP		
Materials	GF	SPSF	PMIA (	
		5151	solid content:25%)	
Cost of raw material	126	27.41	20.55	
(USD m <sup>-2</sup> )	120	27.41	39.33	

### References

- J. Xiao, Q. Li, Y. Bi, M. Cai, B. Dunn, T. Glossmann, J. Liu, T. Osaka, R. Sugiura, B. Wu, J. Yang, J.-G. Zhang and M. S. Whittingham, *Nat. Energy*, 2020, 5, 561-568.
- 2. Y. An, Y. Tian, C. Liu, S. Xiong, J. Feng and Y. Qian, ACS Nano, 2022, 16, 4560-4577.
- 3. J. Li, D. Yan, S. Hou, Y. Li, T. Lu, Y. Yao and L. Pan, J. Mater. Chem. A, 2018, 6, 1234-1243.
- 4. Y. An, Y. Tian, S. Xiong, J. Feng and Y. Qian, *ACS Nano*, 2021, **15**, 11828-11842.
- N. Zhang, S. Huang, Z. Yuan, J. Zhu, Z. Zhao and Z. Niu, Angew. Chem. Int. Ed., 2021, 60, 2861-2865.
- 6. C. Li, J. Qin, M. Sawangphruk, X. Zhang and R. Liu, *Chem. Commun.*, 2018, **54**, 12622-12625.