Electronic Supplementary Information

Cation Selective Separator Induced Cathode Protective Layer and Regulated Zinc Deposition for Zinc Ion Batteries

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Methods

Preparation of active electrode materials

MnO₂ nanowires were synthesized through hydrothermal method.¹ Typically, 3 mmol MnSO₄·H₂O (99 wt%, Aladin) was dissolved in 60 mL of deionized water, and then stirred together with 2 mL 0.5 M H₂SO₄ for 10 min to obtain a clear solution. Next, 20 mL of 0.1 M KMnO₄ (99.5 wt%, Sinopharm Chemical) was added dropwise to the solution with vigorous stirring for 1 h followed by 20 min ultrasonication. The above solution was then transferred into a 100 mL Teflon-lined autoclave at 120 °C for 12 h. After cooling down to room temperature, the obtained dark-brown powder was collected by centrifugation and washed with deionized water 3 times. Finally, the sample was dried in an oven for 24 h at 70 °C.

 V_2O_5 powder (99 wt%) was purchased from Infinity Scientific and used directly as active cathode material. Zinc foil was purchased from Xinye Metal Materials with a thickness of 0.01 mm.

Battery fabrication

The zinc foil was catted into $\Phi 14 \text{ mm}$ discs and used directly as the anode. The active cathode materials, including MnO₂ nanowires and commercial V₂O₅, were mixed with Ketjen black (AkzoNoble) and polytetrafluoroethylene (60 wt%, Aladin) in an agate mortar at a ratio of 7:2:1, using glycol as the solvent. The above slurry was then tableted and cut into pieces. The mass loading of the cathode was about 8.9 mg cm⁻². Glass fiber membrane (Whatman, GF/A) and Nafion membrane (Nafion-211, Dupont) were used as the separator.

Nafion separator was immersed into the 2 M ZnSO₄ electrolyte for 48 h before used.² Stainless Steel Weld Mesh was chosen as the current collector. Finally, the above components were assembled to CR2016-type coin cell (room temperature) to evaluate the electrochemical performance. The fabrication of Zn//Zn symmetric cell, Zn//MnO₂ cell, and Zn//V₂O₅ cell were prepared by 2 M ZnSO₄ electrolyte without any additive.

Characterizations

Material characterizations

The prepared samples were characterized by powder X-ray diffraction (XRD, D8 Discover X-ray diffractometer with Cu K α radiation, $\lambda = 1.5406$ Å). The morphologies and submicroscopic images were collected by a field emission scanning electron microscope (FESEM, JSM-7100F). The 3D height images were obtained via Keyence VR-5000. The stress-strain curves of Nafion and GF separators were characterized by Instron 3360.

Electrochemical characterizations

Galvanostatic discharge-charge test, galvanostatic intermittent titration technique (GITT) (10 min charge/discharge at 0.1 A g⁻¹, followed by a relaxation time of 20 min) and rest test were accomplished by Neware CT 4000. The electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were performed on an electrochemical workstation (CHI760E). All the characterizations were performed at room temperature.

In the Zn//Zn symmetric cell, both cathode and anode were Φ 14 mm zinc foil. The glass fiber separator (Whatman GF/A CAT No. 1820-125) and Nafion-211 (DuPont) were applied as the separator. The Nafion -211 membrane was immersed into 2 M ZnSO₄ before assembling. While in the Zn//MnO₂/V₂O₅ full cell, the cathode plate was cut into a Φ 5 mm

disc. Reversible galvanostatic discharge-charge technology was applied for CE evaluation. The carbon paper was used as the counter electrode versus metallic zinc anode. An aerial capacity of 0.5 mAh cm⁻² was plated on the carbon paper substrate. Then, a reverse of 0.2 V was applied to strip the deposited zinc. The separator recycle test was accomplished by Neware CT 4000 for 25 cycles at 4 A g⁻¹ for each time. The separator was carefully extracted from the cell after the cycling and reassembled into a new cell for the next recycling test.

Calculations

1. The water uptake percentage of the membrane was calculated using Equation (1):

Water uptake =
$$[(W_{wet} - W_{dry})/W_{dry}] \times 100\%(1)$$

where W_{wet} and W_{dry} (g) refer to the weights of the fully hydrated and dry states, respectively. The activated membrane was immersed in deionized (DI) water at 80°C for 12 h. The excess water was carefully wiped off, and the W_{wet} was measured. The membrane was then dried in a vacuum oven at 120°C for 12 h, and weighted to obtain W_{dry} .

2. The calculation of surface parameters in Table S1:

Surface height of irregularities (Sz):

$$Sz = Sp + Sv(2)$$

where *Sp* and *Sv* stands for maximum height and depth of the characterized surface. Arithmetic mean peak curvature (Spc):

$$S_{PC} = -\frac{11}{2n} \sum_{k=1}^{n} \left(\frac{\partial^2 z(x, y)}{\partial x^2} + \frac{\partial^2 z(x, y)}{\partial y^2} \right)_{(3)}$$

)

(Higher Spc indicates that the tips in the characterized area is sharper.)

4 / 30

Developed interfacial area ratio (Sdr):

$$S_{dr} = \frac{1}{A} \left[\iint_{A} \left(\sqrt{\left[1 + \left(\frac{\partial z(x, y)}{\partial x} \right)^{2} + \left(\frac{\partial z(x, y)}{\partial y} \right)^{2} \right]} - 1 \right) dx dy \right]_{(4)}$$

where *A* stands for area of characterized surface. (Higher *Sdr* indicates that the surface change in the characterized area is more aggressive.)

3. The Coulombic efficiency (CE) in Figure 3a was defined as below, according to previous work³:

$$CE = \frac{Discharge \ capacity}{Charge \ capacity} \times 100\% \ (5)$$

The depth of discharge (DOD) in this paper was calculated as below²:

$$DOD = \frac{Capacity of plated zinc}{Capacity of total zinc anode} \times 100\% (6)$$

4. The calculation of cathode cost in Figure 4h: For the fairness of comparison, the price we adopted in calculating the cost of the acive cathode materials were the cheapest price in the all specifications. The V₂O₅, V₂AlC, H₂C₂O₄, rGO, CNTs, NH₄VO₃ and Zn(CF₃SO₃)₂ was obtained from Sigma Aldrich (Sigma Aldrich, https://www.sigmaaldrich.com, accessed October 2020). The components of the raw materials were concluded from the experiment section of the references. The list was shown in Table S2. The cost for the cathode materials are calculated as below:

$$C = PIwt_1\% + P_2wt_2\% + P_3wt_3\%...$$
 (7)

where the *C*, *P* and *wt%* stand for the cost of active materials, the corresponding price, and the percentage of V_2O_5 based cathodes in the synthesize process. (The calculation was based only on raw materials of the V_2O_5 based cathodes)

5. The specific energy density in Figures 4b and 4e were calculated as below:

$$\frac{UIt}{E_{energy \, density}} = \frac{UIt}{m} = \int U(c) dc \tag{8}$$

where *U*, *I*, *t*, *m* and *c* stand for discharge voltage, current, time, the active mass of cathode and specific capacity, respectively. We took the result of 10^{th} cycle in rate performance test in Figure 4d and 4e. The results of the energy densities of V-Nafion/GF and M-Nafion/GF cells are 374.4, 233.9, 240.2 and 114.7 Wh kg⁻¹. Thus, the cathode cost of V-Nafion at 0.1 A g⁻¹ was calculated to be 39.23 US\$ kg⁻¹.

6. The ion diffusion ecoefficiency (D) in Figures 6d and 6e were calculated based on the following equation⁴:

$$D = \frac{4}{\pi\tau} \left(\frac{n_m V_m}{S}\right)^{-2} \left(\frac{\Delta E_s}{\Delta E_\tau}\right)^{-2} \tag{9}$$

where τ is the duration time of the current pulse, n_m is the mole number of the active material, V_m is the molecular volume, S is the contact area between electrode and electrolyte, ΔE_s is related to the change in the steady-state voltage for the corresponding step and ΔE_{τ} is the voltage change during one charge/discharge pulse.

7. For the fairness of comparison, the price we adopted in calculating the cost of Zn-Nafion separator and GF separator were the cheapest price in the all specifications. The price of GF separator was 846.91 US\$ for 25 slices with size of 46 cm \times 57 cm (Whatman glass microfiber filters (GF/A), <u>https://www.krackeler.com/catalog/product/3775/Whatman-8482-Glass-Microfiber-Filters</u>, accessed October 2020). The price of Nafion-211 was 1029 US\$ for 30.5 cm \times 500 cm (NafionTM 211, <u>https://www.fuelcellstore.com/nafion-211?search=Nafion</u> accessed October 2020). GF separator can only stably work for 1 recycle time and the Nafion separator can be recycled for at least 10 times. So, the calculated cost of Nafion and GF are as below:

Cost of GF separator = $846.91 \text{ US}/(46 \text{ cm} \times 57 \text{ cm})/25/1 = 0.0129 \text{ US} \text{ cm}^{-2}$ Cost of Zn-Nafion separator = $1029 \text{ US}/(30.5 \text{ cm} \times 500 \text{ cm})/10=0.0068 \text{ US} \text{ cm}^{-2}$

As a result, the cost of Zn-Nafion separator was 47.3% cheaper than that of GF separator.



Figure S1. Schematic illustration of (a) Molecular formula of Nafion. (b) Cation channel of Nafion. (c) Storage mechanism of water molecules in Nafion. (d) Zn²⁺ substitution

process of Nafion.

As shown in Figure S1a, Nafion consists of a hydrophobic main chain and a hydrophilic side chain, in which negative-charged sulfonic acid groups are attached to the end of the side chain, endowing Nafion with hydrophilicity and cation-selective properties. According to the cluster-net model⁵, the nano-phase separated hydrated ionic aggregates are well connected by nanosized ion-selective channels (Figure 1a). The water molecule and cations can be stored and transported in the hydrophilic microchannels (Figure S1b). In this work, the Nafion membrane was immersed in 2 M ZnSO₄ electrolyte for three days

in order to replace the counterions from protons to zinc ions for reducing the acidity of Nafion membrane (Figure 1b, noted as Zn-Nafion).^{2, 6}



Figure S2. Simulations domains, dimensions, and boundary conditions used in this study. Multi-physic model development for Nafion and GF separator near the surface of zinc anode:

The ion transport for the zinc anode was predicted with a 2D Nernst-Planck formulation accounting for diffusion and migration in the bulk electrolyte and separators. The modeling domain, geometrical dimensions, and major boundary conditions are shown in Figure S2. The governing equations for zinc anode with Nafion membrane were given as

$$\nabla \cdot J_i = 0 \tag{9}$$
$$J_i = -D_i \nabla c_i - z_i F c_i \nabla \emptyset \tag{10}$$
$$\rho_{fix} + F \sum_i z_i c_i = 0 \tag{11}$$

where J_i is the mass flux for each species, D_i is the diffusion coefficient $(3.36 \times 10^{-6} \text{ cm}^2/\text{s})$ for Zn²⁺ and $1.38 \times 10^{-5} \text{ cm}^2/\text{s}$ for SO₄²⁻), c_i is the concertation, z_i is the charge number, and \emptyset is the electrolyte potential. ρ_{fix} is the fix charge density in the Nafion density (1 M for Nafion and 0 M for all other domains). Electroneutrality was assumed throughout the

 $\Delta \phi = -\frac{RT}{Z_{i,membrane}F} ln^{[T]}(\frac{c_{i,electrolyte}}{c_{i,membrane}})$ (12)) was added to all Nafion-Electrolyte interfaces, accounting for potential differences induced by concertation change between membrane and electrolyte. The Zn²⁺ concentration in Figures 1 c-d was the calculated value minus 2 M (2 M ZnSO₄ electrolyte) for the convenience of comparison. The GF was filled with 2 M ZnSO₄ as the liquid electrolyte.

The model was solved in a commercial solver, COMSOL Multiphysics, with a total mesh element of 16889 and a relative error of 0.00001. A fully coupled Newton method was used to solve all coupled PDEs involved.



Figure S3 3D height images for the original zinc anode surface.



Figure S4 Schematic illustration of polarization and voltage hysteresis in Figure 3c.



Figure S5 SEM images of metallic zinc anode after cycled at a current density of 5 mA cm^{-2} (0.5 mAh cm⁻²).

The zinc surface in the Zn-Nafion symmetric cell is smooth without obvious zinc dendrite (Figure S7a). By contrast, the electrode surface in the GF symmetric cell shows a rough surface with unregulated zinc deposition and zinc dendrites.





and GF cell (d, e) with different magnifications after 500 h resting.



Figure S7 XRD patterns of zinc anode after resting for 500 h in Nafion symmetric cell (a) and GF symmetric cell (b).



Figure S8 XRD patterns of cathode materials (a) α -MnO₂ nanowires and (b) V₂O₅.



Figure S9 SEM images of cathode materials (a) α -MnO₂ nanowires and (b) Commercial

V₂O₅.



Figure S10 Cycle performance of MnO_2 cathode at a current density of 2.0 A g⁻¹.



Figure S11 XRD patterns of V_2O_5 cathode after 2000 cycles in the V-Nafion cell (a) and V-GF cell (b).

ZHS is commonly regarded as the byproducts in the study of ARZIBs, and its impact on the electrochemical reaction is still debatable.^{7, 8} Some researchers believed that the ZHS reversible precipitated/dissolved on the cathode surface during the discharge and charge process, as the pH value of electrolyte changed caused by H⁺ reaction of cathode. Moreover, the accumulation of ZHS reduced the reaction area on the electrode and increased the electrochemical impedance.⁹ In the meantime, other researchers agreed that the formation of ZHS was generated from the side reaction between dissolved O₂ and electrolyte, and the capacity of the reversible ZHS contributed to the total capacity of ZHS.⁸



Figure S12 The TEM images of the V_2O_5 cathode in (a) original state and (b) after cycling for 20 cycles.



Figure S13 Photos and SEM images of GF separator (a and c) and Nafion separator (b

and d) by the end of 20^{th} cycle



Figure S14 The CV curves of (a) V-Nafion cell and (b) V-GF cell at different scan rates.



Figure S15 The magnified EIS spectra of the V-Nafion cell and the V-GF cell.



Figure S16 The illustration of GITT characterization.



Figure S17 The GITT curves of the V-Nafion cell and the V-GF cell for the first 5 cycles.



Figure S18 The photos of GF separator and Nafion separator after the recycle testing.

	Sz	Spc	Sdr
Nafion-1	15.62	816.02	0.12
GF-1	35.55	1252.88	0.34
Nafion-20	26.93	767.40	0.22
GF-20	61.27	1414.90	0.56

Table S1 Surface parameters of zinc anode after the first cycle and 20th cycles with Zn-

Nafion and GF as the separator.

Especially, the Spc of Zn-Nafion separator-based zinc symmetric cells slightly decreased after 20 cycles. This is because in the first few cycles, the size zinc dendrites are relatively small, the limitation of zinc dendrites mainly stems from the zinc ion diffusion regulation of the Zn-Nafion separator, the Sz of GF-1 is almost twice as that in Nafion-1 with lager dendrites. However, as the dendrites grow bigger, the high mechanical strength of Zn-Nafion separator inhibits the further growth towards the separator of zinc dendrites, resulting a smoother tip and smaller size of zinc dendrites.

 Table S2 The voltage hysteresis and polarization of zinc symmetric cells applying

Current densities (mA cm ⁻²)	Polarization of Nafion symmetric cell (V)	Polarization of GF symmetric cell (V)	Voltage hysteresis of Nafion separator (V)	Voltage hysteresis of GF separator (V)
1	0.008	0.028	0.058	0.115
2	0.010	0.043	0.015	0.190
5	0.022	0.054	0.167	0.282
10	0.366	0.062	0.217	0.366

different separators at current densities of 1-10 mA cm⁻².

Cathode	Electrolyte	Specific	Raw	Cost of	Synthesize steps	Reference
		capacity	materials	raw		
		(mAh g-		materials		
		1)		(US\$ g ⁻¹)		
$V_2O_5@V_2C$ 2	2.5 M ZnSO ₄	397 at	V ₂ ALC	13.4	Chemical etch;	17
		0.5 A g-	(100%)		hydrothermal	
		1			(2)	
V ₂ O ₅ /Graphene	3 M ZnSO ₄	312 at	V_2O_5	8.0	Hydrothermal;	23
		0.5 A g-	(39.8%);		calcination (2)	
		1	$H_2C_2O_4$			
			(59.1%);			
			rGO			
			(1.1%)			
K ⁺ intercalated	1 M ZnSO ₄	421 at	KOH	0.2	Hydrothermal	44
V_2O_5		0.05 A	(19%);		(1)	
		g ⁻¹	V_2O_5			
		C	(81%)			
V ₂ O ₅ /CNT	1 M ZnSO ₄	312 at 1	V_2O_5	385.9	Vacuum	45
		A g ⁻¹	(70%);		filtration (1)	
		U	CNT			
			(30%)			
NH4 ⁺	2 M ZnSO ₄	404 at	NH ₄ VO ₃	2.5	Hydrothermal	46
intercalated		0.5 A g-	(100%)		(1)	
V_2O_5		1	· · ·			
Porous V ₂ O ₅	3 M	226 at	NH ₄ VO ₃	0.6	Electrospinning;	47
	$Zn(CF_3SO_3)_2$	0.294 A	(27%);		calcination (2)	
	(g ⁻¹	$H_2C_2O_4$			
		U	(73%)			
V ₂ O ₅ nano	2 M ZnSO ₄	375 at	V ₂ O ₅	385.9	Vacuum	48
paper		0.5 A g ⁻	(70%);		filtration; freeze	
1 1		1	MWCNT		dry (2)	
			(30%)		2 . /	
Commercial 7	Zn-Nafion (2	495.8 at	V ₂ O ₅	0.2	Directly applied	This work
V ₂ O ₅	M ZnSO ₄)	0.1 A g-			(0)	
	.,	1			· · ·	

Table S3 Capacity, cost and synthesize complexity comparison between the V-Nafioncell and other ARZIBs with modified V_2O_5 cathode¹⁰⁻¹⁵ or electrolyte (Figure 3h)

Cycles	H ⁺ reaction of V- Nafion cell	Zn ²⁺ reaction of V- Nafion cell	H ⁺ reaction of V-GF cell	Zn ²⁺ reaction of V-GF cell
1	0.841	0.159	0.351	0.649
2	0.925	0.075	0.318	0.682
3	0.826	0.174	0.322	0.678
4	0.849	0.121	0.267	0.733
5	0.928	0.072	0.209	0.781

Table S4 The ratio of H^+ reaction and Zn^{2+} reaction of V-Nafion cell and V-GF cell.

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