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Supplementary Information

Redistributing Zinc-ion Flux by Work Function Chemistry toward Stabilized and Durable Zn Metal Batteries

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Experimental Section Materials

Zn foil (80 µm) and Ti foil (0.02 mm) were purchased from Haoxuan Metal Material Co., Ltd. ZnSO₄·7H₂O (>99.0%), trimesic acid (>99%), Mn(NO₃)₂·4H₂O (>99%), N-methyl-2-pyrrolidone (NMP, 99.5%), tungsten hexachloride (WCl₆; >98%), ammonium vanadate (NH₄VO₃, 98%), hexamethylenetetramine (HMT, (CH₂)₆N₄) (>99.0%), ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O; >98%) and melamine (>99%) were purchased from Aladdin. Sodium dodecyl sulfate (SDS, 99%), Niobium chloride (NbCl₅; >98%), polyvinylidene fluoride (PVDF) and acetylene black were purchased from Sinopharm Chemical Reagent Co., Ltd. Graphene oxide (GO) were purchased from Carbon Solutions Inc. All other reagents were analytical grade and used directly without further purification. Deionized water was used to prepare all aqueous electrolytes.

Preparation of WN $_{0.67}$, VN, Mo₂N and NbN

Firstly, 60 mg of WCl₆ was dissolved in 30 mL of ethanol by vigorous stirring at ambient temperature for 1 h. Next, the suspension was hydrothermally heated at 180 °C for 6 h. The reaction vessel was cooled down to ambient temperature and the obtained solid material was washed with plenty of DI followed by drying at electric oven. Finally, the resulting powder was annealed in ammonia (NH₃) atmosphere at 600 °C for 2 h (heating rate = 5 °C min⁻¹) to obtain WN_{0.67} product.

Secondly, a 200 mL mixed solvent of DI water and ethanol (1:1) consists of ammonium vanadate (585 mg) and hexamethylenetetramine (7 g). Thereafter, the mixed suspension was vigorously stirred for 2 h and dried at 100 °C for 12 h. Asobtained sample was ground evenly before being calcined at 750 °C for 3 h under an argon (Ar) atmosphere with a ramping rate of 5 °C min⁻¹. After natural cooling, the final products were collected and denoted as VN.

Thirdly, ammonium molybdate tetrahydrate (500 mg) was dissolved in DI water (80 mL). The as-prepared solutions were mixed under constant magnetic stirring at ambient temperature to obtain solution A. Subsequently, melamine (1 g) was dissolved in DI water (80 mL) by heating it at 80 °C to obtain solution B. Afterward, solution A and solution B were uniformly mixed under vigorous stirring, followed by heating under the oil bath at 85 °C through reflux for 0.5 h. After finished, the obtained brown precursor was collected by centrifugal washing and subjected to freeze-drying for two days. Finally, the powder sample obtained was annealed at 300 °C for 1 h and 800 °C for 5 h with a heating rate of 5 °C min⁻¹ in an Ar atmosphere to derive Mo₂N.

Fourthly, hexamethylenetetramine (700 mg) were dispersed in deionized (DI) water (30 mL) under constant ultrasonication for 1 h. NbCl₅ (50 mg) was dissolved in ethanol (30 mL) by continuous stirring at ambient temperature, and then transferred to the hexamethylenetetramine solution followed by vigorous stirring for an additional 20 min. Afterwards, the homogeneously dispersed suspension was transferred to a three-neck flask for microwave treatment at 80 °C for 30 min. After cooling down to room temperature in the microwave system, a brown colloidal solution was obtained.

The as-prepared suspension was filtered and rinsed with DI water several times and subjected to freeze-drying for 24 h. The as-obtained powder sample was heated at 800 °C for 5 h at a heating rate of 5 °C min⁻¹ in NH₃ atmosphere to get the NbN products.

Synthesis of modified separator

 $WN_{0.67}@GF$, VN@GF, $Mo_2N@GF$ and NbN@GF modified separators were prepared through a simple vacuum filtration method. In short, GO (30 mg) and four nitrides (30 mg) were ultrasonically dispersed into an ethanolic solution (100 mL) with 0.2 wt.% of LA132 (10 mL). The powder sample was deposited on the glass fiber (GF) separator followed by drying at 60 °C overnight under a vacuum. Finally, the functionalized separator was cut into the 19 nm diameter discs and the areal mass loading weight of coating materials was about 1 mg cm⁻².

Synthesis of the Mn₃O₄@C

First, Mn-MIL-100 was prepared according to the reported method.^[1] In a typical procedure, 12 g of trimesic acid and 2.72 g of $Mn(NO_3)_2 \cdot 4H_2O$ were added into 600 mL methanol, and the resultant solution was stirred for 20 min. Then, the mixture was transferred to a 1000 mL of Teflon-lined stainless-steel autoclave and heated in an oven at 125 °C for 6 h. After cooling down to room temperature, the precipitation was gathered via centrifugation and washed with ethanol. Finally, Mn-MIL-100 was obtained after vacuum drying at 60 °C. The as-prepared Mn-MIL-100 was annealed at 600 °C in Ar atmosphere for 2 h. Then the resultant intermediate was calcined at the temperature of 220 °C in air for 2 h. After cooling down to room temperature, the Mn₃O₄@C was obtained.

 $Mn_3O_4@C$ electrodes were prepared by casting the slurry (by mixing 80 wt% of $Mn_3O_4@C$, 10 wt% of carbon black and 10 wt% of PVDF in NMP) onto stainless steel mesh. The coin-type cell was assembled with the above $Mn_3O_4@C$ electrodes, zinc foils (diameter: 14 mm, thickness: 80 μ m), glass fiber (GF) separators and 2 M ZnSO₄ electrolyte.

Fabrication of Zn//Zn symmetric cell

Two pieces of Zn foil were used as two electrodes for symmetric cell. 90 μ L of 2 M ZnSO₄ were added into the coin cell with a piece of GF as a separator. In order to inhibit hydrogen evolution reactions that may be caused by nitrides and graphene oxide on the anode surface, the two black sides NbN@GF are symmetrically pasted together as a separator. The separator used in the Zn|NbN@GF|Mn₃O₄@C coin cells is also constructed in this way.

Materials Characterization

The morphology of the samples was observed using scanning electron microscopy (SEM, FEI-Quanta 250, USA). The microstructures of the electrodes were analyzed using fieldemission TEM (JEM-ARM200P). XPS measurements were used to characterize the chemical composition by a spectrometer (PerkinElmer PHI 1600 ESCA) with Al K α radiation (hv = 1486.6 eV). The permeability of ions was

measured by a diffusion cell, which was separated into two parts by the separator. One side, 30 mL of 2 M ZnSO₄ electrolyte was added, and 30 mL of deionized water was added in another side. The effective area of separator was 8.04 cm⁻². Solutions in both the reservoirs were stirred vigorously to make homogeneous solution. After 1 h, the sample in H₂O side was collected and analyzed by inductively coupled plasmaatomic emission spectroscopy (ICP-AES; Optima 7300 DV). The elemental analysis of the samples was characterized using a scanning electron microscope (FE-SEM, JSM-7500, Japan) equipped with corresponding energy-dispersive X-ray (EDX) elemental mapping. Ultraviolet photoelectron spectroscopy (UPS, Thermo ESCALAB XI+) and Kelvin probe force microscopy (KPFM, Bruker Dimension Icon) were conducted to investigate the trend of the work function values. The Brunauer-Emmett-Teller (BET, Micromeritics ASAP2020, USA) measurement was conducted to study the differences in specific surface area. The crystal structure of the samples was characterized through the X-ray diffraction analysis (XRD, Smart Lab, Riga ku, Japan) with Cu-Ka ($\lambda = 1.540598$ Å, Smart Lab) source (scan rate of 4° min⁻¹) in the 20 range of 5° ~ 85°. Raman spectroscopic studies were recorded on an Invia/Reflrx Laser Micro-Raman spectroscope (Renishaw, England). Zeta potentials were tested by Malvern Zetasizer Nano ZS90.

Electrochemical Tests

Electrochemical characterizations of symmetrical Zn//Zn cells were conducted using 2032-type coin-cells. For asymmetric batteries (Ti//Zn), Ti foil, Zn foil and GF or NbN@GF were used as the cathode, anode and separators, respectively. EIS of these cells were conducted on an electrochemical workstation (CHI660E, Shanghai, China) over the frequency range of 100 kHz to 0.01 Hz. The Zn|NbN@GF|Mn₃O₄@C coin cells were galvanostatically charged/discharged in the voltage range of 0.8 – 1.8 V vs. Zn/Zn²⁺ at different current densities on a battery testing system (NEWARE, CT-4008Tn-5V10mA-164), and the specific capacities were calculated based on the active mass of Mn₃O₄@C cathode. The mass loading of active material was ~ 1.5 mg cm⁻².

The cumulative plating capacity calculation formula

Cumulative plating capacity = area capacity × cycle number

In this work, the symmetric cells are used to cycle more than 1500 cycles at 0.5 mA cm^{-2} and 0.5 mAh cm^{-2} , so the CPC is 0.5 mAh $m^{-2} \times 1500$ cycles, and the result is 750 mAh cm^{-2} .

Theoretical Calculations

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 Fig. 31, 3m. The governing equations for zinc anode with GF were given as

$$\nabla^{2} \varphi = -F \sum z_{i} C_{i}$$
$$\frac{\partial C_{i}}{\partial t} = \nabla \cdot \left[D_{i} \nabla C_{i} + \frac{D_{i} C_{i}}{RT} z_{i} \nabla \varphi \right]$$

where F, R and T are the Faraday constant, ideal gas constant and temperature, D_i is the diffusion coefficient (1×10^{-10} m²/s for Zn²⁺ and 1.38×10^{-9} m²/s for SO₄²⁻), C_i is the concertation, Z_i is the charge number, and φ is the electrolyte potential. Electroneutrality was assumed throughout the whole domains. In the initial experiments, both the flux of zinc ions and the pore structure of the separator are uniform. The experimental current is 1 mA cm⁻², the electrode length is 22 microns, and the overall diffusion distance of electrolyte is 15 microns. Firstly, considering the situation without NbN, a model with the initial structure is established to obtain the electric field distribution (Fig. 31). The initial structure is a semicircle with a radius of 1 cm. After introducing the NbN@GF, the evolution of electric field distribution is considered (Fig. 3m), which is simulated from the resistance value of the symmetric batteries. The model the processed electrochemistry model was imported into the finite element software COMSOL Multiphysics 6.1, where the material properties were defined and the relevant problems were calculated and analyzed. To solve the discretized transport and electrode deformation kinematics equations, the Parallel Direct Sparse Solver (PARDISO) was employed. Time stepping was handled using 2nd order backward Euler differentiation.

Density functional theory (DFT) calculations were carried out using the projector augmented plane-wave method as implemented in the Vienna Ab initio Simulation Package (VASP).^[2-4] The exchange-correlation functional was treated within the generalized gradient approximation (GGA), employing the Perdew-Burke-Ernzerhof (PBE) scheme.^[5] The plane-wave cutoff energy was set to 500 eV, and the energy convergence criterion for the self-consistent field iterations was established at 10⁻⁵ eV.

The lattice constants of the optimized bulk phases of Mo₂N, NbN, VN, and WN_{0.67} are presented in the following table S1. Based on these, we constructed surface models for their respective (001) facets to investigate surface adsorption phenomena and calculate the work function. During the structural optimization and electronic structure calculations, a K-points mesh was generated with a K-spacing value of 0.040 Å⁻¹, ensuring sufficient sampling in the Brillouin zone. All structures were fully relaxed until the residual forces on each atom were reduced to less than 0.03 eV/Å. To minimize interactions between periodic images in the vertical direction, a vacuum spacing of 15 Å was employed. Furthermore, the DFT-D3 correction method was incorporated to accurately account for weak van der Waals interactions.^[6] For exploring the diffusion barriers of SO42- across different surfaces, the Climbing Image Nudged Elastic Band (CI-NEB) method was utilized.^[7] This approach allowed us to trace the minimum energy path and accurately determine the energy barriers associated with the surface diffusion processes. The work function is defined as $\Phi = E_{vac} - E_F$, where E_{vac} represents the energy of electrons at rest near the surface in vacuum, and $E_{\rm F}$ is the Fermi level of the material.



Fig. S1. XRD patterns of the WN_{0.67}, VN, Mo₂N and NbN powder.



Fig. S2. SEM imags of the $WN_{0.67}$, VN, Mo_2N and NbN powder.



Fig. S3. SEM imags of the $WN_{0.67}$, VN, Mo_2N and NbN powder.



Fig. S4. SEM imags of the $WN_{0.67}$ @GF, VN@GF, $Mo_2N@GF$ and NbN@GF.



Fig. S5. Nyquist plots of symmetrical cells with WN_{0.67}@GF, VN@GF, Mo₂N@GF and NbN@GF.



Fig. S6. UPS spectra of the $WN_{0.67}$, VNF, Mo_2N and NbN.



Fig. S7. Contact potential difference distribution maps measured in the dark for the $WN_{0.67}$, VN, Mo_2N and NbN.

Generally, the work function of gold is considered to be 5.2 eV, and the surface potential of gold measured by this instrument is 0.037 V. The work function of the four nitride materials can be obtained by the following formula:

$$WF_{(material)} = 5.2 - (Mean Potential - 0.037)$$



Fig. S8. Low temperature nitrogen adsorption desorption isotherms curves of the $WN_{0.67}$, VN, Mo₂N and NbN powder.



Fig. S9. Zn²⁺ transference number of the WN_{0.67}@GF, VN@GF, Mo₂N@GF and NbN@GF separator for the symmetrical cells.



Fig. S10. Voltage-time profiles of symmetrical cells with GF, $WN_{0.67}@GF$, VN@GF, $Mo_2N@GF$ and NbN@GF cells at a current density of 2 mA cm⁻² with a cycling capacity of 1 mA h cm⁻².



Fig. S11. XRD patterns of the Zn anodes for symmetrical cells using $WN_{0.67}@GF$, VN@GF, $Mo_2N@GF$ and NbN@GF at a current density of 2 mA cm⁻² with a cycling capacity of 1 mA h cm⁻² after 200 cycles.



Fig. S12. Optical photograph of the GF and NbN@GF.



Fig. S13. TEM images of Zn anode with the GF separator after plating for 60 min.



Fig. S14. XRD patterns of Zn anodes with the untreated GF separator after deposition.



Fig. S15. Nyquist plots collected at open circuit voltage (OCV) over the frequency range of 100 kHz to 1 Hz. The ionic conductivity of the GF separator could be calculated from the bulk electrolyte resistance by the following equation:

$$\sigma = \frac{L}{R_b S}$$

where L is the thickness of the GF separator (0.8 mm), S is the contact area (1.539 cm²), and R_b (GF) = ~3.1 ohm at room temperature. Thus, $\sigma_{GF} = ~16.8 \text{ mS cm}^{-1}$. For the Zn symmetrical cell with NbN@GF (0.95 mm), R_b (NbN@GF) = 1.06 ohm. Therefore, the ionic conductivity of the NbN@GF can be evaluated as $\sigma_{NbN@GF} = ~58.2 \text{ mS cm}^{-1}$.



Fig. S16. Corresponding plating/stripping profiles of CE for Zn|GF|Zn cells at different cycles.



Fig. S17. SEM images of Zn anode with the GF separator and NbN@GF separator after the Zn|GF|Ti and Zn|NbN@GF|Ti cells cycling 94 h.



Fig. S18. XRD patterns of the Zn anodes for symmetrical cells using GF and NbN@GF at a current density of 2 mA cm⁻² with a cycling capacity of 1 mA h cm⁻² after 200 cycles.



Fig. S19. SEM images of Zn anode with the GF separator and NbN@GF separator after 200 cycles.



Fig. S20. Nyquist plots of symmetrical cells with the GF and NbN@GF.



Fig. S21. SEM images of Mn₃O₄@C.



Fig. S22. TEM images of Mn₃O₄@C.



Fig. S23. TEM mapping of Mn₃O₄@C.



Fig. S24. XRD pattern of Mn₃O₄@C powder.



Fig. S25. The activization curves of $Zn//Mn_3O_4@C$ cells at 0.2 mV s⁻¹.



Fig. S26. CV curves of the Zn|GF|Mn₃O₄@C and Zn|NbN@GF|Mn₃O₄@C cells at 0.2-1.2 mV s⁻¹.



Fig. S27. The charge/discharge curves the Zn|GF|Mn₃O₄@C and Zn|NbN@GF|Mn₃O₄@C cells at 0.1-2 A g^{-1} .



Fig. S28. The charge density difference and absorption energy (-1.330 eV) of Mn^{2+} with NbN nanoparticles.



Fig. S29. SEM images of $ZnMn_2O_4@C@C$ after discharging to (a) 1.45 and (b) 0.8V.



Fig. S30. C 1s XPS spectra of ZnMn₂O₄@C@C.

Structur	a /Å	b/Å	c/Å	α	β	γ/°
e				/°	/°	
Mo ₂ N	4.14	4.18	4.18	90	90	90
	8	3	3			
NbN	4.38	4.38	4.38	90	90	90
	7	7	7			
VN	4.09	4.09	4.09	90	90	90
	0	0	0			
WN _{0.67}	4.32	4.32	4.32	90	90	90
	8	8	8			

Table S1. Lattice parameters of the optimized bulk phases of Mo_2N , NbN, VN, and $WN_{0.67}$.

Table S2. Element concentration (g/mL) of Zn and S in H-cell as determined through ICP-AES measurements.

Separator	WN _{0.67}	VN	Mo ₂ N	NbN
Zn	3.96×10 ⁻⁴	4.15×10 ⁻⁴	4.43×10^{-4}	4.88×10 ⁻⁴
S	3.82×10 ⁻⁴	3.10×10 ⁻⁴	1.98×10 ⁻⁴	1.41×10 ⁻⁴

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