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Electronic Supporting Information for

Engineering the Interplanar Spacing of Ammonium Vanadates as High-

performance Aqueous Zinc-ion Battery Cathode

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Experimental section

Material Synthesis:

To synthesize $NH_4V_4O_{10}$,¹ 1.170 g NH_4VO_3 was dissolved in 80°C deionized water to form a light yellow solution. Subsequently, 1.891 g $H_2C_2O_4$ ·2 H_2O solid powders were added to the solution under magnetically stirring until it became black-green. The solution was transferred to a 50 mL autoclave and kept in an oven at 140 °C for 48h. The products were collected and washed repeatedly with de-ionized water after the sample was cooled to room temperature naturally. The final product was dried at 60°C for 12h to obtain the $NH_4V_4O_{10}$.

 $NH_4V_3O_8$ was prepared modified by reported method.² 0.936 g NH_4VO_3 was dissolved in 100 mL deionized water (80°C), then an appropriate amount of dilute hydrochloric acid was added dropwise under continuous stirring to adjust the desired pH value of the solution to about 2.0. Then, the resulting solution was maintained at 90°C for 2.5h with oil-bath and then allowed to cool down to room temperature naturally. The product was washed several times with deionized water, and then dried at 60 °C for 12h to obtain $NH_4V_3O_8$.

 $(NH_4)_2V_3O_8$ was prepared by a hydrothermal method.³ At first, 1.275 g NH_4VO_3 was dissolved in 35 ml deionized water(80°C) to form a light-yellow solution. 0.687 g $H_2C_2O_4$ ·2 H_2O was added and the solution turned orange. The solution was then transferred into a 50 ml Teflon lined stainless steel autoclave, sealed and maintained at 180 °C for 24h. After that, the autoclave was cooled to room temperature. The precipitate was washed with water and dried in air at 60 °C for 12h to obtain $(NH_4)_2V_3O_8$.

Cathode: To prepare the working electrode, the active material, acetylene black and polyvinylidene fluoride (PVDF) binder were mixed in a weight ratio of 7:2:1 with N-methyl-2-

pyrrolidone (NMP) solvent to form a homogeneous slurry. This slurry was then coated on a Stainless Steel Wire Mesh (SSWM) and then dried at 80°C in a vacuum oven for 12 h.

Electrochemical Measurements: Electrochemical experiments were performed using 2016 type coin cells with Zn metal as the anode, the ammonium vanadates as cathode and 2 mol L⁻¹ ZnSO₄ solutions as the electrolyte. The areal loading density of NH₄V₄O₁₀ is ~1.0 mg cm⁻². The galvanostatically tests were performed on a battery testing system (LAND CT2001A) in the voltage window of 0.4–1.4 V. Cyclic voltammetry (CV) tests were carried out using the CHI 660e electrochemical station. Galvanostatic intermittence titration techniques (GITT) technique based on chronopotentiometry is proved to be helpful for the detailed study of the electrode kinetic behaviors of ammonium vanadates. In this method the Zn²⁺ diffusivity (D_{GITT}) was obtained based on the formula;^{4, 5}

$$D = \frac{4L^2}{\pi\tau} \left(\frac{\Delta Es}{\Delta Et}\right)^2 \tag{1}$$

Where *L* denotes the Zn ion diffusion length (cm), τ is the relaxation time (s), and ΔE s is the steady-state potential change (V) by the current pulse. ΔE t is the total change of cell voltage during the constant current pulse after eliminating the iR drop. During GITT process, current pulse of 50 mA g⁻¹ was applied for 600 s while the followed relaxation time is 1800 s. The GITT measurement continues until coming to the cut-off voltage (0.4 V/1.4 V). All electrochemical tests were performed after the battery was allowed to stand for 4 hours and the test temperature was maintained at 28 °C.

Characterization: X-ray diffraction (XRD) patterns of the as-prepared products were performed on an X-ray diffractometer (XRD, Rigaku D/max2500). The morphological studies of the products were conducted using scanning electron microscopy (SEM, Quanta FEG 250). TEM,

SAED, and TEM–EDS elemental mapping measurements were carried out on the Tecnai G2 F20 transmission electron microscope. X-ray photoelectron spectroscopy (XPS) measurements were performed using a spectrometer (Escalab 250xi, Thermo Scientific).

Preparation operations for *ex-situ* XRD and XPS analysis:

Ex-situ analysis was conducted during the charge/discharge cycle within the potential window of 0.4-1.4 V at a current density of 100 mA g⁻¹.

The cells were disassembled after discharge/charge to specific voltages to obtain the corresponding cathode. Then, rinse the electrode thoroughly with plenty of distilled water after removing the adhered white fibers from it. These cathode electrodes were dried at 60 °C for 12 h.

Figures and Tables

Electrode Materials	Electrochemical Performance (Capacity retention)	Ref.
$\mathrm{NH_4V_4O_{10}}$	255.5 mA h g ⁻¹ at 10 A g ⁻¹ after 1000 cycles (~100%)	Our work
$Zn_3V_2O_7(OH)_2 \cdot 2H_2O$	101mA h g ⁻¹ at 0.2 A g ⁻¹ after 300 cycles (68%)	6
$K_2V_8O_{21}$	128.3 mA h g ⁻¹ at 6 A g ⁻¹ after 300 cycles (83%)	7
ZnMn ₂ O ₄	106.5 mA h g ⁻¹ at 0.1 A g ⁻¹ after 300 cycles (<60%)	8
Na _{1.1} V ₃ O _{7.9} @rGO	171 mA h g ⁻¹ at 0.3 A g ⁻¹ after 100 cycles (77%)	9
MnO ₂	135 mA h g ⁻¹ at 2 A g ⁻¹ after 2000 cycles (94%)	10
β-MnO ₂	135 mA h g ⁻¹ at 0.2 A g ⁻¹ after 200 cycles (75%)	11
VS ₂	110.9 mA h g ⁻¹ at 0.5 A g ⁻¹ after 200 cycles (98%)	12
α-Mn ₂ O ₃	82.2 mA h g ⁻¹ at 2 A g ⁻¹ after 1000 cycles (<92%)	13
Mn ₃ O ₄	106.1 mA h g ⁻¹ at 0.5 A g ⁻¹ after 300 cycles (<76%)	14
VO _{1.52} (OH) _{0.77}	105 mA h g ⁻¹ at 0.015 A g ⁻¹ after 50 cycles (<70%)	15
LiV ₃ O ₈	140 mA h g ⁻¹ at 0.133 A g ⁻¹ after 65 cycles (<80%)	16
ZnHCF@MnO ₂	69 mA h g ⁻¹ at 0.5 A g ⁻¹ after 1000 cycles (77%)	17
Fe ₅ V ₁₅ O ₃₉ (OH) ₉ ·9H ₂ O	100 mA h g ⁻¹ at 5 A g ⁻¹ after 300 cycles (80%)	18
Na ₃ V ₂ (PO ₄) ₂ F ₃	63.8 mA h g ⁻¹ at 6 A g ⁻¹ after 600 cycles	19

 Table S1 The electrochemical performance of previous reported cathode materials in aqueous zinc
 ion batteries.

Figures and Captions



Figure S1. Crystal structures of $NH_4V_4O_{10}$, $NH_4V_3O_8$ and $(NH_4)_2V_3O_8$.



Figure S2. a) The XRD pattern, b) TEM image, c) SEAD pattern and d) TEM elemental mapping images of $NH_4V_4O_{10}$.

The X-ray diffraction (XRD) pattern (Figure S2a) shows no impurities and can be indexed to monoclinic $NH_4V_4O_{10}$ (JPCDS no. 31-0075). Examination of transmission electron microscopy (TEM) data shown in Fig. S2c indicates that $NH_4V_4O_{10}$ exhibits a flake-like morphology structure. The selected area electron diffraction (SAED) pattern suggests the single-phase of $NH_4V_4O_{10}$. The homogeneous distributions of N, V, and O in $NH_4V_4O_{10}$ were evidenced by TEM elemental mapping images in Figure S2d.



Figure S3. The XRD patterns and morphology of a) $NH_4V_3O_8$ and b) $(NH_4)_2V_3O_8$.

The X-ray diffraction (XRD) patterns show single-phase of $NH_4V_3O_8$ and $(NH_4)_2V_3O_8$ phases (JCPDS no. 89-6614 and JCPDS No. 88-1473). Moreover, the magnified XRD patterns of the $NH_4V_3O_8$ and $(NH_4)_2V_3O_8$ are displayed. All observed diffraction peaks in the magnified XRD patterns of the $NH_4V_3O_8$ were well matched to the monoclinic $NH_4V_3O_8$ phase, with lattice parameters of a=4.99, b=8.42, c=7.86 nm, and β =96.41°. The intensity of the (-111) and (120) peaks appeared inconsistent with the standard JCPDS pattern because the anisotropic growth of crystal. ^{20, 21} The (00*l*) peaks of $(NH_4)_2V_3O_8$ show an obviously increased relative intensity to other peaks, indicative of a preferential c-axis orientation of $(NH_4)_2V_3O_8$. The anisotropic growth and preferential orientation of the $NH_4V_3O_8$ and $(NH_4)_2V_3O_8$ lead to changes in morphology without affecting the interplanar spacing of the (001) plane. ^{21, 22}

Both of $NH_4V_3O_8$ and $(NH_4)_2V_3O_8$ display flake-like morphology. The EDS spectrum data of $NH_4V_3O_8$ and $(NH_4)_2V_3O_8$ are shown in Fig. S3. The N, V ratios of them are about 1:3 and 2:3, respectively, which further confirmed that the product was stoichiometric $NH_4V_3O_8$ and $(NH_4)_2V_3O_8$ phases.



Figure S4. The charge/discharge curves at 500 mA g^{-1} of a) $NH_4V_4O_{10}$, b) $NH_4V_3O_8$ and c) $(NH_4)_2V_3O_8$.



Figure S5. The cycling performance of a) $NH_4V_4O_{10}$, b) $NH_4V_3O_8$ and c) $(NH_4)_2V_3O_8$. at 100 mA h g⁻¹.



Figure S6. The Zn^{2+} diffusion coefficient of $NH_4V_3O_8$ at the second, fourth and eighth discharge/charge cycles.



Figure S7. a) CV curves of the NH₄V₄O₁₀ cathode at different sweep rates. b) log(i) versus log(v)plots at specific peak currents. c) Bar chart showing the percent of pseudocapacitive contribution at different scan rates and (d) CV curve with the pseudocapacitive fraction shown by the shaded area at a scan rate of 0.2 mV s⁻¹ of NH₄V₄O₁₀.

To further investigate the electrochemical kinetics of NH₄V₄O₁₀ cathode, sweep voltammetry at various scan rates from 0.1 to 1 mV s⁻¹ was performed (Figure S5a).

Generally, the measured peak current (i) has a relationship with the scan rate (v) which can be described by the following equations²³:

$$i=av^{b}$$

$$log(i)=b \times log(v)+log(a)$$
(2)
(3)

 $log(i)=b \times log(v)+log(a)$

where a and b refer to adjustable parameters, and in general, b-value ranges from 0.5 to 1.0, which can be determined by the plots of log(i) and log(v). The coefficient b of 0.5 indicates an absolute diffusion-controlled process, corresponding to a faradaic insertion/extraction reaction, ²⁴ whereas 1.0 means a complete surface-controlled capacitive process,^{25, 26} The *b*-values of NH₄V₄O₁₀ are calculated to be 0.83, 0.65, 0.83, and 0.72, respectively (Figure S5b). This implies that the electrochemical reactions of $NH_4V_4O_{10}$ are partially controlled by the surface-controlled capacitive behavior.

The pseudocapacitive contributions at different scan rates can be calculated by the equations described as below:

$$i = k_1 v + k_2 v^{1/2} \tag{4}$$

$$i/v^{1/2} = k_1 v^{1/2} + k_2 \tag{5}$$

where k_1 and k_2 are constants for a given potential. Figure S5c displays the calculated contribution ratios of two capacity mechanism at different scan rates ranging from 0.1 to 1.0 mV s⁻¹. As the scan rates increase, the capacitive contribution ratios of NH₄V₄O₁₀ gradually raises from 38.6% to 67.3%, revealing that the NH₄V₄O₁₀ electrode have favorable charge transfer kinetics, which can be responsible for its high-rate capability. A shaded region related to the surface-controlled capacity contributions is illustrated at the scan rate of 0.2 mV s⁻¹, comprising about 46.2% of the total capacity.



Figure S8. The cyclic voltammogram (CV) curves of 0.5 mV s⁻¹ with various discharge/charge cycles at 10 A g^{-1} of $NH_4V_4O_{10}$.



Figure S9. The aqueous ZIBs using $NH_4V_4O_{10}$ cathode successfully power the blue lamp bead for at least 150 min.



Figure S10. Ex situ XRD patterns with various discharge/charge cycles at 100 mA g^{-1} of NH₄V₄O₁₀.



Figure S11. Ex situ XRD patterns with various discharge/charge cycles at 10 A g^{-1} of $NH_4V_4O_{10}$.



Figure S12. Ex situ XRD patterns at different discharge/charge states of NH₄V₃O₈.



Figure S13. Ex situ XRD patterns at different discharge/charge states of (NH₄)₂V₃O₈.



Figure S14. V2p XPS spectra of $NH_4V_4O_{10}$ electrode at different electrochemical stages.



Figure S15. TEM-EDX element mapping images at a full discharge state.

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