Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2021

Supporting Information for

Suppressing Vanadium Dissolution *via* Guest Engineering for Durable Aqueous Zinc-Ion Batteries

Lishang Zhang^a, Jisong Hu^a, Bao Zhang^a, Jia Liu^a Houzhao Wan^{b*}, Ling Miao^{a*} Jianjun Jiang^a

^aSchool of Optical and Electronic Information, Huazhong University of Science and Technology,

Wuhan 430074, China

^b Hubei Key Laboratory of Ferro & Piezoelectric Materials and Devices, Faculty of Physics and

Electronic Science, Hubei University, Wuhan 430062, China.

*Corresponding authors: <u>houzhaow@hubu.edu.cn</u> (H. Wan); <u>miaoling@hust.edu.cn</u> (L. Miao).

Experimental

Synthesis

Synthesis of $(NH_4)_2V_6O_{16} \cdot 1.5H_2O$: In a typical procedure, 0.364 g V₂O₅ was dissolved in 55 mL deionized water, followed by the addition of 5 mL 30% H₂O₂ under continuous magnetic stirring at room temperature for 20 min. Then, 0.48 g urea (CH₄N₂O) and 0.08 g NaOH was added to the above solution and continuously stirred for another 20min before transferred into a 100 mL Teflonlined sealed autoclave and maintained at 180 °C for 32 h. After cooling down to room temperature naturally, the products were collected and washed with deionized water and absolute ethanol for 3 times, respectively. The powders were obtained by freeze-drying, which is designated as NH–V.

Synthesis of $V_2O_5 \cdot 1.5H_2O$: $V_2O_5 \cdot 1.5H_2O$ was synthesized via a similar procedure as above mentioned except for the addition of urea. The final bright yellow compound was obtained and denoted as H–V.

Synthesis of $NH_4V_3O_8$: $NH_4V_3O_8$ cannot be obtained through the direct heat treatment of NH_-V due to the inferior thermal stability of NH_4^+ , the $NH_4V_3O_8$ was synthesized by a method reported elsewhere¹. Typically, 0.468 g commercial NH_4VO_3 powder was dissolved in 50 mL deionized water at 70 °C, followed by adjusting the pH to about 2 with dilute hydrochloric acid. Afterward, the mixture was maintained at 90 °C for 2.5 h in an oil bath. After cooling down to room temperature naturally, the products were collected and washed with deionized water, and the final $NH_4V_3O_8$ was obtained after drying at 60 °C for 24 h in air. The obtained red-brown powder is denoted as N-V. **Characterization**

The phase formation was identified using powder XRD (Philips X'pert PRO; Cu K α , λ = 0.1524 nm). Fourier transform infrared spectroscopy (FTIR) were conducted on a Bruker ALPHAT FTIR spectrometer. The morphologies of as-prepared samples were observed by Field emission scanning electron microscope (ZEISS Gemini SEM 300) and transmission electron microscopy (TEM, Titan G2 60-300 with image corrector). X-ray photoelectron spectroscopy (XPS) spectra were measured on an Escalab 250Xi system equipped with a monochromatic Al K α (1486.6 eV) as an X-ray source.

Electrochemical measurement

The batteries were assembled in the form of 2032 coin cells in the ambient atmosphere and aged overnight before electrochemical data collection. The working electrode slice was prepared by mixing the active material, acetylene black and polyvinylidene fluoride (PVDF) at a weight ratio of 7: 2: 1 with N-Methyl pyrrolidone (NMP) dispersant. The slurry was evenly ground and coated onto a stainless steel mesh (500 mesh) as the current collector, followed by drying in a vacuum oven at 60 °C for 8 h, finally, the working electrode was cut into circular discs of 12 mm in diameter. Notably, the active material mass loading was about 2.4 (\pm 0.2) mg cm⁻² of all electrodes. Zn metal pellet with a diameter of 12 mm was used as the anode, glass fiber membrane with a diameter of 16 mm served as the separator, and 2 M ZnSO₄ aqueous solution was used as the electrolyte. The fabricated cells were tested on a multichannel battery testing system (LAND CT2001A, China) with Galvanostatic charge/discharge and Galvanostatic intermittent titration technique (GITT) measurements (2 min charge/discharge and followed by a relaxation period of 30 min) in the voltage range between 0.2 and 1.7 V *vs.* Zn²⁺/Zn. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were conducted on an electrochemical workstation (CHI760E). All the tests were performed at room temperature.

Calculation methods and models

All calculations were performed by generalized gradient approximation (GGA) within the Perdew-Burke-Ernzerhof (PBE) exchange-correlation implemented in the Vienna ab Initio Simulation Package (VASP)^{2,3}. The projector augmented wave (PAW) method was used to describe the interaction between core electrons and valence electrons^{4,5}. The valence configurations include 1s1 for H, 2s22p3 for N, 2s22p4 for O, 3s1 for Na and 3p63d44s1 for V. A cutoff energy of 400 eV was set for planewave function. The DFT+U formalism of Anisimov et al. was employed to account for strong on-site Coulombic interactions of the V 3d-electrons, with a specific on-site potential of U = 3.25 eV^{6,7}. The lattice constants and atomic positions were both fully relaxed until a maximum energy difference and residual force on atoms converge were reached at 10–4 eV and 0.05 eV/Å, respectively. A Monkhorst-Pack grid of $2 \times 7 \times 6$ for V_2O_5 , $2 \times 7 \times 2$ for V_2O_5 ·1.5H₂O, $3 \times 5 \times 3$ for NH₄V₃O₈ and $3 \times 9 \times 2$ for (NH₄)₂V₆O₁₆·1.5H₂O were used, respectively. To explicitly account for van der Waals' interactions between layers and structural water, van der waals corrected D2 method of Grimme was used for all calculations⁸. Crystal structure diagrams were drawn with Visualization for Electronical and Structural Analysis (VESTA)⁹.

Equation S1

The current of CV curves obeys an empirical power-law relationship with the scan rate.

$$i = a v^b$$

where i is current, v is scan rate, and a and b are adjustable parameters (b=0.5 indicating a diffusioncontrolled process, and b=1.0 taking a stand of a capacitive storage process)^{10, 11}.

Equation S2

To quantify the exact ratio of capacitive contribution, equation

$$i(V) = k_1 v + k_2 v^{1/2}$$
(2)

(1)

is used. According to the equation, the current (i) at a fixed potential (V) is divided into two parts: the capacitive contributions effect $(k_1 v)$ and diffusion-controlled effect $(k_2 v^{1/2})$, k_1 and k_2 value can be derived from the $i/v^{1/2} vs. v^{1/2}$ plot^{12, 13}.

Equation S3

The D_{Zn} can be calculated based on the simplified equation

$$D_{Zn^{2+}} = \frac{4}{\pi \tau} \left(\frac{n_m V_m}{S} \right)^2 \left(\frac{\Delta E_s}{\Delta E_\tau} \right)^2$$
(3)

where τ is the duration time of the current pulse, nm is the mole number of the active material, Vm is the molecular volume (cm³ mol⁻¹), S is the contact area between electrode and electrolyte, Δ Es is related to the change of steady-state voltage for the corresponding step, and Δ E τ is the voltage change during one charge/discharge pulse^{14, 15}.



Fig. S1 Side views of optimized structures of (a) V_2O_5 , (b) H–V and (c) N–V.

	<i>a</i> /Å	b /Å	c /Å	lpha /°	β /°	γ /°
V_2O_5	11.60	3.55	4.12	90.00	90.00	90.00
V ₂ O ₅ @ 1.5H ₂ O	11.59	3.64	11.22	90.52	90.80	89.86
$NH_4V_3O_8$	8.24	4.91	7.35	83.96	90.00	90.00
$(NH_4)_2V_6O_{16}$ @ $1.5H_2$	11.92	3.55	8.34	91.06	99.11	89.78
0						

Table S1. The optimized lattice parameters of V_2O_5 , H–V, N–V and NH–V.

Table S2. Calculated interlayer binding energies of V_2O_5 , H–V, N–V and NH–V.

	Interlayer binding energy/ meV Å-2
V_2O_5	17.44
V ₂ O ₅ @ 1.5H ₂ O	21.15
NH ₄ V ₃ O ₈	158.43
(NH ₄) ₂ V ₆ O ₁₆ @ 1.5H ₂	208.01
0	



Fig. S2 FTIR curve of NH-V sample.



Fig. S3 XRD spectrums of different samples (a) V₂O₅, (b) H–V and (c) N–V.



Fig. S4 Voltage variation of the four cathodes during OCV-3Days test



Fig. S5 Voltage *vs.* time curves of (a) V_2O_5 , (b) H–V, (c) N–V and (d) NH–V of the 3 days OCV rest. Dis/charge profiles of (e) H–V and (f) N–V before/after 3 days OCV rest.

Sample	Capacity loss per	Recharge capacity	Capacity loss caused	
	GCD cycle (structure	loss after OCV-	by the vanadium	
	deformation)	3days	dissolution after	
			OCV-3days	
V_2O_5	5.68%	25%	19.3%	
V ₂ O ₅ @ 1.5H ₂ O	2.47%	5.9%	3.5%	
NH ₄ V ₃ O ₈	5.53%	12.6%	7.1%	
NH-V	0.49%	1.5%	1.45%	

Table S3 The calculated capacity loss caused by vanadium dissolution after OCV



Fig.S6 (a) CV curves at scan rate ranging from 0.1 to 1 mV s⁻¹ with a voltage window between 0.2 and 1.7 V vs. Zn^{2+}/Zn . (b) Plots of log (i) vs. log (v) at specific peak currents extracted from the CV scans. (c) Capacitive contribution to the total charge storage at 1 mV s⁻¹. (d) Contribution ratio of the capacitive-controlled and diffusion-controlled capacities at various scan rates.



Fig. S7 (a) GITT curves at a current density of 0.5 A g⁻¹, (b) Schematic illustration of selected steps of the GITT curve during charging, (c) The linear relationship between ΔE_{τ} and $\tau^{1/2}$, and (d) Zn²⁺ diffusivity *vs*. the de/intercalation state.



Fig. S8 (a) XPS spectra of cathode in origin state, 1st discharged to 0.2V and 1st recharged to 1.7V.



Fig. S9 SEM image (a) and EDS mapping images (b-d) of the 1st discharged NH–V cathode.



Fig. S10 SEM image (a) and EDS mapping images (b-d) of the 1st recharged NH–V cathode.

Reference

- X. Wang, B. Xi, Z. Feng, W. Chen, H. Li, Y. Jia, J. Feng, Y. Qian and S. Xiong, *Journal of Materials Chemistry A*, 2019, 7, 19130-19139.
- 2. J. P. Perdew, K. Burke and M. Ernzerhof, *Physical Review Letters*, 1997, 78, 1396-1396.
- 3. Kresse and Furthmuller, *Physical review. B, Condensed matter*, 1996, **54**, 11169-11186.
- 4. G. Kresse and D. Joubert, *Physical Review B*, 1999, **59**, 1758-1775.
- 5. Blochl, *Physical review. B, Condensed matter*, 1994, **50**, 17953-17979.
- 6. V. I. Anisimov, F. Aryasetiawan and A. I. Lichtenstein, *Journal of Physics: Condensed Matter*, 1997, **9**, 767-808.
- 7. T. Wu, K. Zhu, C. Qin and K. Huang, *Journal of Materials Chemistry A*, 2019, 7, 5612-5620.
- 8. S. Grimme, Journal of Computational Chemistry, 2006, 27, 1787-1799.
- 9. K. Momma and F. Izumi, *Journal of Applied Crystallography*, 2008, 41, 653-658.
- 10. Y. Ruan, C. Wang and J. Jiang, *Journal of Materials Chemistry A*, 2016, 4, 14509-14538.
- V. Augustyn, J. Come, M. A. Lowe, J. W. Kim, P.-L. Taberna, S. H. Tolbert, H. D. Abruña, P. Simon and B. Dunn, *Nature Materials*, 2013, 12, 518.
- H.-S. Kim, J. B. Cook, H. Lin, Jesse S. Ko, Sarah H. Tolbert, V. Ozolins and B. Dunn, *Nature Materials*, 2016, 16, 454.
- 13. T. Brezesinski, J. Wang, S. H. Tolbert and B. Dunn, *Nature Materials*, 2010, 9, 146.
- 14. T. Sasaki, Y. Ukyo and P. Novák, *Nature Materials*, 2013, 12, 569.
- 15. W. Weppner and R. A. Huggins, *Journal of The Electrochemical Society*, 1977, **124**, 1569-1578.