

Supporting information

Multi-Functional Potassium Ion Assists Ammonium Vanadium Oxide Cathode for High-Performance Aqueous Zinc-Ion Batteries

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Material characterization of KNVO

The crystallographic structure of the as-prepared KNVO product was analyzed using an X-ray diffractometer (XRD, SmartLab9KW). Scanning electron microscopy (SEM, JEOL JSM-7500F) and high-resolution transmission electron microscopy (HRTEM, FEITalosF200XG2) were applied to acquire the microcosmic crystal morphologies and sizes. X-ray photoelectron spectroscopy (XPS, PHI5000VersaProbeESCALAB250xi) was used to characterize the valence of V, N, O in the sample and the intermediates at various charge/discharge states. The IR spectra of KNVO were obtained by attenuated total reflection-Fourier transform infrared (ATR-FTIR, Bruker Tensor II Sample Compartment RTDLaTGS) spectroscopy.

Electrochemical tests and mechanism study of KNVO

The KNVO electrodes were prepared by mixing KNVO, Ketjen black (KB), and polytetrafluoroethylene (PTFE) at an appropriate weight ratio of 7:2:1, and pressed onto stainless-steel mesh. Then the electrode films were dried at 80 °C for 12 h under vacuum. The KNVO mass loading was 1-2 mg cm⁻². For the fabrication of ZIBs, zinc metal as the anode, 3 mol L⁻¹ Zn(CF₃SO₃)₂ was used as the electrolyte, stainless-steel mesh as the current collector and glass fiber as the separator. A 2032-type coin cell was assembled under an air atmosphere to perform the galvanostatic charge/discharge tests on a LAND battery testing system (LAND CT2001A). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out on an electrochemical workstation (CHI660E) in the voltage range of 0.2-1.6 V (*vs.* Zn²⁺/Zn). The current density and specific capacity were based on the mass of KNVO in each electrode. The test used for ex-situ FTIR, SEM, TEM, and XPS are all tested at the current density of 0.2 A g⁻¹ over the voltage range of 0.2–1.6 V during the second charge and discharge cycle.

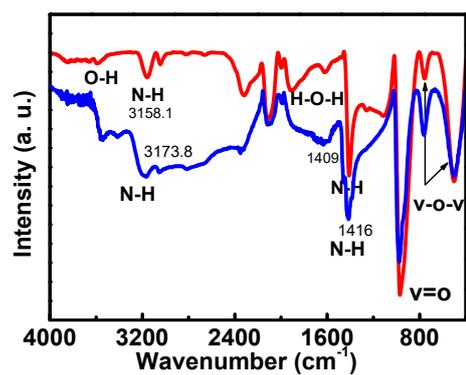


Figure S1. FTIR spectra of KNVO (red) and NVO (blue), respectively.

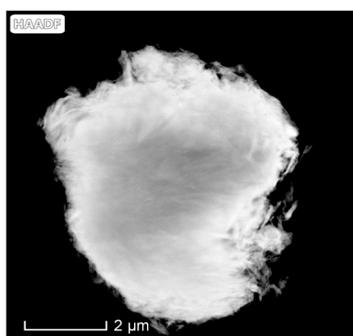


Figure S2. HAADF of KNVO.

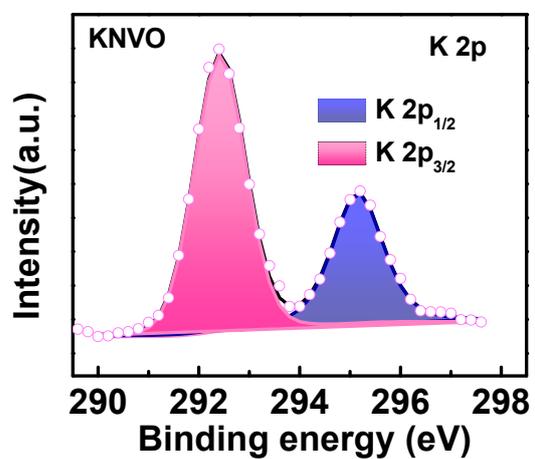


Figure S3. K_{1s} XPS spectrum of KNVO.

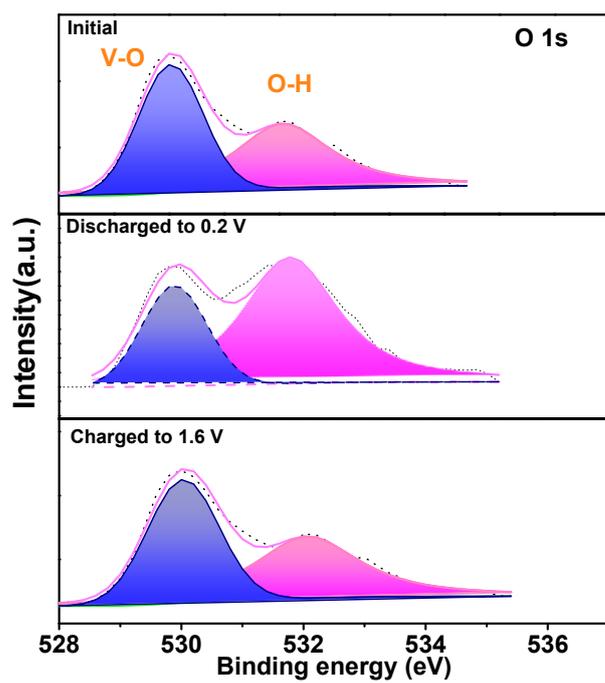


Figure S4. O 1s XPS spectrum of KNVO in different states.

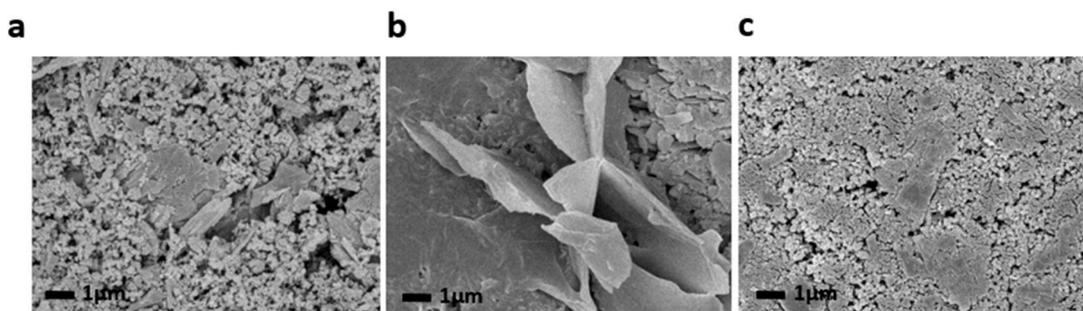


Figure S5. SEM image of KNVO in initial (S4a), discharged (S4b) and charged state (S4c), respectively.

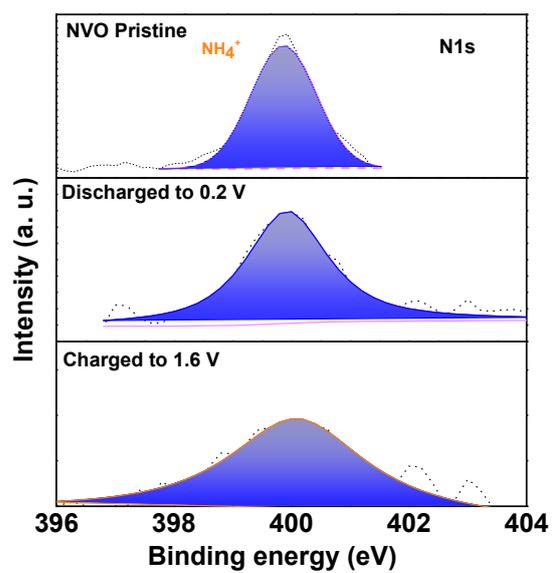


Figure S6. N 1s XPS spectrum of NVO in different states.

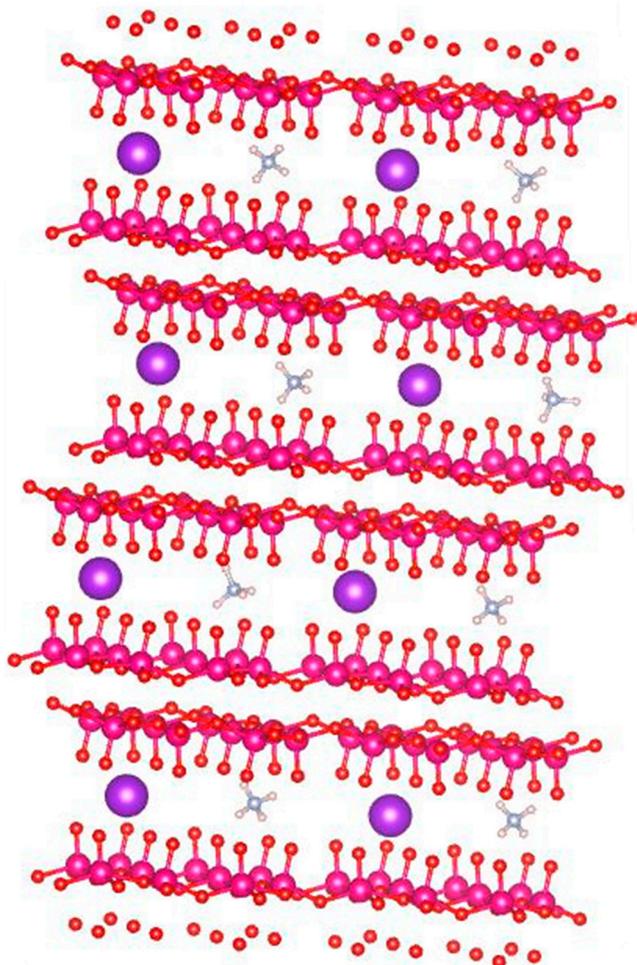


Figure S7. Crystal structural illustration of KNVO.

Table S1. The comparisons of our work and previous reports.

Cathode	Electrolyte	Voltage window(V)	Specific capacity (mA h g ⁻¹)	Cycling performance	Ref
(NH ₄) _x V ₂ O ₅	3M Zn(CF ₃ SO ₃) ₂	0.3-1.6	382/0.1 A g ⁻¹	50 cycles at 0.1 A g ⁻¹ , 59.0%	[1]
(NH ₄) _{0.38} V ₂ O ₅	3M Zn(CF ₃ SO ₃) ₂	0.3-1.6	500/0.1 A g ⁻¹	200 cycles at 0.2 A g ⁻¹ , 41.0%	[2]
NH ₄ V ₄ O ₁₀	3M Zn(CF ₃ SO ₃) ₂	0.1-1.6	457/0.1 A g ⁻¹	100 cycles at 0.2 A g ⁻¹ , 25.0%	[3]
K _{0.23} V ₂ O ₅	3M Zn(CF ₃ SO ₃) ₂	0.2-1.6	284/0.1A g ⁻¹	500 cycles at 2 A g ⁻¹ , 92.8%	[4]
K _{1.1} V ₃ O ₈	3M Zn(CF ₃ SO ₃) ₂	0.3-1.4	386/0.1 A g ⁻¹	2000 cycles at 5 A g ⁻¹ , 97.0%	[5]
KMgV ₂ O ₅	3M Zn(CF ₃ SO ₃) ₂	0.5-1.4	420/0.1 A g ⁻¹	2000 cycles at 5 A g ⁻¹ , 95.0%	[6]
KNVO	3M Zn(CF ₃ SO ₃) ₂	0.2-1.6	432/0.4 A g ⁻¹	2000 cycles at 5 A g ⁻¹ , 94.2%	This Work

Table S2. Element distribution and atomic percentage of KNVO and NVO in discharged and charged state, respectively.

Atomic Percentage (%)	V	O	N	K	Zn
KNVO Discharge	6.21	17.47	1.11	0.35	15.08
KNVO Charge	6.36	16.30	1.26	0.45	1.11

References

- Xu, L.; Zhang, Y.; Zheng, J.; Jiang, H.; Hu, T.; Meng, C., Ammonium Ion Intercalated Hydrated Vanadium Pentoxide for Advanced Aqueous Rechargeable Zn-Ion Batteries. *Mater. Today Energy*. **2020**, *18*, 100509.
- Jiang, Y.; Wu, Z.; Ye, F.; Pang, R.; Zhang, L.; Liu, Q.; Chang, X.; Sun, S.; Sun, Z.; Hu, L., Spontaneous Knitting Behavior of 6.7-nm Thin (NH₄)_{0.38}V₂O₅ Nano-Ribbons for Binder-Free Zinc-Ion Batteries. *Energy Storage Mater.*, **2021**, *42*, 286-294.
- Tang, B.; Zhou, J.; Fang, G.; Liu, F.; Zhu, C.; Wang, C.; Pan, A.; Liang, S., Engineering the Interplanar Spacing of Ammonium Vanadates as a High-performance Aqueous Zinc-Ion Battery Cathode. *J. Mater. Chem. A.*, **2019**, *7*, 3, 940-945.
- Zhang, W.; Tang, C.; Lan, B.; Chen, L.; Tang, W.; Zuo, C.; Dong, S.; An, Q.; Luo, P., K_{0.23}V₂O₅ as A Promising Cathode Material for Rechargeable Aqueous Zinc Ion Batteries with Excellent Performance. *J. Alloys Compd.* **2020**, *819*, 152971.
- Zhang, G.; Wu, T.; Zhou, H.; Jin, H.; Liu, K.; Luo, Y.; Jiang, H.; Huang, K.; Huang, L.; Zhou, J., Rich Alkali Ions Preintercalated Vanadium Oxides for Durable and Fast Zinc-Ion Storage. *ACS Energy Lett.* **2021**, *6*, 2111-2120.

- Feng, Z.; Zhang, Y.; Sun, J.; Liu, Y.; Jiang, H.; Cui, M.; Hu, T.; Meng, C., Dual Ions Enable Vanadium Oxide Hydration with Superior Zn²⁺ Storage for Aqueous Zinc-Ion Batteries. *Chem. Eng. J.* **2022**, *433*, 133795.