

Electronic Supplementary Information

Engineering crystal water in potassium ammonium vanadate for fast Zn-ion storage

Experimental section

Synthesis of potassium ammonium vanadate (KNVO) nanoribbons: All chemical reagents were purchased from Kelong Chemical Reagent Factory (Chengdu, China) and used without any further purification. Firstly, 20 mmol of NH_4VO_3 and $\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ were dissolved in deionized water (150 ml), and then 30 mmol of $\text{K}_2\text{S}_2\text{O}_8$ was added to the above mixture under magnetic stirring for 10 min. After that, the mixture was transferred into a 200 ml Teflon-lined autoclave and kept at 180 °C for 3 hours. Using vacuum filtration, the brick-red precipitate was collected, rinsed with deionized water and anhydrous ethanol, and dried at 60 °C. The as-obtained KNVO nanoribbons were sintered at 200 °C, 300 °C, 400 °C, and 550 °C, respectively, for 3 hours in the atmosphere to obtain the final products.

Material characterization: X-ray diffraction (XRD) data of the samples were measured on an Empyrean X-ray diffractometer (Cu $\text{K}\alpha$ radiation, 40 kV and 40 mA). High-resolution transmission electron microscope (HRTEM) images were acquired by transmission electron microscope (Talos F200S G2, 200 kV). Vacancy data were determined by electron paramagnetic resonance spectrometry (Bruker A300). X-ray photoelectron spectroscopy (XPS) data were acquired by

a Thermo Fisher Escalab Xi+ instrument. Thermogravimetric curves were obtained utilizing the thermal gravimetric analyzer (TGA).

Electrochemical characterization: Electrochemical characterization was carried out in a coin-type cell (CR2032). The working electrodes were prepared as follows: KNVO nanoribbons were thoroughly mixed with carbon black (Super P) and polytetrafluoroethylene (PTFE) in a mass ratio of 70:20:10 in the presence of ethanol. After drying at 60 °C for 2h, the mixture was pressed into films and cut into discs. The electronic balance (Sartorius BSA124S) was used to measure the mass of the cathode. KNVO discs with a mass loading of 3-8 mg cm⁻² were selected as the cathode, 80 μm thick zinc foils as the anode, and 3 M zinc trifluoromethanesulfonate (Zn(OTF)₂) as the electrolyte to assemble the button cell. The LANHE battery tester (Wuhan, China) was used for charge and discharge (0.2-1.6 V vs. Zn/Zn²⁺) tests at room temperature. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were carried out using a CorrTest (CS310H) electrochemical workstation in the frequency range of 10⁵ and 0.01 Hz. It is worth noting that all electrochemical tests were preceded by 2 hours resting process for all cells. The apparent chemical diffusion coefficients of the materials were determined during the galvanostatic intermittent titration technique (GITT).

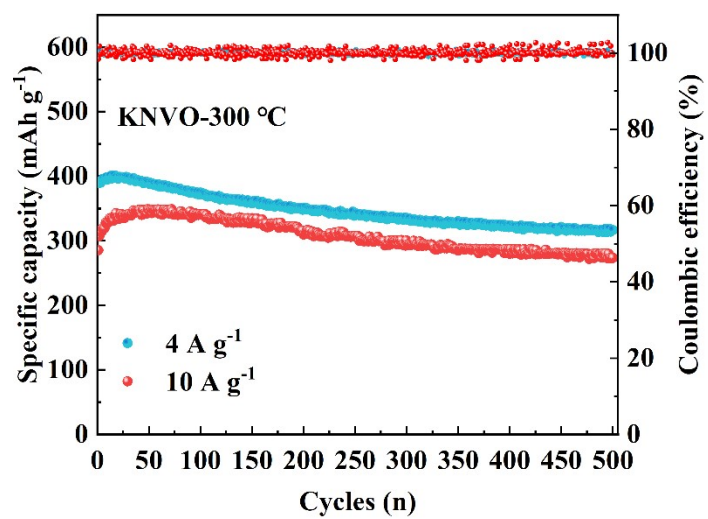


Fig. S1 Cycling performance at 4 and 10 A g⁻¹.

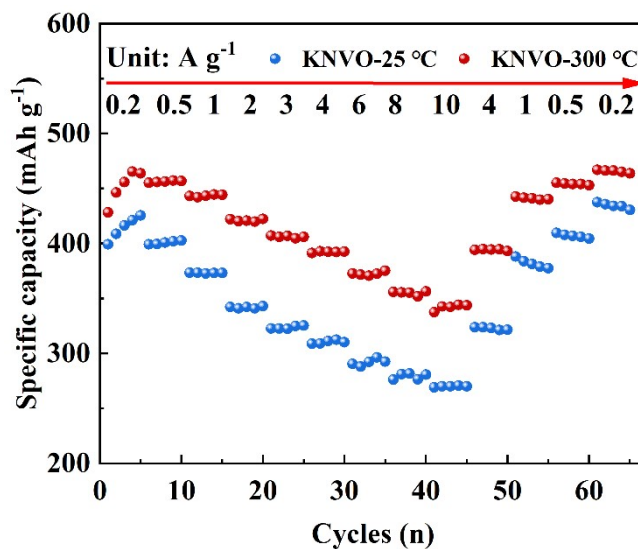


Fig. S2 Discharge capacity at different current densities in aqueous electrolytes after normalization, where the mass of crystal waters and the removed ammonium before 300 °C in the KNVO-25 °C does not count.

Note S1. We have normalized the KNVO-25 °C specific capacity by combining the TGA test data in Fig. 1b (as shown in Fig. S2), where the mass of crystal waters and the removed ammonium before 300 °C in the KNVO-25 °C does not count. The improved electrochemical performance of the annealed KNVO-300 °C still can be identified.

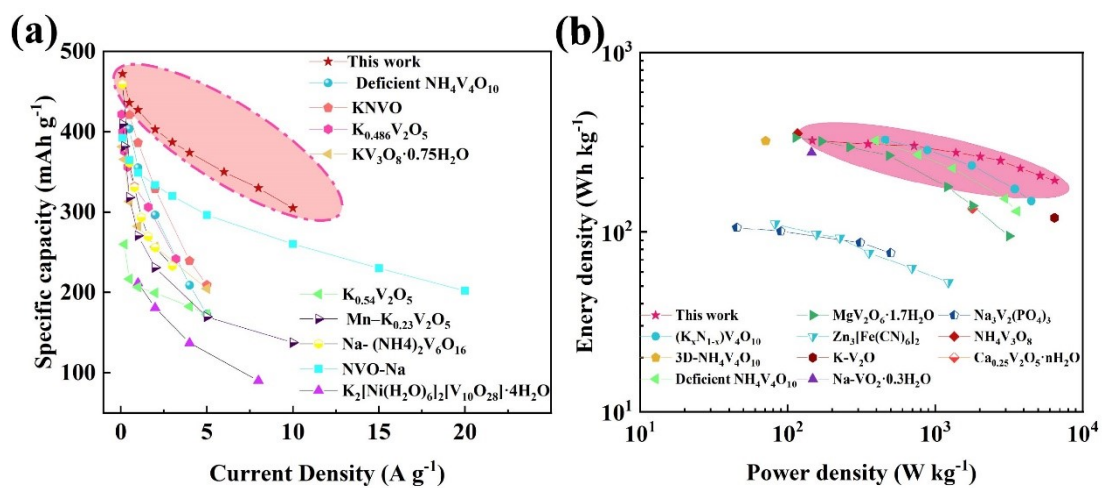


Fig. S3 (a) Comparison of electrochemical performance of cathode materials between this work and other previous reports.¹⁻⁹ (b) Ragone plot of KNVO samples compared to the previously reported performance of AZIBs cathode materials.^{1, 2, 7-11}

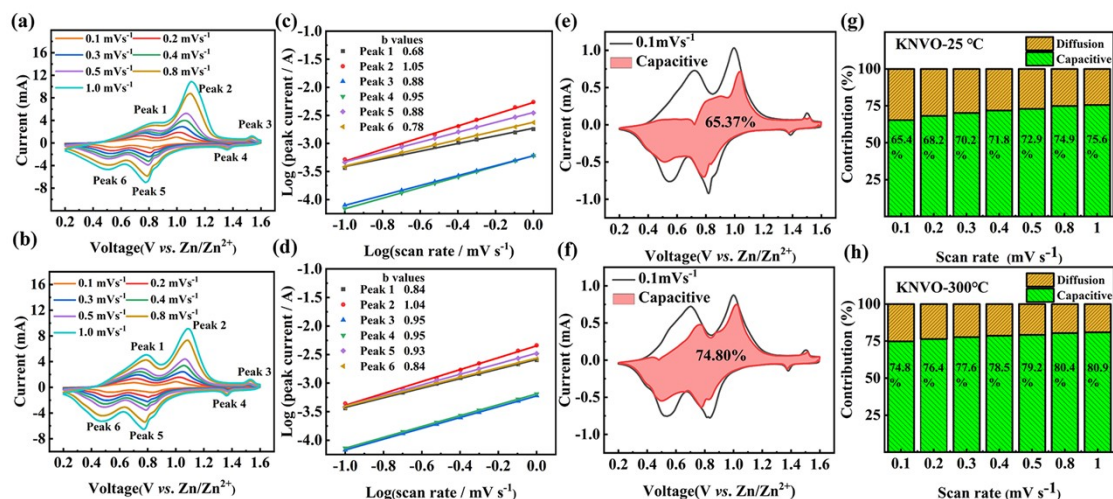


Fig. S4 CV curves at different current densities for (a) KNVO-25 °C and (b) KNVO-300 °C. The plot of peak current versus scan rate for the CV curves of (c) KNVO-25 °C and (d) KNVO-300 °C. The b values are the slope values of the fitted curves. CV curves of pseudocapacitance fraction calculated for (e) KNVO-25 °C and (f) KNVO-300 °C at a scan rate of 0.1 mV s⁻¹. Capacitance contribution of (g) KNVO-25 °C and (h) KNVO-300 °C at different scan rates.

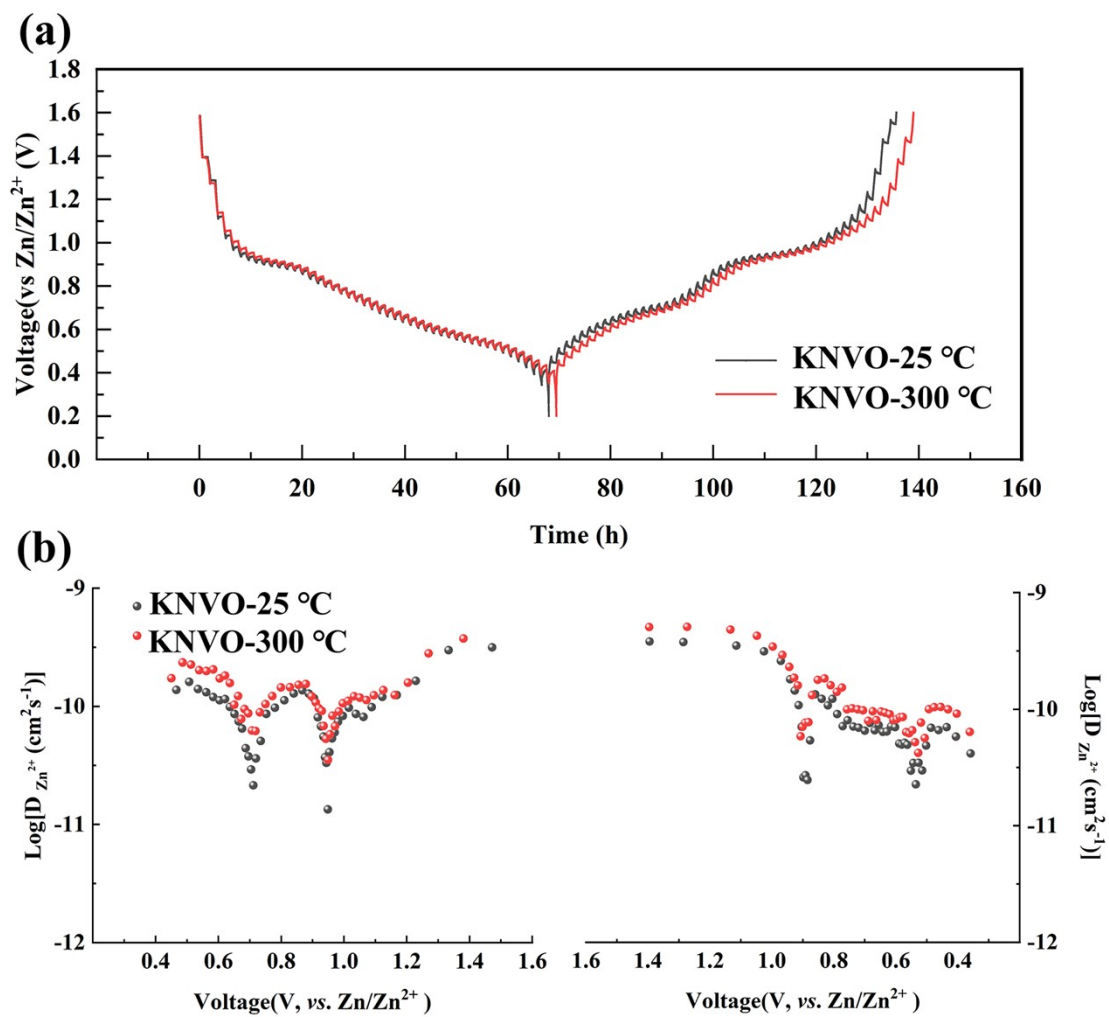
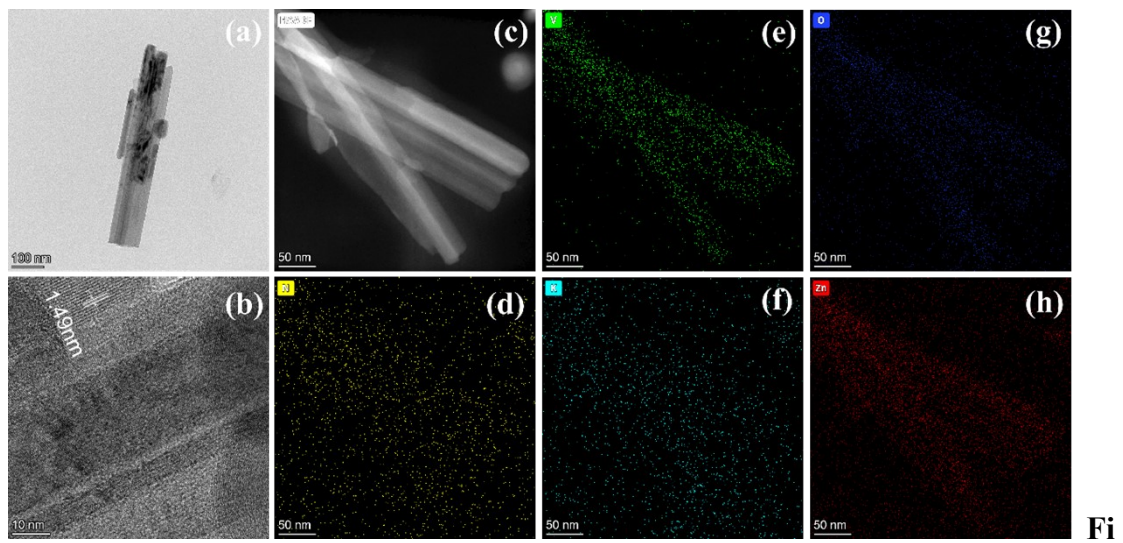


Fig. S5 (a) GITT charge and discharge curves. (b) Ion diffusion coefficients corresponding to KNVO-25 °C and KNVO-300 °C.



g. S6 Structural and morphological of KNVO-25 °C charged to 1.6 V.

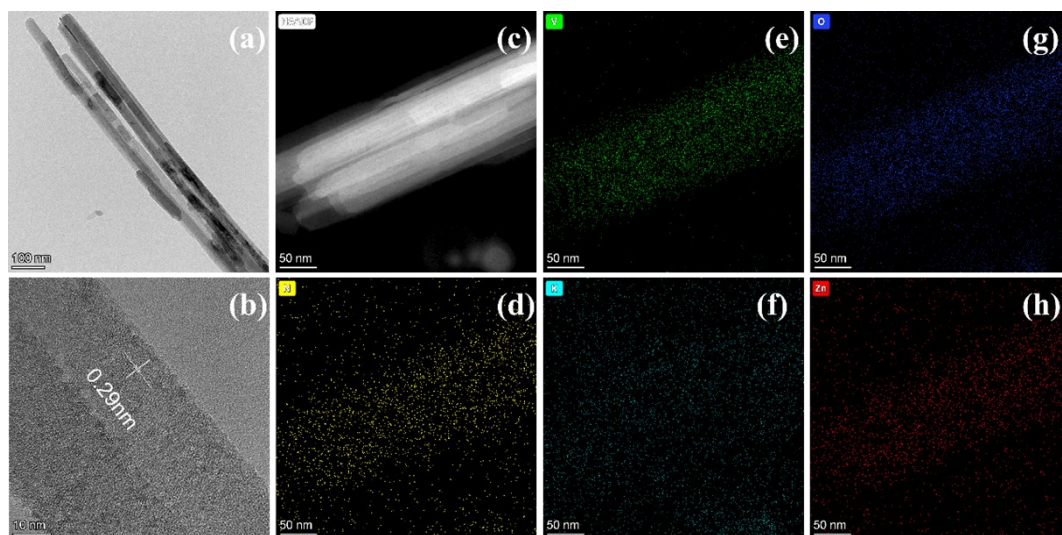


Fig. S7 Structural and morphological of KNVO-300 °C charged to 1.6 V.

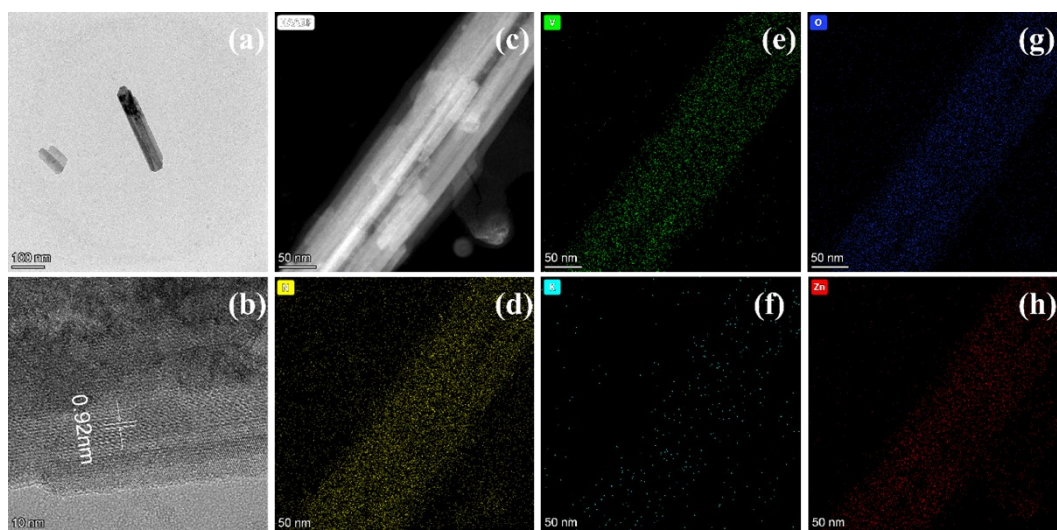


Fig. S8 Structural and morphological of KNVO-300 °C discharged to 0.2 V.

Based on the data from the GITT test, the ionic diffusion coefficient (D) inside the battery can be calculated with the following formula¹²:

$$D_{zn} = \frac{4}{\pi\tau} \left(\frac{m_B V_M}{M_B A} \right)^2 \left(\frac{\Delta E_s}{\Delta E_\tau} \right)^2 \quad (1)$$

where τ represents the duration of the constant current (s), m_B is the mass of the active material, V_M is the molar volume ($\text{cm}^3 \text{mol}^{-1}$), M_B is the molar mass, A is the total contact area between the electrode and the electrolyte, ΔE_s represents the voltage difference (V) between the steady-state voltage after the retardation and the previous steady-state voltage, while ΔE_τ represents the value of the voltage change (V) due to the duration of the constant current.

Supplementary References

1. Q. Zong, W. Du, C. Liu, H. Yang, Q. Zhang, Z. Zhou, M. Atif, M. Alsalhi and G. Cao, *Nanomicro Lett*, 2021, **13**, 116.
2. Q. Zong, Q. Wang, C. Liu, D. Tao, J. Wang, J. Zhang, H. Du, J. Chen, Q. Zhang and G. Cao, *ACS Nano*, 2022, **16**, 4588-4598.
3. P. Wu, T. Xu, Y. Chen, Q. Yang, J. Wang, Y.-N. Liu and Y. Li, *ACS Applied Energy Materials*, 2022, **5**, 1656-1661.
4. X. Wang, A. Naveed, T. Zeng, T. Wan, H. Zhang, Y. Zhou, A. Dou, M. Su, Y. Liu and D. Chu, *Chem Eng J*, 2022, **446**, 137090.
5. Z. Shi, W. Xu, Q. Ru, M. Zheng, J. Zhang, F. Chi-Chun Ling and L. Wei, *J Power Sources*, 2021, **516**, 230699.
6. F. Wan, S. Huang, H. Cao and Z. Niu, *ACS Nano*, 2020, **14**, 6752-6760.
7. X. Wang, Z. Zhang, S. Xiong, F. Tian, Z. Feng, Y. Jia, J. Feng and B. Xi, *Small*, 2021, **17**, e2100318.
8. C. Xia, J. Guo, P. Li, X. Zhang and H. N. Alshareef, *Angew Chem Int Ed Engl*, 2018, **57**, 3943-3948.
9. Q. Li, X. Rui, D. Chen, Y. Feng, N. Xiao, L. Gan, Q. Zhang, Y. Yu and S. Huang, *Nanomicro Lett*, 2020, **12**, 67.
10. H. Jiang, Y. Zhang, Z. Pan, L. Xu, J. Zheng, Z. Gao, T. Hu, C. Meng and J. Wang, *Materials Chemistry Frontiers*, 2020, **4**, 1434-1443.
11. G. Li, Z. Yang, Y. Jiang, C. Jin, W. Huang, X. Ding and Y. Huang, *Nano Energy*, 2016, **25**, 211-217.
12. F. Liu, Z. Chen, G. Fang, Z. Wang, Y. Cai, B. Tang, J. Zhou and S. Liang, *Nanomicro Lett*, 2019,

11, 25.