Electronic supplementary information

A high-power and long-life aqueous rechargeable Zn-ion battery based on hierarchically porous sodium vanadate

Experimental Procedures

Synthesis of NVO nanowires: All chemical reagents were purchased from Aladdin Reagent Company (Shanghai, China) and used without any further purification. The synthetic procedure was conducted as follows: first, NaVO₃ (1.84 g) and 15 mmol of H₂C₂O₄·H₂O (1.89 g) were dissolved in deionized water (50.00 g), and then Na₂S₂O₈ (7.50 g)was added into the above mixture under magnetic stirring for 30 min. Then, the mixture was transferred into a 100 ml Teflon-lined autoclave and kept at 180 °C for 180 min. The precipitate was collected by filtration, washed with water and ethanol, and dried at 80 °C.

Materials characterization: X-ray diffraction (XRD) patterns of the samples were recorded on an Empyrean X-ray diffractometer using filtered Cu K α radiation at 40 kV and 40 mA. The morphologies of the samples were characterized by SEM using a field emission scanning electron microscope (FE-SEM, JEOL, JSM-7500F). Transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) images were obtained using a JEOL JEM-2100 field emission transmission electron microscope operating at 200 kV. X-ray photoelectron spectroscopy (XPS) experiments were performed in a Kratos XSAM 800 instrument. The N₂ adsorption/desorption isotherms were measured on Micromeritics ASAP 2460 at liquid nitrogen temperature (77 K). The Barrett–Joyner–Halenda (BJH) model was employed to compute pore size distribution curves from the desorption branches.

Electrochemical measurements: The electrochemical tests were carried out in coin-type cells (CR2032). The working electrodes were prepared as follows: the as-prepared NVO was mixed with carbon black (Super P) and polymer binder (polytetrafluoroethylene, PTFE) in a weight ratio of 70:20:10 with the help of ethanol. After drying, the mixture was pressed into a film and cut into disk. The mass of cathode was measured by an electronic balance (Sartorius BSA124S, 0.1mg resolution). Several films were weighed and then used as cathode. The NVO mass loading is 3-6 mg cm⁻². The coin cells were assembled in open air atmosphere using an NVO electrode as the cathode, a glass fiber (GF/D, Whatman) as the separator and a zinc foil (Alfa Aesar) as the anode. $3M Zn(OTF)_2$ in H₂O was used as the electrolyte without oxygen removal. All of the cells were aged for 2 h before any electrochemical processes. The charge-discharge (0.2-1. 6 V vs. Zn/Zn^{2+}) tests were conducted on a LANHE battery tester (Wuhan, China) at room temperature. The cyclic voltammetry (CV) and electrochemical impedance spectra (EIS) tests in a frequency range between 10⁵ and 0.01 Hz were carried out using a CorrTest (CS310H) electrochemical work station.

Detail information about GITT test for the apparent chemical diffusion coefficients:

For GITT analyses, the cells were cycled in the potential window of 0.2-1.6 V vs. Zn/Zn²⁺ at 20 mA g⁻¹. The duration time for each applied galvanostatic current was 30 min and then the cell was relaxed for 1 hour.

The apparent chemical diffusion coefficients values can be calculated according to the following equation:

$$D_{GITT} = \frac{4}{\pi\tau} \left(\frac{m_B V_M}{M_B S}\right)^2 \left(\frac{\Delta E_s}{\Delta E_\tau}\right)^2$$

 $\tau \ll \frac{L^2}{D_{GITT}}, \text{ where } m_B, V_M \text{ and } M_B \text{ are the mass, molar volume and molecular}$ weight of the NVO, respectively; τ is the time for an applied galvanostatic current; S is the contacting area of the electrode; ΔE_s and ΔE_{τ} are the quasi-equilibrium potential and the change of cell voltage during the galvanostatic current pulse, respectively. *L* is the thickness of electrode.





Figure S1. SEM image and EDS profile of pristine NVO.



Figure S2. TGA profile of pristine NVO from 100 to 600 $\,^\circ\!\!\mathbb{C}$



Figure S3. a) N_2 adsorption–desorption isotherms (BET surface area is 10.77 m²/g) and b) BJH pore size distribution curve of NVO. Based on Barrett–Joyner–Halenda plots, the average pore size of the cathode material is about 21.0 nm.



Figure S4. The normalized contribution ratio of the first (high) plateau and the second (low) plateau in capacities at different scan rates.



Figure S5. (a) The corresponding current response with voltage of NVO electrodes at a scan rate of 0.1 mV s⁻¹ (the contribution ratio is about 53.9%). Capacitive current (shaded blue region) was calculated using $i(V) = k_1 v + k_2 v^{1/2}$. (b) The normalized contribution ratio of diffusion controlled and pseudocapacitive capacities at different scan rates.



Figure S6. XRD pattern of the cycled NVO at 4 A g⁻¹. The crystallite size has been estimated by the broadening of the diffraction peak around 50° using the Scherrer formula. This estimated value is 10.0 nm, which show the crystal size of NVO is slightly decreased after repeated charge-discharge processes.



Figure S7. Storage performance of aqueous Zn-ion cell based on Zn/NVO. (a) charge-discharge and OCV test curves of Zn-ion cell based on Zn/NVO. (b) charge curve of Zn-ion cell based on Zn/NVO between 0.2-1.6 V vs. Zn/Zn^{2+} at the current of 0.1 A g⁻¹; (c) open-circuit voltage (OCV) test of Zn-ion cell based on Zn/NVO for 24 h; (d) discharge curve of Zn-ion cell based on Zn/NVO between 0.2-1.6 V vs. Zn/Zn^{2+} at the current of 1 A g⁻¹. The current density (A g⁻¹) and the capacity (mAh g⁻¹) is calculated based on the weight of cathode material.

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Materials	Electrolyte	voltage window	Capacity	Cycling performance	Reference
Zn _{0.25} V ₂ O ₅ ·n H ₂ O	1M ZnSO ₄	0.5-1.4 V	300, 260 and 223 mA h g ⁻¹ at 0.05, 0.3 and 4.5 A g ⁻¹ , respectively	189 mA h g 1 after 1000 cycles at 4.5 A g 1	1
Ca _{0.25} V ₂ O ₅ ·n H ₂ O	1M ZnSO4	0.6-1.6 V	340 and 289 mA h g ⁻¹ at 0.05 and 0.25 A g ⁻¹ , respectively	72 mA h g-1after 5000 cycles at 20 A g-1	2
Na _{0.33} V ₂ O ₅	3M Zn(OTF) ₂	0.2-1.6 V	253.7, 173.4, 137.5 and 96.4 mA h g ⁻¹ at 0.2, 0.5, 1 and 2 A g ⁻¹ , respectively	128 mA h g ⁻¹ after 1000 cycles at 1 A g ⁻¹	3
NaV₃O ₈ ·1.5H₂ O	1M Na ₂ SO ₄ + 1M ZnSO ₄	0.3-1.25 V	380, 250 and 165 mA h g ⁻¹ at 0.05, 1 and 4 A g ⁻¹ , respectively	221 mA h g ⁻¹ after 100 cycles at 1 A g ⁻¹ 135 mA h g ⁻¹ after 1000 cycles at 4 A g ⁻¹	4
Na ₂ V ₆ O ₁₆ ·1.63 H ₂ O	1M ZnSO4	0.4-1.4 V	352, 261, and 219 mA h g ⁻¹ at 0.05, 0.5 and 1 A g ⁻¹ , respectively	228 mA h g ⁻¹ after 300 cycles at 5.4 A g ⁻¹ 182 mA h g ⁻¹ after 500 cycles at 9.0 A g ⁻¹ 108 mA h g ⁻¹ after 1000 cycles at 14.4 A g ⁻¹	5
VS ₂	1M ZnSO ₄	0.4-1.0 V	190.3, 136.8 and 121.5 mA h g ⁻¹ at 0.05, 0.5 and 1 A g ⁻¹ , respectively	110.9 mA h g $^{-1}$ after 200 cycles at 0.5 A g $^{-1}$	6
Zn ₂ (OH)VO ₄	2M ZnSO ₄	0.4-1.5 V	204, 160 and 101 mA h g ⁻¹ at 0.1, 2 and 10 A g ⁻¹ , respectively	125 mA h g $^{\rm l}$ after 2000 cycles at 4 A g $^{\rm l}$	7
NH4V4O10	2M ZnSO4	0.4-1.4 V	380.3, 361.6 and 252.8 mA h g ⁻¹ at 0.1, 1 and 10 A g ⁻¹ , respectively	125.6 mA h g ⁻¹ after 100 cycles at 0.1 A g ⁻¹ 275 mA h g ⁻¹ after 100 cycles at 1 A g ⁻¹ 255.5 mA h g ⁻¹ after 1000 cycles at 10 A g ⁻¹	8
(NH ₄) ₂ V ₄ O ₉	3M Zn(OTF) ₂	0.3-1.3 V	376, 336 and 259 mA h g ⁻¹ at 0.1, 0.2 and 1 A g ⁻¹ , respectively	328 mA h g ⁻¹ after 100 cycles at 0.1 A g ⁻¹ 125 mA h g ⁻¹ after 2000 cycles at 5 A g ⁻¹	9
MnVO	3M Zn(OTF) ₂	0.2-1.6 V	415, 380, 347, 310, 268 and 214 mA h g ⁻¹ at 0.05, 0.5, 1, 2, 4, and 8 A g ⁻¹ , respectively	260 mA h g ⁻¹ after 2000 cycles at 4 A g ⁻¹	10
NaV ₈ O ₂₀ ·1.85 H ₂ O	3M Zn(OTF)2	0.2-1.6 V	417.5, 376.4, 352.3, 320.3, 295.3, 279.6, 255.7, 241.8 and 234.5 mA h g ⁻¹ at 0.2, 0.5, 1, 2, 3, 4, 6, 8 and 10 A g ⁻¹ , respectively	322.6 mA h g ⁻¹ after 500 cycles at 1 A g ⁻¹ 283.3 mA h g ⁻¹ after 2000 cycles at 4 A g ⁻¹ 255.3 mA h g ⁻¹ after 6000 cycles at 10 A g ⁻¹	This work

 $Zn(OTF)_2$: Zinc trifluoromethanesulfonate



Figure S8. EIS spectra of NVO cathode before and after the initial several cycles with a small current density.

Table S2. Selected parameter values of the equivalent circuit components to a measured impedance spectrum before
and after the initial several cycles with a small current density.

	CPE1-T	CPE1-P	R2	CPE2-T	CPE2-P	R3	Ws-R	Ws-T	Ws-P
Initial	0.038	0.266	1.814	0.023	0.881	737.50	-	-	-
1th	0.00287	0.464	1.569	0.028	0.806	29.33	125.9	34.87	0.834
2nd	0.00362	0.440	1.761	0.038	0.742	10.40	89.9	34.52	0.825
3rd	0.00312	0.466	1.845	0.038	0.742	9.49	86.46	33.25	0.830
10th	0.00237	0.481	2.901	0.043	0.674	7.81	89.61	31.54	0.825
11th	0.00216	0.504	2.773	0.043	0.676	8.37	89.22	31.81	0.826



Figure S9. EIS spectra of NVO cathode at selected depth of discharge state.

Table S3. Selected parameter values of the equivalent circuit components to a measured impedance spectrum at selected depth of discharge state.

	CPE1-T	CPE1-P	R2	CPE2-T	CPE2-P	R3	Ws-R	Ws-T	Ws-P
A	0.0022	0.504	2.773	0.043	0.676	8.37	89.22	31.81	0.826
В	0.0023	0.509	3.083	0.053	0.663	7.78	47.03	34.49	0.832
С	0.0029	0.487	3.515	0.048	0.682	10.91	32.12	33.01	0.852
D	0.0033	0.476	3.738	0.037	0.709	20.63	35.19	35.19	0.842
E	0.0042	0.449	4.030	0.029	0.697	43.26	149.7	39.14	0.822
F	0.0057	0.419	4.475	0.029	0.697	60.87	192.7	36.41	0.842
G	0.0119	0.345	6.741	0.028	0.819	153.2	227.4	30.34	0.867
н	0.0435	0.214	27.17	0.026	0.853	191.5	366.3	29.52	0.877

Supplementary note:

Details of the calculations for energy and power densities of the Zn/NVO battery in Fig. 2e. The energy and power densities of the Zn/NVO battery is based on positive electrodes. The energy densities of the cathode at various current densities are directly obtained from the ratio test. The power densities are calculated using "energy densities" divided into "processing time". For example, the NVO delivered an energy density of 180.9 W h kg⁻¹ at 8 A g⁻¹, and

$$\frac{180.9 W h kg^{-1}}{\frac{109}{3600} h} = 5974.6 W kg^{-1}$$

the process was completed within 109 seconds, and the power density is

the case of 10 A g⁻¹, the power density is 7139 W kg⁻¹.

Supplementary References:

- 1. D. Kundu, B. D. Adams, V. Duffort, S. H. Vajargah and L. F. Nazar, *Nat. Energy*, 2016, **1**, 16119.
- 2. C. Xia, J. Guo, P. Li, X. Zhang and H. N. Alshareef, *Angew. Chem., Int. Ed.*, 2018, **57**, 3943-3948.
- P. He, G. Zhang, X. Liao, M. Yan, X. Xu, Q. An, J. Liu and L. Mai, *Adv. Energy Mater.*, 2018, DOI: 10.1002/aenm.201702463, 1702463.
- 4. F. Wan, L. Zhang, X. Dai, X. Wang, Z. Niu and J. Chen, *Nat. Commun.*, 2018, **9**, 1656.
- 5. V. Soundharrajan, B. Sambandam, S. Kim, M. H. Alfaruqi, D. Y. Putro, J. Jo, S. Kim, V. Mathew, Y.-K. Sun and J. Kim, *Nano Lett.*, 2018, **18**, 2402-2410.
- P. He, M. Y. Yan, G. B. Zhang, R. M. Sun, L. N. Chen, Q. Y. An and L. Q. Mai, *Adv. Energy Mater.*, 2017, 7, 1601920.
- D. Chao, C. Zhu, M. Song, P. Liang, X. Zhang, N. H. Tiep, H. Zhao, J. Wang, R. Wang, H. Zhang and H. J. Fan, *Adv. Mater.*, 2018, **30**, 1803181.
- 8. B. Tang, J. Zhou, G. Fang, F. Liu, C. Zhu, C. Wang, A. Pan and S. Liang, *J. Mater. Chem. A*, 2019, **7**, 940-945.
- 9. Y. Zhang, H. Jiang, L. Xu, Z. Gao and C. Meng, ACS Applied Energy Materials, 2019, **2**, 7861-7869.
- Liu, Chaofeng; Neale, Zachary; Zheng, Jiqi; Jia, Xiaoxiao; Huang, Juanjuan; Yan, Mengyu; Tian, Meng; Wang, Mingshan; Yang, Jihui; Cao, Guozhong, *Energy & Environmental Science*, 2019, 12 (7), 2273-2285.