Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Porous Hydrated Ammonium Vanadate as Novel Cathode for Aqueous Rechargeable Zn-Ion Batteries

Experimental Procedures

Synthesis of AVO nanorods: 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, 10 mmol of NH_4VO_3 and 15 mmol of $H_2C_2O_4$ were dissolved in 50 ml of deionized water, and then 31.5 mmols of $(NH_4)_2S_2O_8$ 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 ℃ for 180 min. The precipitate was collected by filtration, washed with water and ethanol, and dried at 60 °C.
Materials characterization: X-ray diffraction (XRD) patterns of the samples were recorded on an Empyrean X-ray diffractometer using filtered Cu Kα 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 N_2 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 AVO nanorods 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 cathode were weighed and then used. The AVO mass loading is 3-6 mg cm^{-2}. The coin cells were assembled in open air atmosphere using an AVO electrode as the cathode, a glass fibre (GF/D, Whatman) as the separator and a zinc foil (Alfa Aesar) as the anode. 2M $ZnSO_4$ with/without 1M Na_2SO_4 in H_2O was used as the electrolyte without oxygen removal. All of the cells were aged for 2 h before any electrochemical processes. The charge-discharge (0.3-1.5V vs. Zn/Zn^{2+}) tests were conducted on a LANHE battery tester (Wuhan, China) at room temperature. The cyclic voltammetry (CV) tests 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 0.3-1.5 V vs. Zn/Zn^{2+} 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:

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

This equation is valid when $\tau \ll \frac{L^2}{D_{GITT}}$, where m_B, V_M and M_B are the mass, molar volume and molecular weight of the AVO, 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.

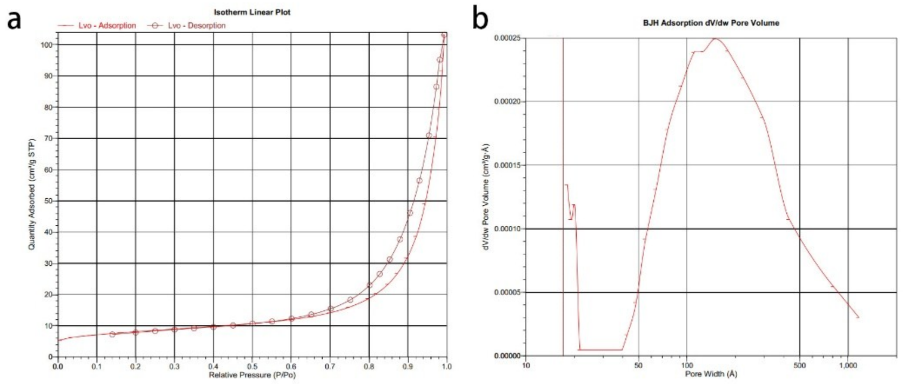

Figure S1. a) N_2 adsorption–desorption isotherms and b) BJH pore size distribution curve of AVO. Based on Barrett–Joyner–Halenda plots, the average pore size of the cathode material is about 25 nm.

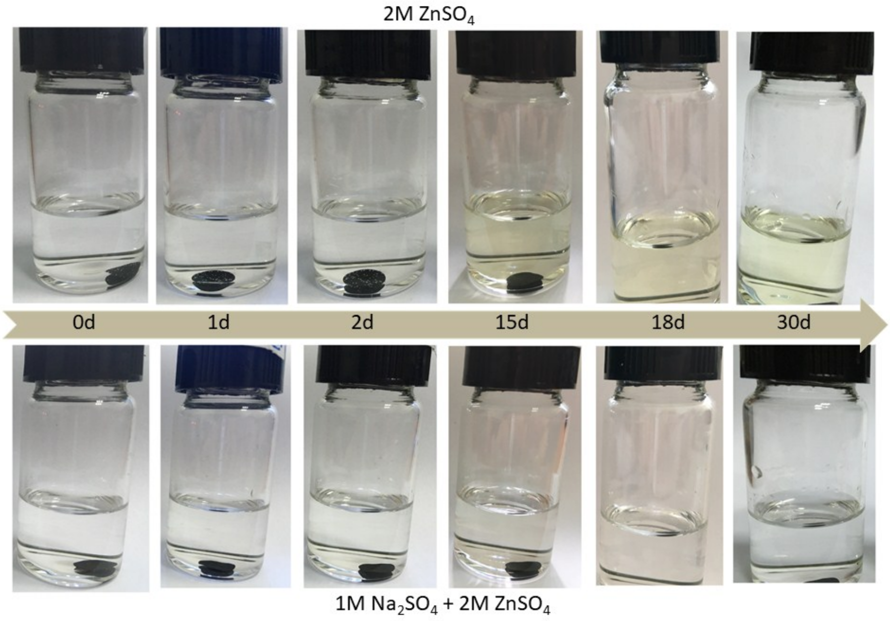

Figure S2. Optical images of AVO electrodes in $ZnSO_4$-based electrolytes for different periods. The addition of Na^+ into the electrolyte can effectively suppresses the dissolution of the AVO electrode.

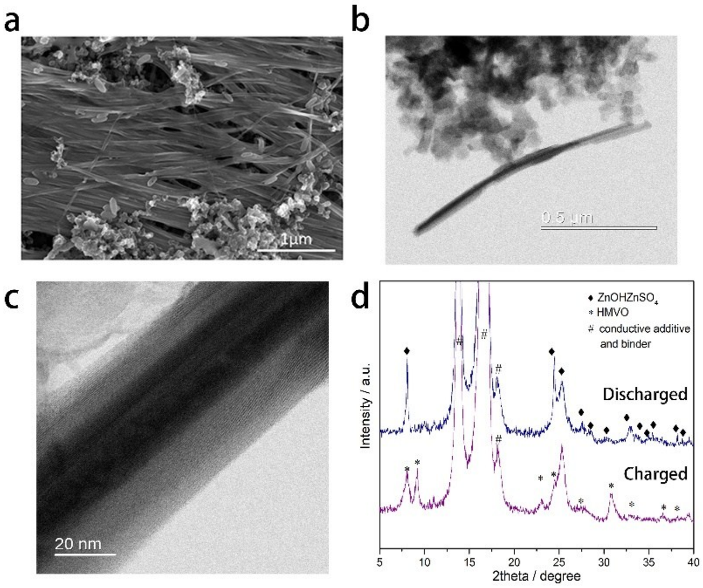

Figure S3. SEM (a) and TEM (b,c) images of AVO electrode, which was experienced 2000 cycles at 4 A g^{-1} in 1M Na_2SO_4 + 2M $ZnSO_4$ electrolyte. XRD patterns of the cycled AVO electrode.

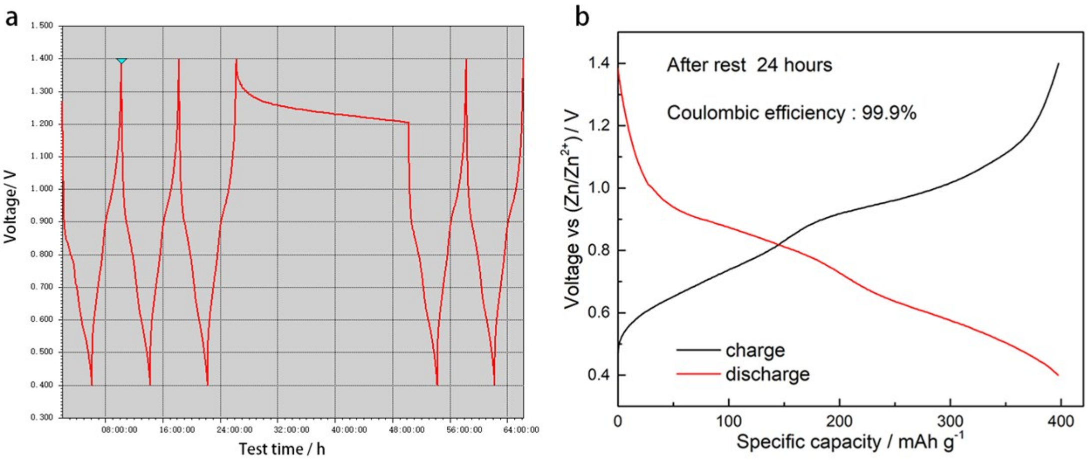

Figure S4. Storage performance of Zn/AVO. The cell was charged at 0.1 A g^{-1}, rested for 24 hours, and then discharged at the same rate. a) voltage profile and b) charge/discharge profiles of Zn/AVO before and after rest at charged state.

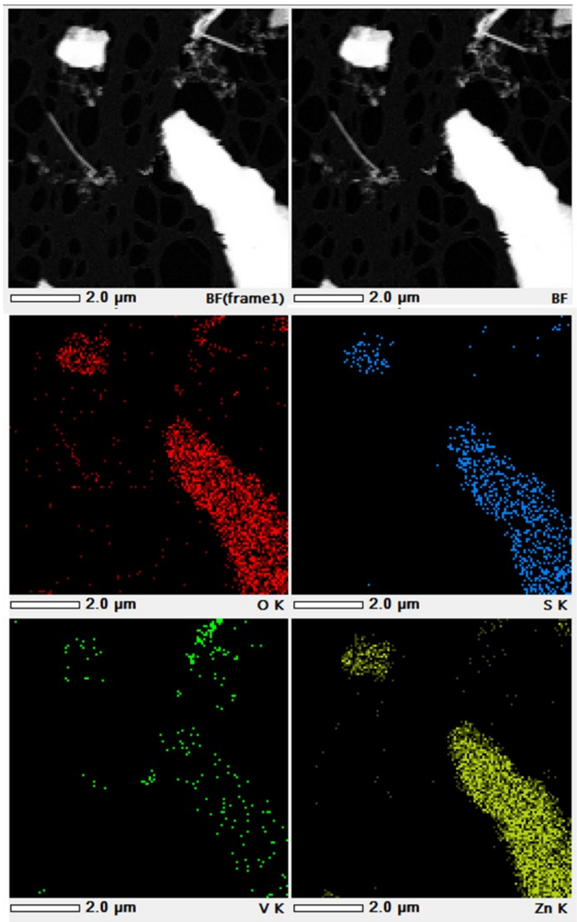

Figure S5. TEM images and the corresponding EDS mapping of the $Zn_4SO_4(OH)_6 \cdot xH_2O$ in the discharged state.

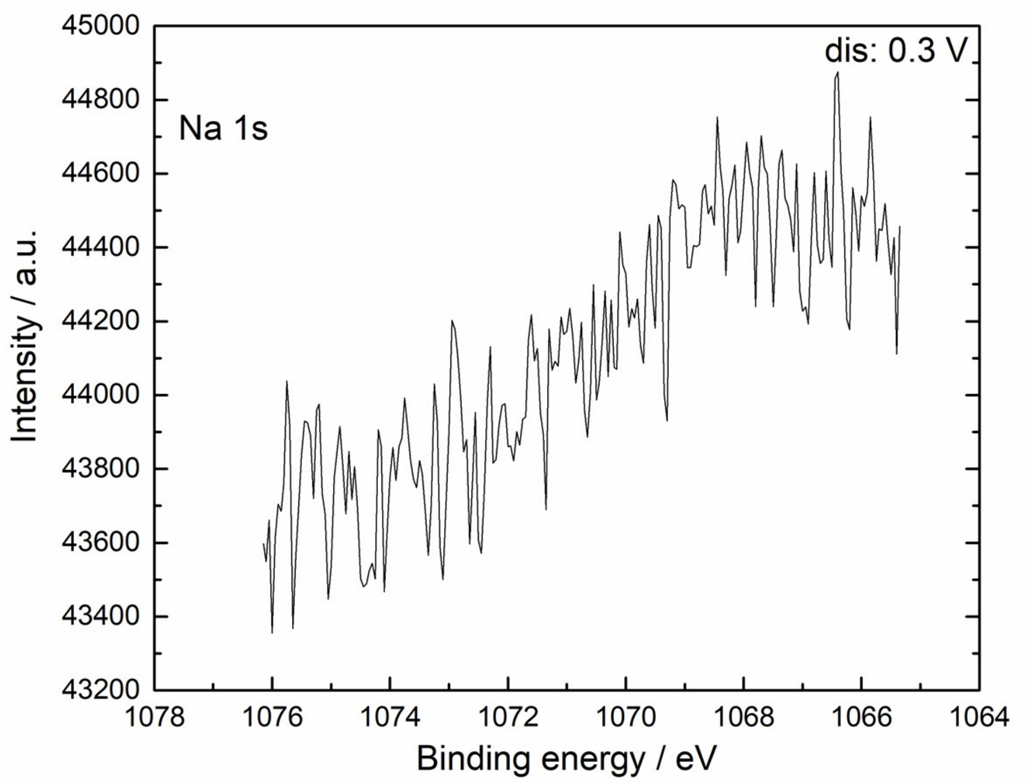

Figure S6. The XPS spectrum of Na 1s of AVO in the discharged state. The result indicates that Na^+ ions do not involve in the electrochemical reaction, servicing as a stabilizer in the electrolyte.

Table S1. Comparison of electrochemical properties of AVO with previously reported V-based cathode materials.

Materials	Electrolyte	Capacity	Cycling performance	Reference
$Zn_{0.25}V_2O_5\cdot n\ H_2O$	1M $ZnSO_4$	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
$Ca_{0.25}V_2O_5\cdot n\ H_2O$	1M $ZnSO_4$	340 and 289 mA h g^{-1} at 0.05 and 0.25 A g^{-1}, respectively	72 mA h g^{-1}after 5000 cycles at 20 A g^{-1}	2
$Na_{0.33}V_2O_5$	3M Zn(OTF)$_2$	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
$NaV_3O_8\cdot 1.5H_2O$	1M Na_2SO_4 + 1M $ZnSO_4$	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
$Na_2V_6O_{16}\cdot 1.63H_2O$	1M $ZnSO_4$	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 $ZnSO_4$	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
Zn2(OH)VO4	2M $ZnSO_4$	204, 160 and 101 mA h g^{-1} at 0.1, 2 and 10 A g^{-1}, respectively	125 mA h g^{-1} after 2000 cycles at 4 A g^{-1}	7
$NH_4V_4O_{10}$	2M $ZnSO_4$	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
$(NH_4)_2V_4O_9$	3M Zn(OTF)$_2$	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
AVO	1M Na_2SO_4 + 2M $ZnSO_4$	405,397,367,330,286,240,218,204 and 194 mA h g^{-1} at 0.1, 0.2,0.5, 1, 2, 4, 6, 8 and 10 A g^{-1}, respectively	340 mA h g^{-1} after 200 cycles at 0.2 A g^{-1} 278 mA h g^{-1} after 1000 cycles at 1 A g^{-1} 215 mA h g^{-1} after 2000 cycles at 4 A g^{-1}	This work

Zn(OTF)$_2$: Zinc trifluoromethanesulfonate

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.

3. 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.
6. 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.
7. 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.