

Electronic Supplementary Information

Layered Iron Vanadate Cathode for High-Capacity Aqueous Rechargeable Zinc Battery

Zhuo Peng,^a Qiulong Wei,^b Shuangshuang Tan,^a Pan He,^a Wen Luo,^a Qinyou An,^{a*} and Liqiang Mai^{a*}

^a *State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, International School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, Hubei, China.*

^b *Department of Materials Science and Engineering, University of California Los Angeles, CA 90095-1595, USA.*

Experimental

Synthesis of FVO nanosheets. The FVO nanosheets were synthesized via a simple water bath method. In a typical process, 3 mmol NH_4VO_3 (Aladdin, 99%) was dissolved in 100 mL deionized water after water bath at 90 °C, and 1 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Aladdin, 99.99%) was dissolved in 10 mL deionized water. Then the $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution was added into the NH_4VO_3 solution dropwise with water bath for 1 h. The precipitation was separated by centrifugation and washed by water and ethanol for three times. At last, it was dried in oven at 70 °C over night.

Materials characterization. *Ex-situ* XRD and *in-situ* XRD measurements were performed to investigate the crystallographic structure using a Bruker D8 Discover X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The IR was obtained by NEXUS 670 FTIR spectrometer. TG analysis and DSC were performed using NETZSCH-STA449c/3/G thermoanalyzer. The SEM images were collected by a JEOL-7100F microscope at an acceleration voltage of 20 kV. TEM, EDS element mapping and HRTEM images were recorded using a Titan G2 60–300 transmission electron microscope. The chemical states of elements were evaluated by XPS (VG MultiLab 2000).

Electrochemical measurements. The electrochemical properties were characterized by assembling 2016 coin cells in air, using zinc metal as anode and 0.3 M $\text{Zn}(\text{TFSI})_2$ (zinc(II) bis(trifluoromethanesulfonyl) imide, Sigma-Aldrich, 95%) as electrolyte. The cathodes were prepared with mass ratio of 70% active material, 20% acetylene black, and 10% polytetrafluoroethylene (PTFE), whose loading density of active material is about 0.62 g cm^{-2} . Galvanostatic charge/discharge tests and GITT were performed over the potential range from 0.4 to 1.6 V vs. Zn/Zn^+ using a multichannel battery testing system (LAND CT2001A). CV was conducted using an electrochemical workstation (CHI600E and Autolab PGSTAT 302N).

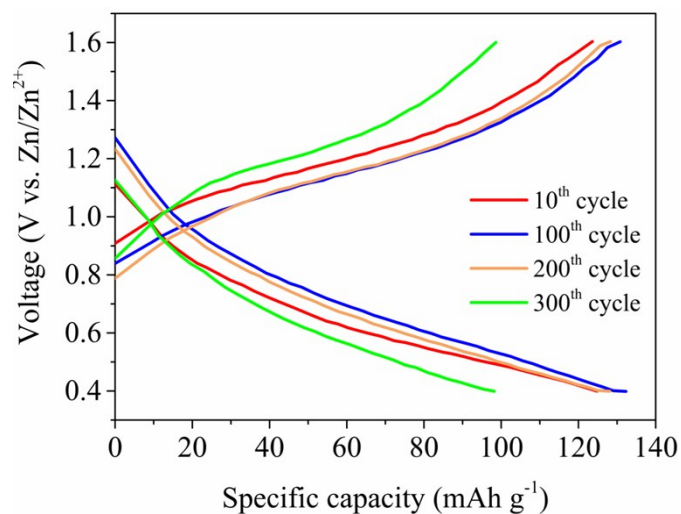


Fig. S1 Charge and discharge curves of FVO in Zn(TFSI)₂ electrolyte at 5 A g⁻¹.

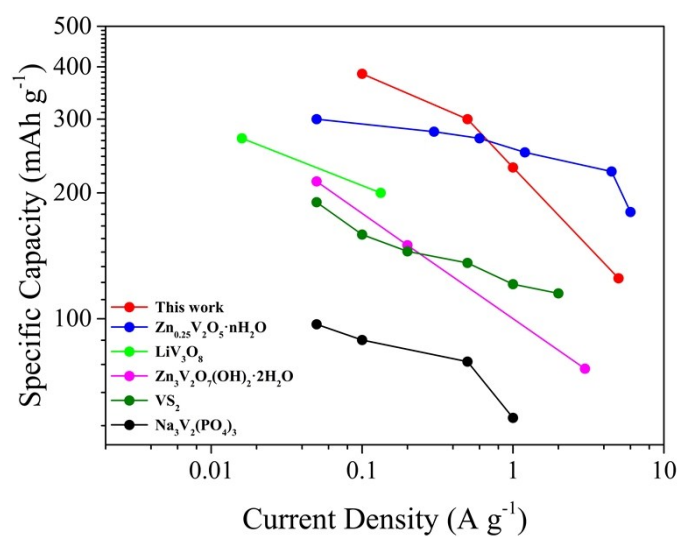


Fig. S2 Comparison of Zn-ion storage capacity of layered FVO to the state-of-the-art reported vanadium based cathodes: Zn_{0.25}V₂O₅·nH₂O,¹ LiV₃O₈,² Zn₃V₂O₇(OH)₂·2H₂O,³ VS₂,⁴ Na₃V₂(PO₄)₃.⁵ It can be clearly seen that FVO cathode in this work delivers relatively high specific capacity and could tolerate much higher current density.

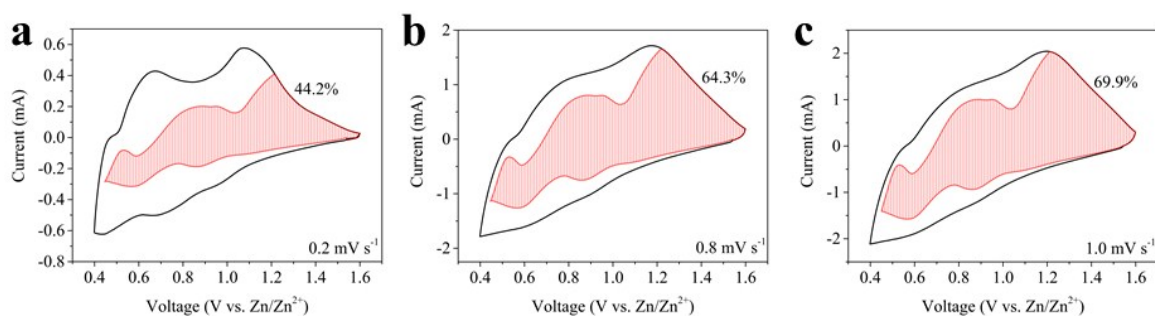


Fig. S3 Capacity separation curves at 0.2, 0.8 and 1.0 mV s^{-1} , calculated from data in Fig. 3a.

GITT test. Fig. S4 shows the GITT curves during the 4th cycle. The cell was discharged/charged at a constant current flux (0.2 A g^{-1}) with intervals of 10min. Two charge steps during the GITT experiment at around 0.9 V is shown in Fig. S5, with schematic labeling of different parameters. The values of chemical diffusion coefficients (D) can be obtained via following equation⁶:

$$D = \frac{4}{\pi\tau} \left(\frac{m_B V_M}{M_B S} \right)^2 \left(\frac{\Delta E_S}{\Delta E_t} \right)^2$$

Where τ is the pulse duration, M_B is the molar mass of FVO, V_M is the molar volume, m_B and S are the active mass and electrode/electrolyte contact area. ΔE_S and ΔE_t can be obtained from the GITT curves. The Zn ion diffusion coefficient (about 10^{-11} - $10^{-10} \text{ cm}^2 \text{ s}^{-1}$) as a function of cell voltage are plotted in Fig. S6.

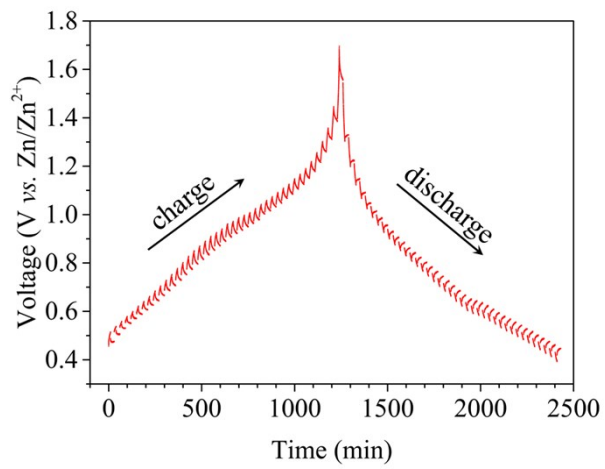


Fig. S4 GITT curves of FVO/Zn system during the 4th cycle.

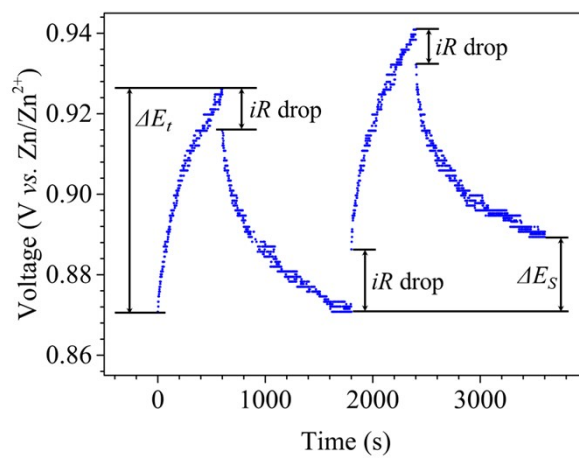


Fig. S5 Scheme of two charge steps during the GITT experiment at around 0.9 V.

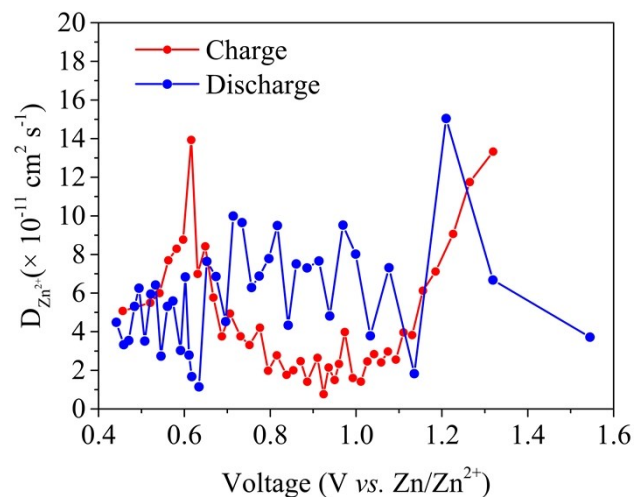


Fig. S6 Diffusion coefficients of Zn ion calculated from GITT.

References

1. D. Kundu, B. D. Adams, V. Duffort, S. H. Vajargah and L. F. Nazar, *Nature Energy*, 2016, **1**, 16119.
2. M. H. Alfaruqi, V. Mathew, J. Song, S. Kim, S. Islam, D. T. Pham, J. Jo, S. Kim, J. P. Baboo and Z. Xiu, *Chemistry of Materials*, 2017, **29**, 1684-1694.
3. C. Xia, J. Guo, Y. Lei, H. Liang, C. Zhao and H. N. Alshareef, *Advanced Materials*, 2017, 1705580.
4. P. He, M. Yan, G. Zhang, R. Sun, L. Chen, Q. An and L. Mai, *Advanced Energy Materials*, 2017, **7**, 1601920.
5. G. Li, Z. Yang, Y. Jiang, C. Jin, W. Huang, X. Ding and Y. Huang, *Nano Energy*, 2016, **25**, 211-217.
6. Y. Zhu, T. Gao, X. Fan, F. Han and C. Wang, *Accounts of Chemical Research*, 2017, **50**, 1022.