

Supporting Information for

## **V<sub>2</sub>O<sub>5</sub> Nanospheres with Mixed Vanadium Valences as High Electrochemically Active Aqueous Zinc-ion Battery Cathode**

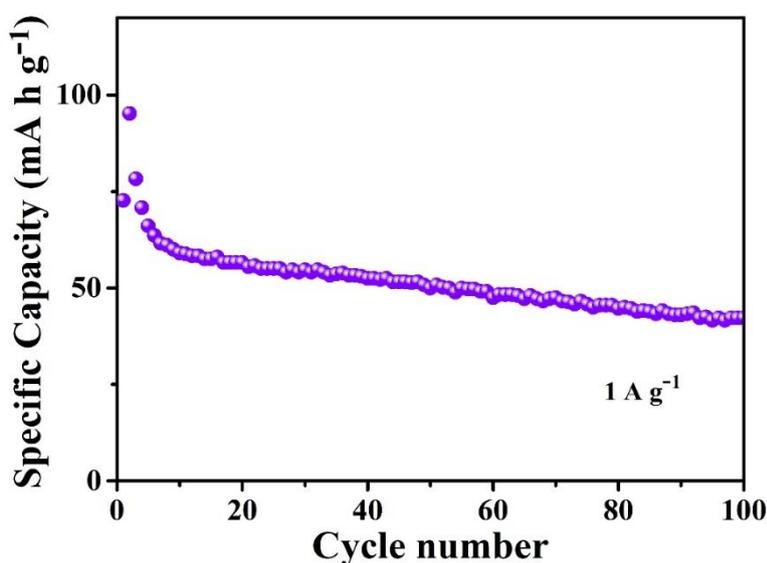
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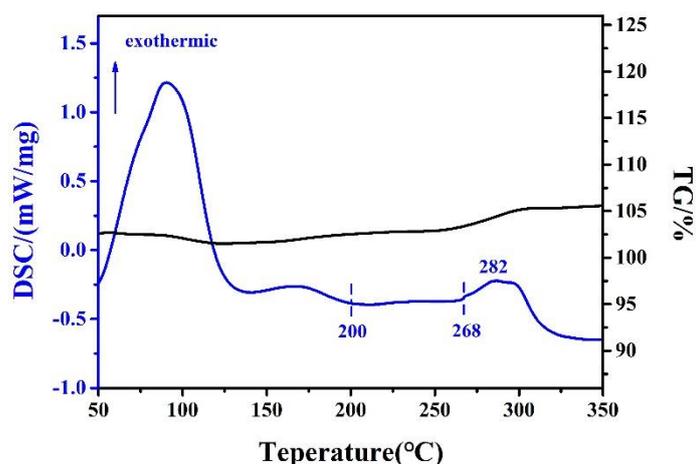
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### **Supplementary Figures and Table**



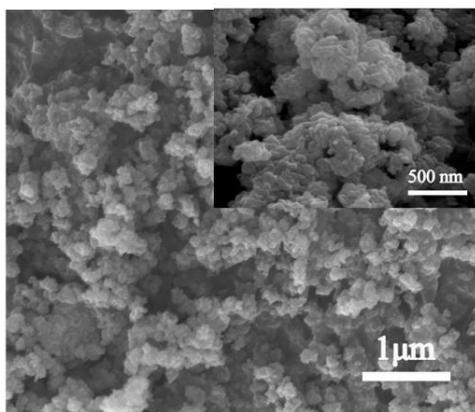
**Fig. S1** Cycle performance at 1 A g<sup>-1</sup> of VOOH electrode

When the current density is 1 A g<sup>-1</sup>, the first discharge specific capacity of the Zn/VOOH coin cell is 75 mA h g<sup>-1</sup>. After 100 cycles, the specific capacity drops to 50 mA h g<sup>-1</sup>. Obviously, VOOH is not suitable to be used as the cathode material for ZIBs.



**Fig. S2** TG and DSC results of VOOH dried at 50 °C. The temperature ramp rate was set to 10 °C min<sup>-1</sup>

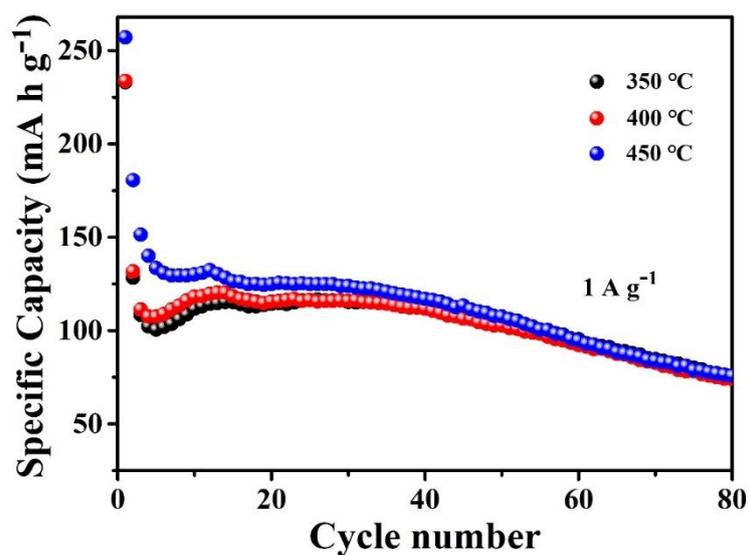
**Figure S2** shows the TG-DSC results of the VOOH and we can divide the heating process into three parts for analysis. First, before heating to 200 °C, V<sup>3+</sup> is slowly oxidized to V<sup>4+</sup> in air. Second, the substance is a mixed valence state of V<sup>4+</sup> and V<sup>5+</sup> within the temperature range of 200-270 °C as indicated in **Fig. S2**. Third, after heating to 282 °C, the substance in mixed valence state of V<sup>4+</sup> and V<sup>5+</sup> is converted into V<sub>2</sub>O<sub>5</sub> in pure pentavalent gradually. During the oxidation process, the mass is slightly increased due to the absorption of oxygen in air. And then the quality is unchanged, implying that the vanadium in substance is completely oxidized, which corresponds to the stable vanadium pentoxide phase in the temperature-controlled *in-situ* XRD (**Fig. 1b**).



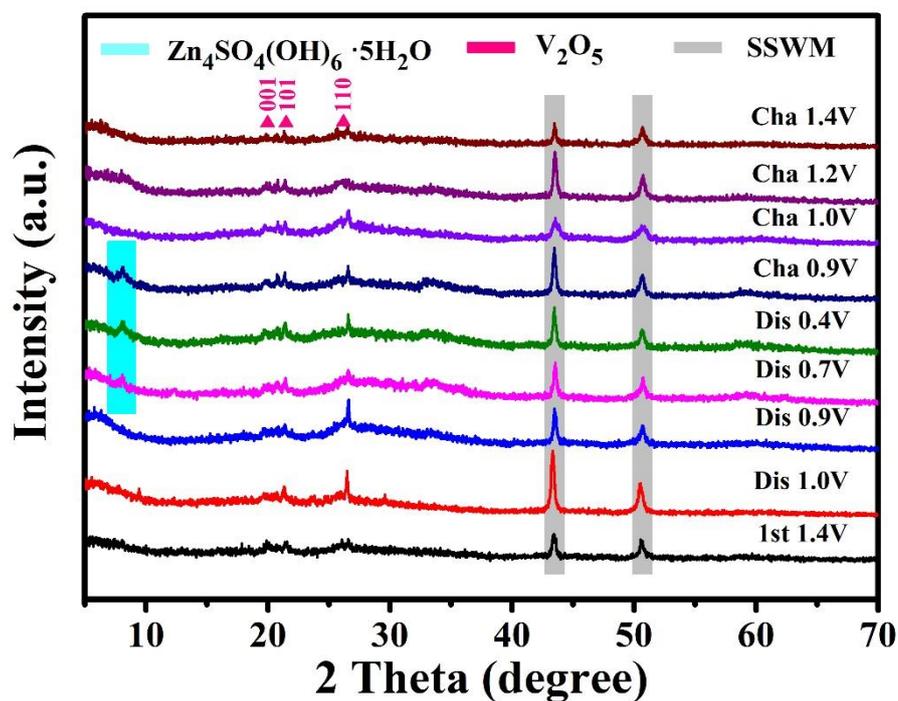
**Fig. S3** SEM image of V<sub>2</sub>O<sub>5</sub>

**Table S1** EIS primary simulation parameters of as-prepared V<sup>4+</sup>-V<sub>2</sub>O<sub>5</sub> and V<sub>2</sub>O<sub>5</sub>

Samples	$R_s$ ( $\Omega$ )	$R_{ct}$ ( $\Omega$ )
V <sup>4+</sup> -V <sub>2</sub> O <sub>5</sub>	1.212	203.5
V <sub>2</sub> O <sub>5</sub>	2.456	377.3



**Fig. S4** Cycling performance of samples obtained at 350 °C, 400 °C, and 450 °C at the discharge current density of 1 A g<sup>-1</sup>



**Fig. S5** Ex-situ XRD patterns of V<sup>4+</sup>-V<sub>2</sub>O<sub>5</sub> electrodes discharged or charged to different voltage states at the current density of 100 mA g<sup>-1</sup> in the second cycle

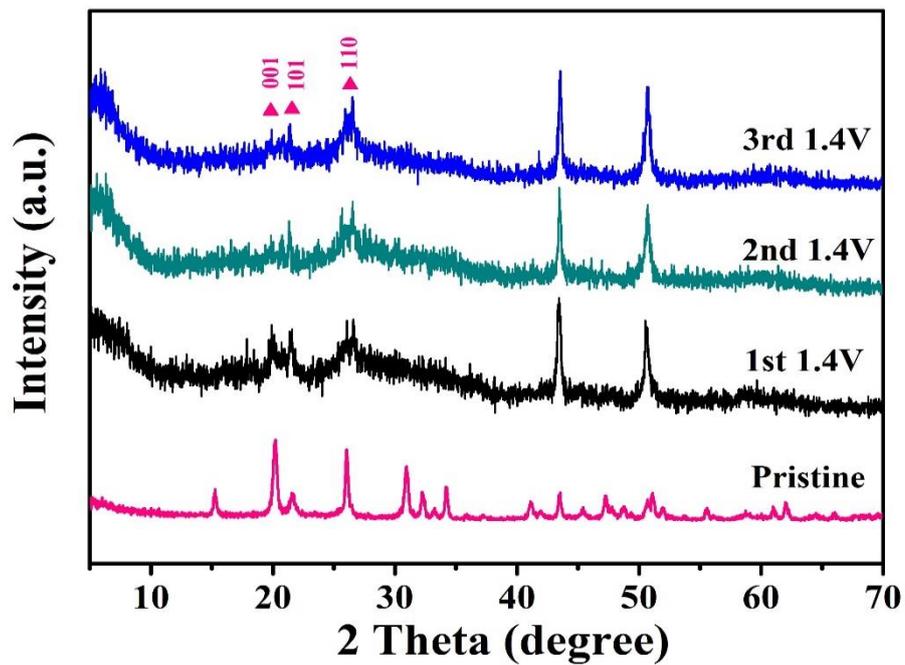


Fig. S6 Ex-situ XRD patterns of  $V^{4+}$ - $V_2O_5$  electrodes charged to 1.4 V at different cycles

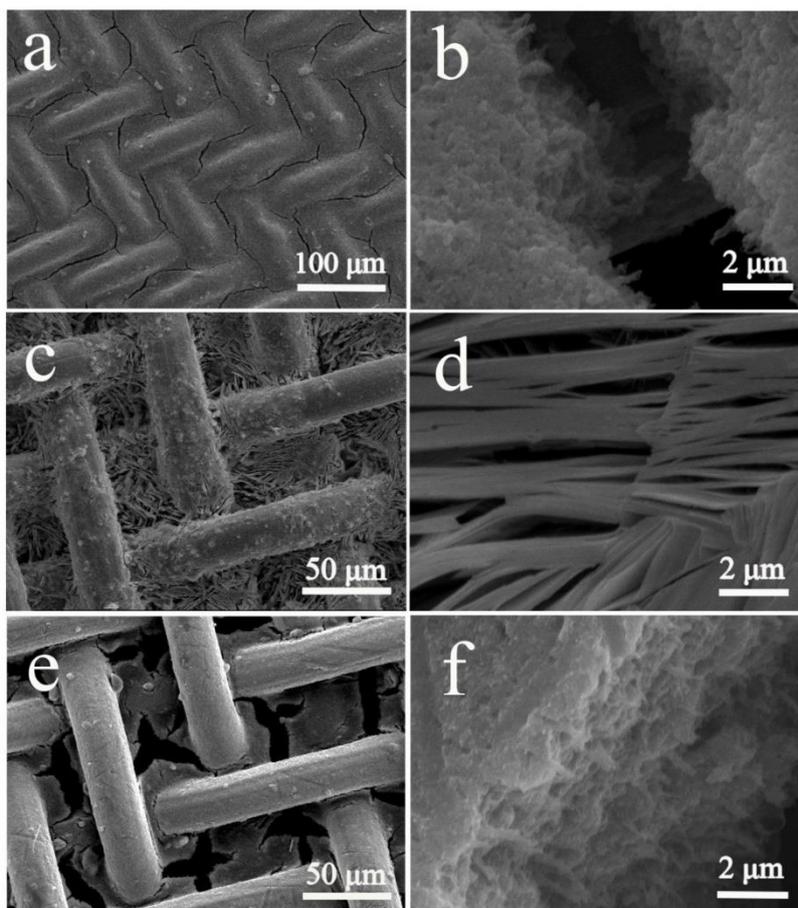
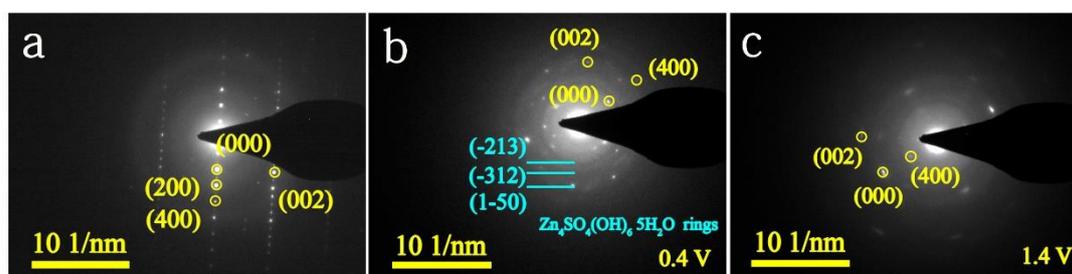


Fig. S7 SEM images with different magnifications of  $V^{4+}$ - $V_2O_5$  electrode film at **a, b** original state. **c, d** discharge to 0.4 V. **e, f** charge to 1.4 V

The scanning electron microscopy (SEM) images of  $V^{4+}$ - $V_2O_5$  electrodes at different states are shown in **Fig. S7**. The SEM image of initial  $V^{4+}$ - $V_2O_5$  electrode is presented in **Fig. S7a**. Furthermore, the SEM images of the surface and cross-section of electrode (**Fig. S7b**) also reflect that the surface and internal structure of the mixture are relatively loose, which is beneficial to the  $Zn^{2+}$  diffusion. When discharged to 0.4 V, it can be seen that the morphology of the material on the surface of the electrode film changed a lot. There are many layered flakes emerged compared to the initial state (**Fig. S7c, d**), these layered flakes vanished during charging process (**Fig. S7e**). The highly reversible morphologic transformation during the discharge/charge process is well consistent with the evolution observed in ex-situ XRD patterns (**Fig. 5**), which corresponding to the formation/disappearance of  $Zn_4SO_4(OH)_6 \cdot 5H_2O$  phase. What's more, such phenomenon has been reported in some previous reports[S1-S3]. The flakes at discharge states may be due to the formation of  $Zn_4SO_4(OH)_6 \cdot 5H_2O$ . When charged to 1.4 V, it is obviously that the morphology of  $V^{4+}$ - $V_2O_5$  electrode film is not as regular as the original state, it becomes a little messy (**Fig. S7e, f**), which may further explain the phenomenon that the cycling stability in low current density is not very good.



**Fig. S8** SAED images of  $V^{4+}$ - $V_2O_5$  **a** powder **b** discharged to 0.4 V and **c** charged to 1.4 V

## Supplementary References

- [S1]M. Chamoun, W.R. Brant, C.-W. Tai, G. Karlsson, D. Noréus, Rechargeability of aqueous sulfate Zn/MnO<sub>2</sub> batteries enhanced by accessible Mn<sup>2+</sup> ions. *Energy Storage Mater.* **15**, 351-360 (2018). <https://doi.org/10.1016/j.ensm.2018.06.019>
- [S2]J. Huang, Z. Wang, M. Hou, X. Dong, Y. Liu, Y. Wang, Y. Xia, Polyaniline-intercalated manganese dioxide nanolayers as a high-performance cathode material for an aqueous zinc-ion battery. *Nat. Commun.* **9**(1), 2906 (2018). <https://doi.org/10.1038/s41467-018-04949-4>
- [S3]C. Zhu, G. Fang, J. Zhou, J. Guo, Z. Wang, C. Wang, J. Li, Y. Tang, S. Liang, Binder-free stainless steel@Mn<sub>3</sub>O<sub>4</sub> nanoflower composite: a high-activity aqueous zinc-ion battery cathode with high-capacity and long-cycle-life. *J. Mater. Chem. A* **6**(20), 9677-9683 (2018). <https://doi.org/10.1039/c8ta01198b>