

## Supporting Information

# Achieving High Performance in Aqueous Iron-Ion Batteries using Tunnel-Like VO<sub>2</sub> as a Cathode Material

*Yu-Shuang Xu<sup>a</sup>, Chang Li<sup>a</sup>, Wen-Jun Deng<sup>a</sup>, Jin-Lin Zhu<sup>a</sup>, Yi Zhou<sup>a</sup>, Run-Duo Zhu<sup>a</sup>, Chao Huang<sup>a</sup>, Wen-Xia Zou<sup>a</sup>, and Rui Li<sup>a,\*</sup>*

<sup>a</sup>*School of Advanced Materials, Peking University Shenzhen Graduate School, Shenzhen 518055, China*

E-mail: [liruisz@pku.edu.cn](mailto:liruisz@pku.edu.cn)

## Experimental Section

### 1. Preparation of Materials

The VO<sub>2</sub> was synthesized by the hydrothermal method as follows: 0.36 g of V<sub>2</sub>O<sub>5</sub> and 0.37 g of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O were added to 30 mL of deionized water. The solid-liquid mixture was dispersed by ultrasound for 30 min. The dispersion was transferred into a 100 mL Teflon-lined stainless steel autoclave, and a moderate amount of deionized water was added. The autoclave was then heated at 180 °C for 48 h. The resulting product was collected by filtration and washed three times with deionized water, followed by drying at 60 °C overnight under a vacuum.

### 2. Materials Characterization

X-ray diffraction (XRD, Bruker D8 Advance diffractometer with Cu K $\alpha$  radiation ( $\lambda$ = 1.5405 Å)) was used to characterize the structural properties of VO<sub>2</sub>. Scanning electronic microscopy (SEM, ZEISS Supra 55) and transmission electron microscope (TEM, FEI Talos F200x) were used to obtain information about the morphology and dimensions of VO<sub>2</sub>. TGA measurements were performed in a nitrogen atmosphere at a heating rate of 5 °C min<sup>-1</sup> to evaluate the thermostability of the samples (from 30 to 800 °C). Raman spectroscopy (Thermo Fischer DXR) was used for substance characterization and identification of crystalline forms. X-ray photoelectron spectroscopy (XPS, Thermo Scientific, Nexsa) was used to evaluate the vanadium valence of the VO<sub>2</sub> cathodes in the initial, discharged, and charged states.

### 3. Electrochemical Characterization

The VO<sub>2</sub> electrodes were composed of active materials (VO<sub>2</sub> powder, 70 wt%), Ketjen black (20 wt%), and polytetrafluoroethylene (10 wt%), which were then pressed onto Ti meshes. The average mass loading of VO<sub>2</sub> cathode is about 4.5 mg cm<sup>-2</sup>. The AIBs (CR2032-type coin cells) consisted of an electrolyte (3 m Fe(OTF)<sub>2</sub>), a separator (glass fiber, Whatman), an anode (Fe plate), and a cathode (VO<sub>2</sub> electrode), assembling in the air atmosphere. The amount of electrolyte in each coin cell is 100  $\mu$ L. AIBs were used for all tests. Cyclic voltammetry (CV) and Galvanostatic Intermittent Titration Technique (GITT) tests were conducted using the CHI660E electrochemical workstation (Chenhua Instrument Company, Shanghai, China). CV tests were conducted at various scan rates within the potential of 0 - 1.0 V (vs. Fe<sup>2+</sup>/Fe). GITT was applied to analyze the diffusion kinetics at a specific current of 0.02 A g<sup>-1</sup> and a charge/discharge time and interval of 30 min for each step. The electrochemical tests (GCD, rate capability, and cycling performance) were evaluated using the NEWARE system. The electrochemical tests were measured at various specific currents over a potential range of 0 - 1.0 V (vs. Fe<sup>2+</sup>/Fe). All tests were done at room temperature and air

atmosphere. Generally, each test was performed for three times, three cells were assembled for each time, and the data with consistent repeatability was selected.

#### 4. Equation

The contribution ratio of capacitive control ( $k_1v$ ) and diffusion control ( $k_2v^{1/2}$ ) can be evaluated through the following equation<sup>1</sup>:

$$i = k_1v + k_2v^{1/2} \quad \#(1)$$

$$\frac{i}{v^{1/2}} = k_1v^{1/2} + k_2 \quad \#(2)$$

Where  $v$  represents a specific scan rate,  $i$  refers to the current density during the cyclic voltammetry test.

The  $D_{Fe^{2+}}$  in electrodes can be calculated using the following equation<sup>2</sup>:

$$D = \frac{4L^2}{\pi\tau} \left( \frac{\Delta E_s}{\Delta E_t} \right)^2 \quad \#(3)$$

Where  $\tau$  represents the constant current pulse time (s),  $L$  refers to the ion diffusion length (cm),  $\Delta E_s$  denotes the steady-state potential change (V), and  $\Delta E_t$  signifies the potential (V) during the constant current pulse of a single GITT step.

## Supporting Figures and Tables

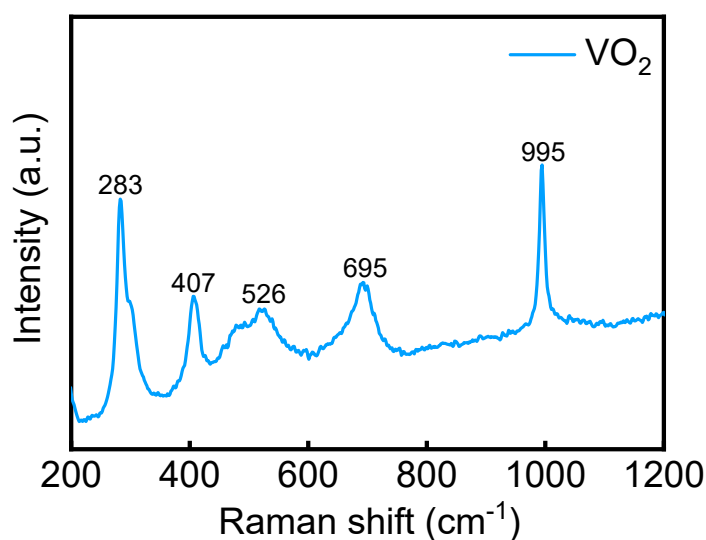


Fig. S1 Raman spectrum of VO<sub>2</sub>.

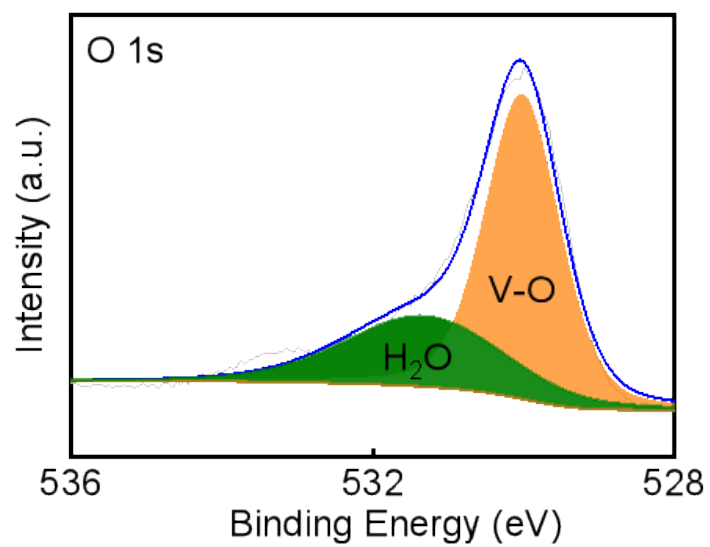


Fig. S2 XPS spectrum of VO<sub>2</sub> (O 1s).

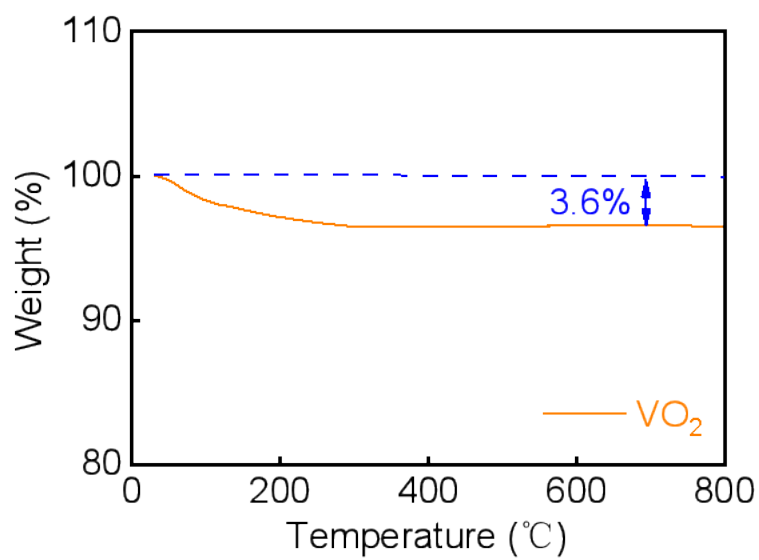


Fig. S3 TGA curve of VO<sub>2</sub>.

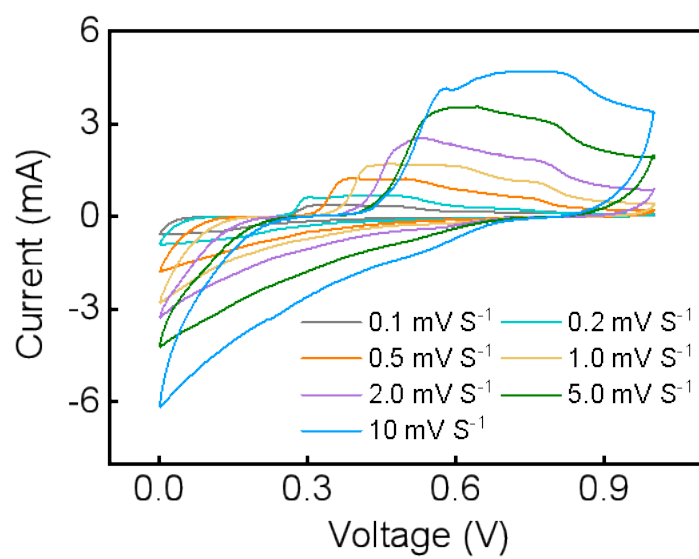


Fig. S4 CV curves of the full battery at a scan rate of 0.1-10 mV s<sup>-1</sup>.

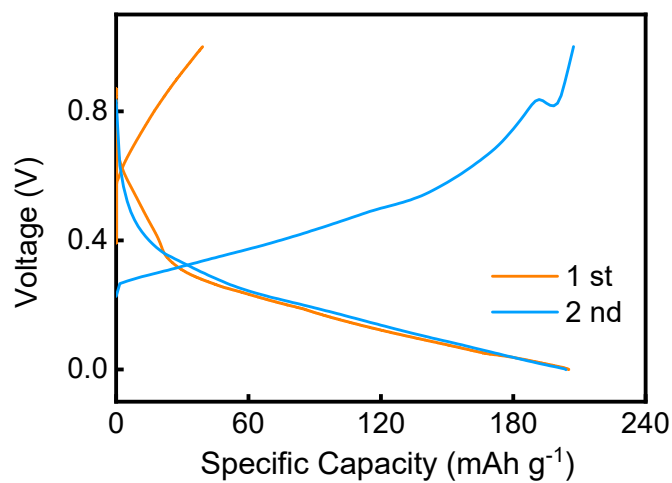


Fig. S5 GCD curves of AIIB at first cycle and second cycle.

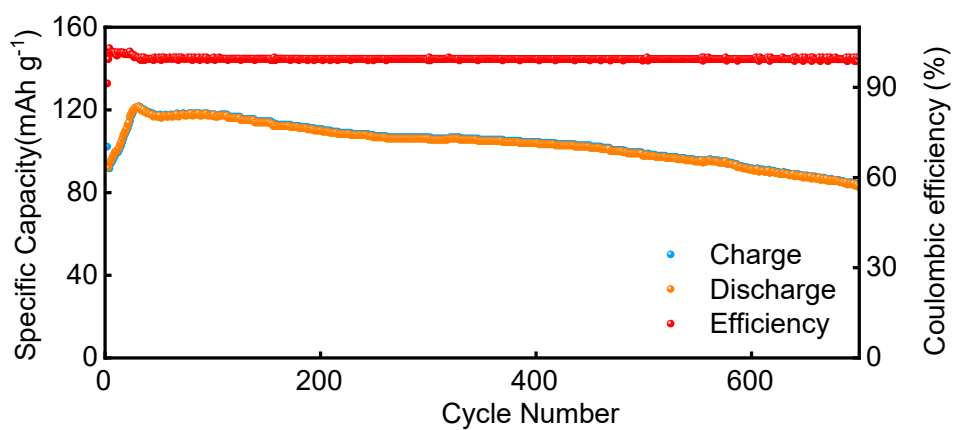


Fig. S6 Long-term cycling performance of the battery at 2 A g<sup>-1</sup>.

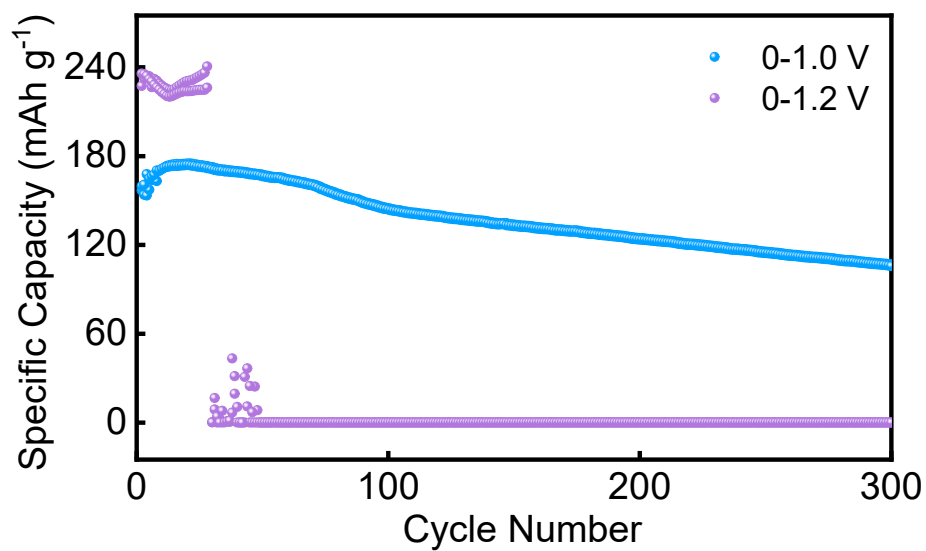


Fig. S7 Cycling performance of AIIB at different ranges of operating voltage.

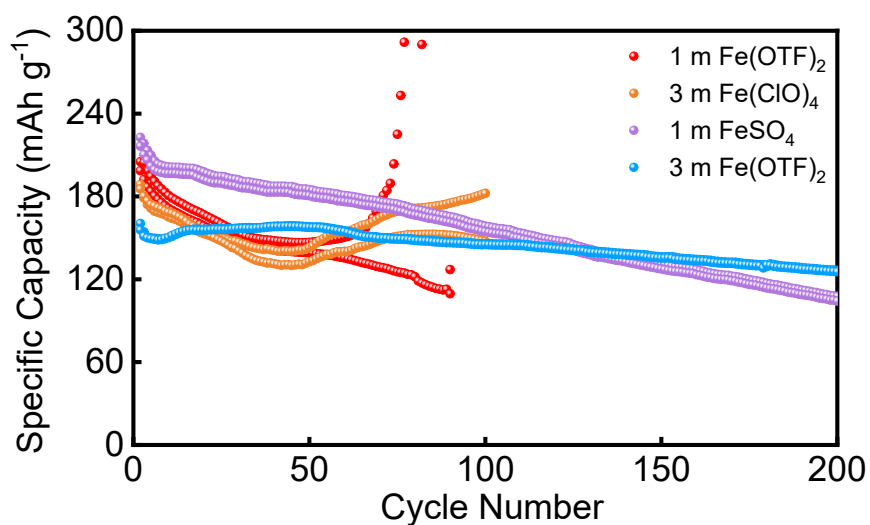


Fig. S8 Cycling performance of AIIB at different electrolytes.

Table S1.

Comparison of the performance with the previous works

Cathode	Active mass loading of cathode	Anode	Electrolyte	Capacity	Cycling Performance
VO <sub>2</sub> (This work)	~4.5 mg cm <sup>-2</sup>	Fe	Fe(OTF) <sub>2</sub>	198 mAh g <sup>-1</sup> at 0.2 A g <sup>-1</sup>	~78.9% after 200 cycles at 0.5 A g <sup>-1</sup>
V <sub>2</sub> O <sub>5</sub> <sup>3</sup>	~5 mg cm <sup>-2</sup>	Fe	Fe(ClO <sub>4</sub> ) <sub>2</sub> in TEGDME	18 mAh g <sup>-1</sup> at 0.2 A g <sup>-1</sup>	~43.7% after 173 cycles at 0.1 A g <sup>-1</sup>
VOPO <sub>4</sub> ·2H <sub>2</sub> O <sup>4</sup>	~9 mg cm <sup>-2</sup>	Fe	FeSO <sub>4</sub>	100 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup>	~81% after 50 cycles at 0.1 A g <sup>-1</sup>
Prussian blue analogues <sup>5</sup>	~1.5 mg cm <sup>-2</sup>	Fe	FeSO <sub>4</sub>	56 mAh g <sup>-1</sup> at 0.24 A g <sup>-1</sup>	~80% after 1000 cycles at 0.6 A g <sup>-1</sup>

#### Reference

1. X. Pu, D. Zhao, C. Fu, Z. Chen, S. Cao, C. Wang and Y. Cao, *Angew. Chem. -Int Edit*, 2021, **60**, 21310-21318.

2. Q. Zong, W. Du, C. Liu, H. Yang, Q. Zhang, Z. Zhou, M. Atif, M. Alsalhi and G. Cao, *Nano-Micro Lett.*, 2021, **13**, 116.
3. A. P. Vijaya Kumar Saroja, S. S. Samantaray and R. Sundara, *Chem. Commun.*, 2019, **55**, 10416-10419.
4. Y. Xu, X. Wu, S. K. Sandstrom, J. J. Hong, H. Jiang, X. Chen and X. Ji, *Adv. Mater.*, 2021, **33**, e2105234.
5. X. Wu, A. Markir, Y. Xu, C. Zhang, D. P. Leonard, W. Shin and X. Ji, *Adv. Funct. Mater.*, 2019, **29**, 1900911.