

Supporting Information

B-doped Layered VOPO₄·2H₂O Cathode for High-performance Zinc-Ion Batteries with H⁺/Zn²⁺ Co-insertion Mechanism

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Experiments Section

1. Preparation of B-doped VOPO₄·2H₂O material

In a typical synthesis, 4.8 g of V₂O₅, 26.6 mL of H₃PO₄ and 115.4 mL deionized water were added to a three-neck flask, respectively. Then 10 mL of HNO₃ was added with magnetic stirring for 30 min to stabilize the oxidation state of vanadium. The mixture was then heated at 110 °C for 16 h. The yellow precipitate was collected by centrifugation from the bottom after cooling to the room temperature, and washed three times with deionized water and acetone, respectively. The resulting bright yellow VOPO₄·2H₂O samples were dried in a vacuum oven at 60 °C.

Then 0.5 g of synthesized VOPO₄·2H₂O was taken, 0.5 g of boric acid was added and dispersed in 50 mL of N-methyl pyrrolidone. After VOPO₄·2H₂O and boric acid

were mixed evenly, the mixture was transferred into a 100 mL of Teflon-lined stainless-steel autoclave and kept at 120 °C for 2 h. After cooling down, the product was also washed with ultra-pure water and collected by centrifugation, named B-doped $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$.

2. Characterization

The crystalline phase of B-doped $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ were investigated by powder X-ray diffraction (XRD) with Bruker D8 Advance diffractometer (Cu K α radiation, $\lambda = 0.15418 \text{ \AA}$) over the range 10-50° at a scan rate of 10°·min⁻¹. Fourier transform infrared (FT-IR) spectra were collected on a Nicolet Avatar 370 spectrometer with KBr tablets. The chemical states of each element in the prepared samples were analyzed by X-ray photoelectron spectroscopy (XPS) on EscaLab 250 (USA) using a monochromatic Al-K source. The weight change of the samples was investigated by a differential thermal thermogravimetry analyzer (DSC-TG, STA 449 F5). The high-angle annular dark-field (HAADF) and its super-X EDS were carried out with FEI Talos F200X G2. The morphology and microstructure of B-doped $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ were observed by high-resolution transmission electron microscopy (HRTEM, JEM-2100F) and field-emission scanning electron microscopy (FESEM, JEOL JSM-6700F).

3. Electrochemical measurements

The cathode material was prepared by mixing the active materials, acetylene black and polyvinylidene fluoride (PVDF) in N-methyl pyrrolidone (NMP) solutions in mass ratio of 7:2:1. The smooth ink was evenly coated on the stainless-steel net, and dried in

a vacuum oven at 60 °C for 12 h. The anode material was commercial zinc foil, and the electrolyte was 3 mol L⁻¹ of Zn(CF₃SO₃)₂ aqueous solution. The electrochemical performance of B-doped VOPO₄·2H₂O and VOPO₄·2H₂O electrode materials were evaluated by cyclic voltammetry (CV) performed on the CHI 760E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd.). A series of 100 mA g⁻¹ constant-current pulses were used in constant-current batch titration (GITT) that allowed to rest for 0.5 h. The galvanostatic charge-discharge (GCD) tests were completed on the Neware electrochemical workstation, the voltage window of GCD is between 0.2 and 1.9 V, and the current density was set in the range of 0.1~1 A g⁻¹.

The capacity recorded by the Neware software is calculated according to equation of “ $C=I\times\Delta t/m$ ” (S1), in which I , Δt , and m are the current (mA), the discharge time (h), and the mass of active material (g), respectively. The energy density (E) and power density (P) of AZIBs were separately evaluated by the equations of “ $E=C\times V/m$ ” (S2) and “ $P=3600E/t$ ” (S3), in which C , V , m , t is the capacitance, average discharge voltage, mass and discharge time, respectively.

Results Section

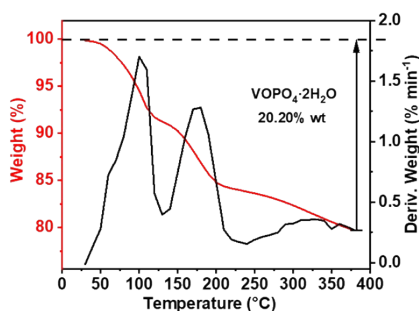


Figure S1 DSC-TG curves of VOPO₄·2H₂O.

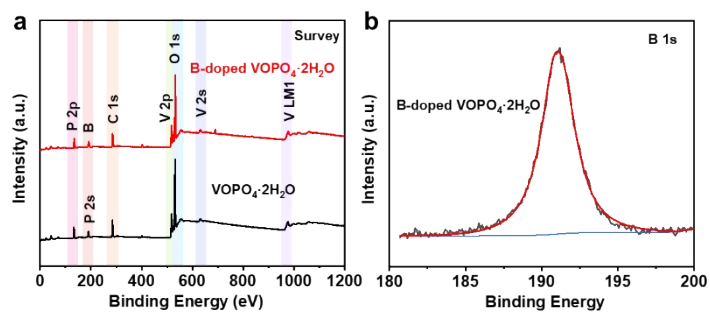


Figure S2 (a) Survey XPS spectra of B-doped $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$, (b) High-resolution XPS spectra of B in B-doped $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$.

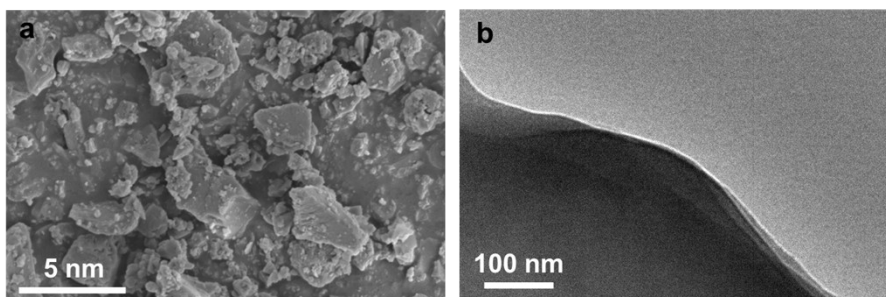


Figure S3 (a) FESEM and (b) HRTEM images of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$.

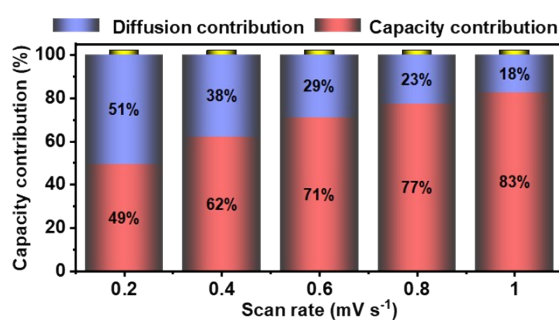


Figure S4 Contribution ratio of capacitance at various scan rates in $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$.

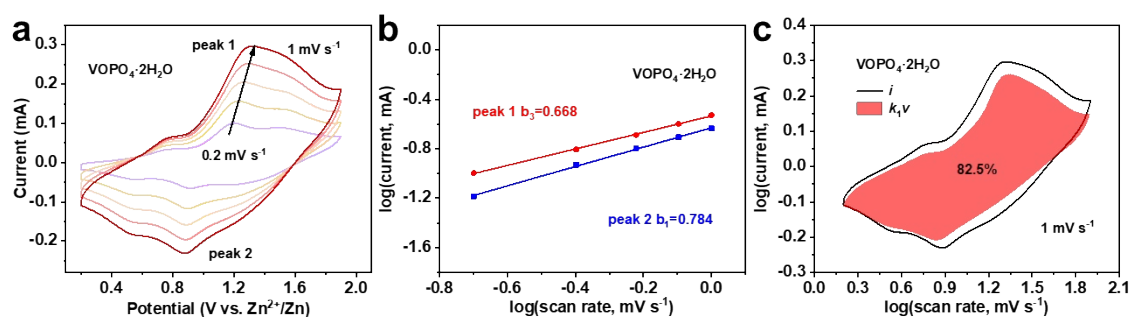


Figure S5 (a) CV curves of VOPO₄·2H₂O at different scanning speeds, (b) Relationship between scan rates and peak currents, (c) CV fitting of pseudo-capacitance.

Table S1 Comparison of electrochemical performance of VOPO₄-based cathodes.

Materials	Current density (A g ⁻¹)	Capacity (mAh g ⁻¹)	Reference
VOPO ₄ /C	0.1	140	<i>ACS Appl. Mater. Interfaces</i> , 2022, 14(40): 45494-45502
NaVOPO ₄ ·0.83H ₂ O	0.1	187	<i>Small</i> , 2023, 19: 2303227
Na _x VOPO ₄ ·nH ₂ O	0.3	100	<i>Energy Fuels</i> , 2022, 36(12): 6520-6531
PPy-VOPO ₄	0.1	65	<i>ACS Appl. Energy Mater.</i> , 2019, 2(12): 8667-8674
Li ₃ V ₂ (PO ₄) ₃	0.3	128	<i>Chem Comm.</i> , 2021, 57: 6253-6256
δ-VOPO ₄	0.3	122.6	<i>Chem. Sci.</i> , 2023, 14: 8206-8213
B-doped VOPO₄	0.1	234.5	This work