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Supplementary Information for

Unveiling the Role of Structural Water and Achieving Enhanced Zn-Ion Storage via Thermal Dehydration of a Ni-Containing Heteropolyvanadate Cathode

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1. Experimental Section

1.1 Materials and methods

$NaVO_3$ (99%), $NiSO_4$ (99.5%), NaS_2O_8 (99%) and $Zn(CF_3SO_3)_2$ (98.0%) were all from Shanghai McLean Biochemical Technology Co. HNO_3 (68%), N−methylpyrrolidone (NMP, 99.9%), ethanol, polyvinylidene fluoride (PVDF) and aniline were all purchased from National Medicine Chemical Reagent Co, Ltd.

X-ray powder diffraction (XRD) patterns of all samples were obtained using a D/max2500 X-ray powder diffractometer at a scan rate of 2°/min between 5 and 50°. The Fourier Transform infrared spectroscopy (FT−IR) was determined on a Nicolet 6700 Fourier transform infrared spectrometer. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer TG−7 thermogravimetric analyzer in nitrogen at a scan rate of 10 °C min^{-1}. X-ray photoelectron spectroscopy (XPS, ESCALAB Xi) was performed using an Al Kα radiation source. All XPS data were calibrated using the adventitious carbon C 1s peak at 284.8 eV for binding energy correction.[1] The morphology and microstructure of the samples were analyzed by scanning electron microscopy (SEM, S−5500 model) and transmission electron microscopy (TEM, FEI Talos−F200S).

1.2 Synthesis of $Na_7[NiV_{14}O_{40}]$ (Ni-NVO)

$Na_7[NiV_{14}O_{40}]$ was synthesized using a simple and reproducible solution method [2]. The detailed procedures were as follows: First, 31.7 g of $NaVO_3$ was dissolved in 700 mL of deionized water preheated to 80 °C with continuous stirring until complete dissolution, followed by filtration to remove undissolved impurities. Subsequently, 20 mL of 1 M HNO_3 and 20 mL of 1 M $NiSO_4$ solutions were sequentially added to the filtrate. After thorough stirring, 9.52 g of $Na_2S_2O_8$ was slowly introduced. The resulting mixed solution was continuously stirred and heated at 80 °C until its volume was reduced to 300 mL, during which the solution color gradually changed. After cooling the solution to approximately 25 °C, filtration was performed again. The filtrate was transferred to a clean container and stored in a refrigerator for two days. The precipitated black crystals were then collected by filtration,

washed multiple times with deionized water to remove surface impurities, and air−dried initially. Finally, the product was placed in a tube furnace at 200 °C for 12 h to obtain a reddish−brown Ni-NVO material.

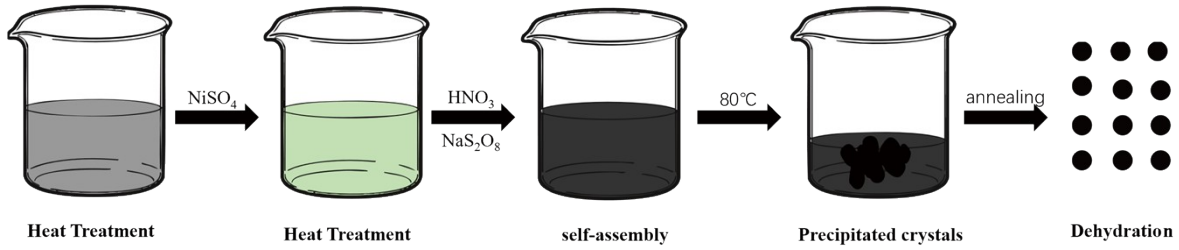

Figure. S1 Schematic synthesis of Ni-NVO

1.3 Electrochemical tests

The cathode slurry was prepared by mixing the active material, acetylene black, and PVDF binder in N-methyl-2-pyrrolidone (NMP) at a mass ratio of 7:2:1, followed by stirring for 12 hours. The homogeneous slurry was then coated onto a titanium foil current collector (thickness: 0.01 mm) using a doctor blade. The coated electrode was dried at 60 °C under dynamic vacuum for 12 hours in a vacuum oven. The resulting cathode had an average active material mass loading of 1 mg cm^{-2}, with an estimated total coating thickness (including all solid components) of approximately 30–50 μm. The button cells (CR2025) were assembled in air with zinc foil as the anode, 3 M $Zn(CF_3SO_3)_2$ as the electrolyte. The cyclic voltammetry curves (CV) and electrochemical impedance spectroscopy (EIS) were tested using the Princeton electrochemical workstation. Constant current charge−discharge tests were conducted on the battery automated testing system (LAND, CT2100A, Wuhan, China) in the voltage range of 0.2−1.8 V.

2. Supplementary Characterization

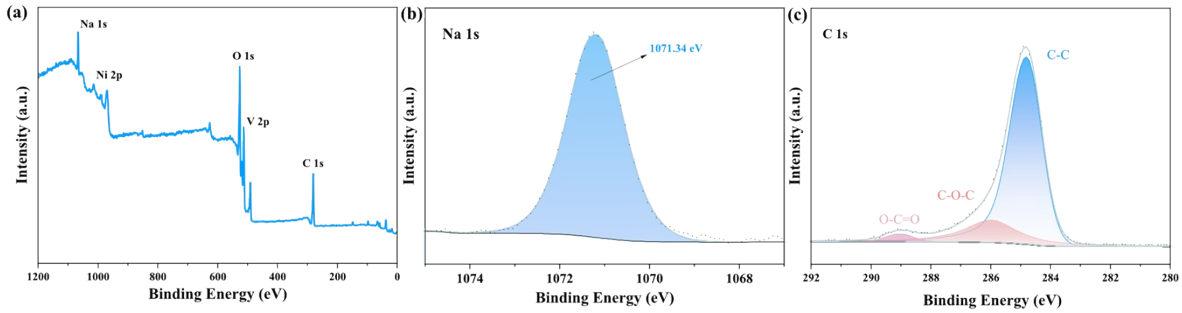

Figure. S2 (a) Full XPS spectra of Ni-NVOH, (b) Na 1s spectrum, (b) C 1s spectrum.

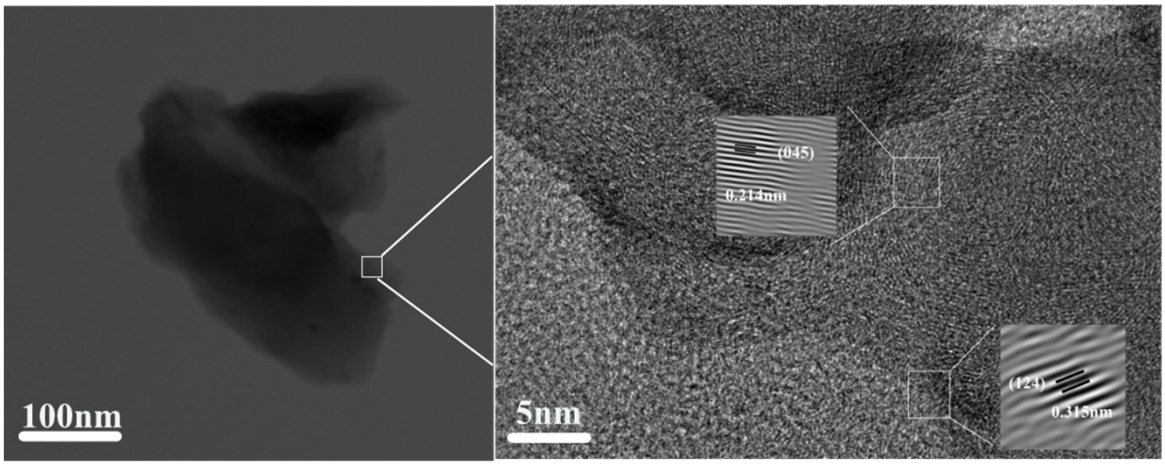

Figure. S3 HRTEM images of Ni-NVOH.

3. Supplementary measurements

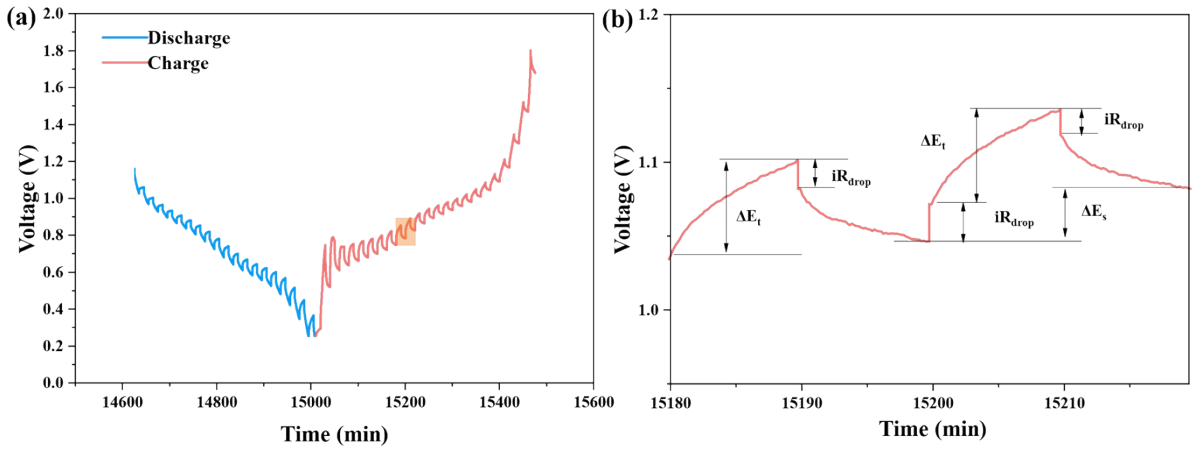

Figure. S4 Schematic illustration of a single step of the GITT profile during the charge process and discharge−charge GITT profiles at 0.1 A g^{-1}.

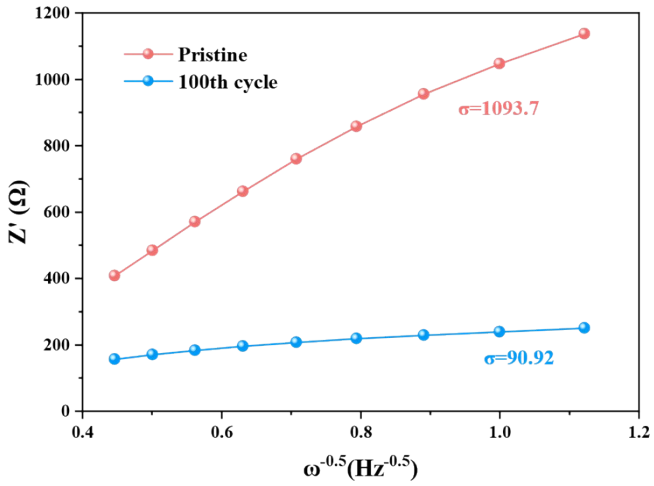

Figure. S5 The linear relationship graph between $\omega^{-0.5}$ and Z′.

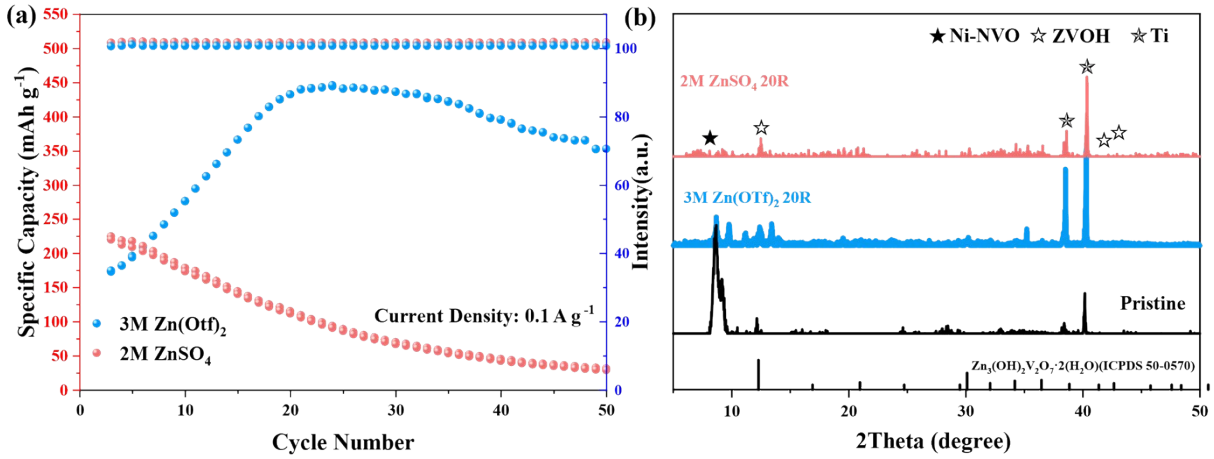

Figure. S6 Comparative electrochemical performance and structural evolution of the Ni-NVO cathode in different electrolytes: (a) Long-term cycling performance at 0.1 A g^{-1} in 2 M $ZnSO_4$ and 3 M $Zn(CF_3SO_3)_2$ electrolytes. (b) Ex-situ XRD patterns of the cathodes after the 20th cycle at 0.1 A g^{-1} in the respective electrolytes.

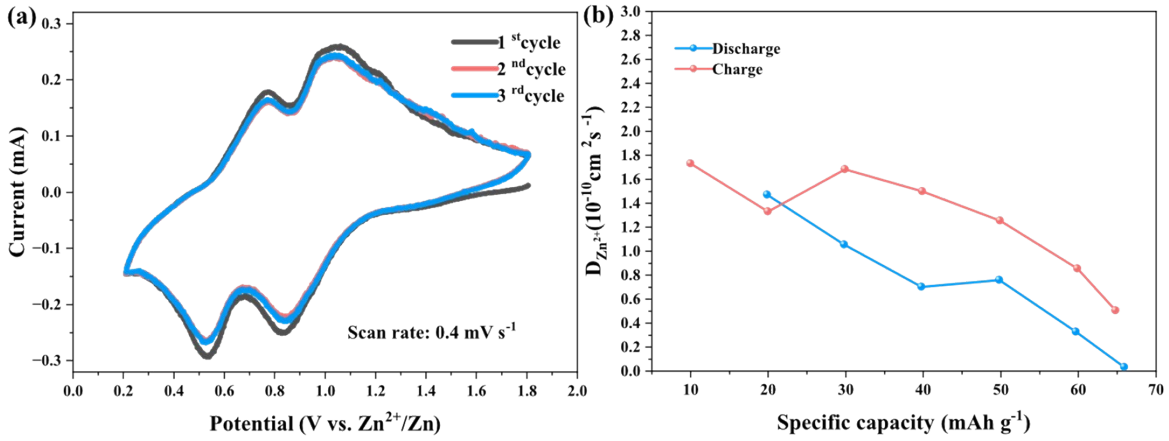

Figure. S7 Electrochemical activity and Zn^{2+} diffusion kinetics of the pristine hydrated material (Ni-NVOH): (a) The first three cyclic voltammetry (CV) curves at 0.4 mV s^{-1}. (b) The corresponding Zn^{2+} diffusion coefficient (D_{Zn}^{2+}) of Ni-NVOH.

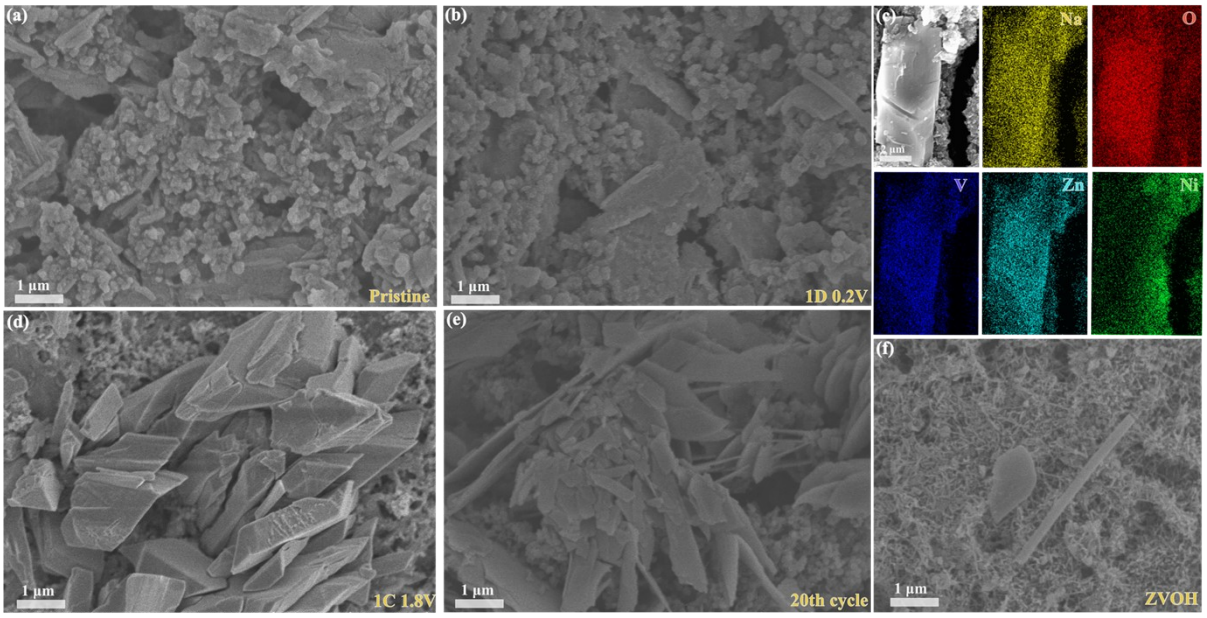

Figure. S8 Ex-situ SEM images of (a) initial electrode, (b) 1st fully discharged, (d) 1st fully charged and (e-f) 20th cycle states. (c) EDS mapping at the 1st fully discharged state.

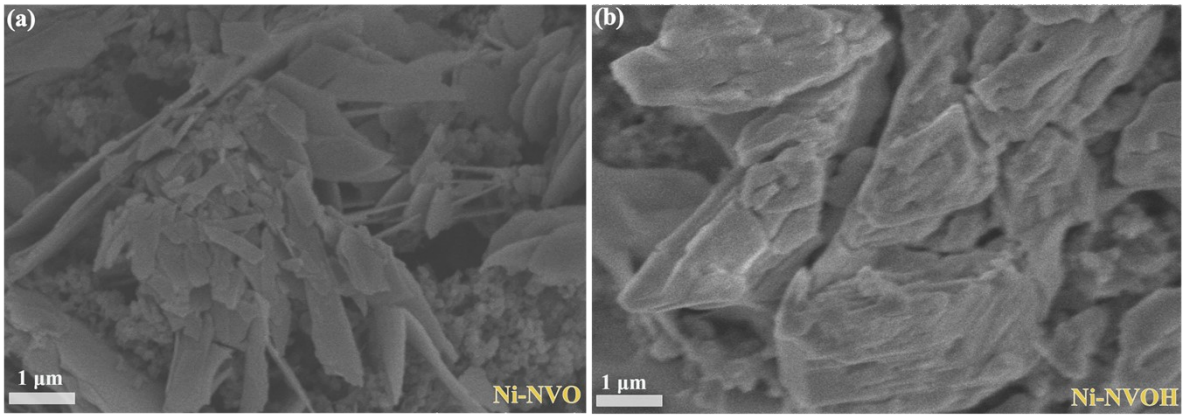

Figure. S9 Ex-situ SEM after 20th cycle states images of (a) Ni-NVO, (b) Ni-NVOH.

Table S1. Comparison of Zn−ion storage properties of NVO with currently reported cathode materials.

Cathode materials	Electrolyte	Voltage (V)	Specific capacity (mAh g^{-1})	Capacity retention (cycle numbers)	Ref.
$K_2Zn_2V_{10}O_{28}$	3 M $Zn(CF_3SO_3)_2$	0.2−1.9	223.4 (0.1 A g^{-1})	97.6% (50)	3
$Na_6[V_{10}O_{28}]$•$2.6H_2O$	3 M $Zn(CF_3SO_3)_2$	0.2−1.8	119.4 (10 A g^{-1})	89.7% (1000)	4
$K_4Na_2V_{10}O_{28}$	3 M $Zn(CF_3SO_3)_2$	0.2−1.8	102.5 (1.0 A g^{-1})	100% (1000)	5
$[Co_3(H_2O)_{12}][V_{10}^{IV}V_8^{V}O_{42}(SO_4)]\cdot 24H_2O$	2 M $Zn(CF_3SO_3)_2$	0.2−1.6	217.5 (10 A g^{-1})	90.4% (1500)	6
$(NH_4)_6(V_{10}O_{28})(H_2O)_6$/TPA	3 M $Zn(CF_3SO_3)_2$	0.2-1.8	300 (0.1 A g^{-1})	100% (100)	7
$KxH_9(PV_{14}O_{42})$	3 M $Zn(CF_3SO_3)_2$/PAM-LDH	0.3-1.5	413.3 (0.05 A g^{-1})	97.96% (2000)	8
$[H_6Mn_3V_{19}O_{46}(H_2O)_{12}]\cdot 30H_2O$	3 M $Zn(CF_3SO_3)_2$	0.2-1.9	170.5 (0.05 A g^{-1})	81.6% (100)	9
$K_2[Ni(H_2O)_6]_2[V_{10}O_{28}]\cdot 4H_2O$	7 M $ZnSO_4$	0.2-1.8	229.4 (0.1 A g^{-1})	99.1% (4500)	10
$Li_7[V_{15}O_{36}(CO_3)]$	3 M $Zn(CF_3SO_3)_2$	0.2-1.9	369.6 (0.1 A g^{-1})	99% (4500)	11
$K_7MnV_{13}O_{38}$	3 M $Zn(CF_3SO_3)_2$	0.2-1.9	150 (0.1 A g^{-1})	91.2% (1000)	12
$(NH_4)_8[V_{19}O_{41}(OH)_9]\cdot 11H_2O$	2.5 M $Zn(CF_3SO_3)_2$	0.2-1.6	413 (0.2 A g^{-1})	94% (2000)	13
$K_{10}[V_{34}O_{82}]\cdot 20H_2O$	3 M $Zn(CF_3SO_3)_2$	0.2-1.5	401 (0.05 A g^{-1})	93% (4000)	14

$Ag_x[V_{34}O_{82}]$	2.5 M $Zn(CF_3SO_3)_2$	0.2-1.6	383 (0.2 A g^{-1})	97.4% (7000)	15
$Fe_5V_{15}O_{39}(OH)_9 \cdot 9H_2O$	2 M $Zn(CF_3SO_3)_2$	0.2-1.6	409.6 (0.1 A g^{-1})	87.5% (3000)	16
PANI-$V_{10}O_{28}$	3 M $Zn(CF_3SO_3)_2$	0.2-1.6	355 (0.1 A g^{-1})	82% (2000)	17
S-doped V_2O_5	2 M $ZnSO_4$	0.4-1.5	370 (0.1 A g^{-1})	93.4% (5000)	18
Li_3VO_4–LiV_2O_5-based	3 M $ZnSO_4$	0.4-1.6	310.4 (1 A g^{-1})	85.13% (10000)	19
$NH_4V_4O_{10}$	2M $ZnSO_4$-1M Na_2SO_4	0.4-1.4	407.8 (0.1 A g^{-1})	79.5% (2000)	20
$Na_7[NiV_{14}O_{40}]$	3 M $Zn(CF_3SO_3)_2$	0.2−1.8	440 (0.1 A g^{-1})	79.5% (50)	This work

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