Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplemental Information

Impact of Sodium Vanadium Oxide (NaV_3O_8, NVO) Material Synthesis Conditions on Charge Storage Mechanism in Zn-ion Aqueous Batteries

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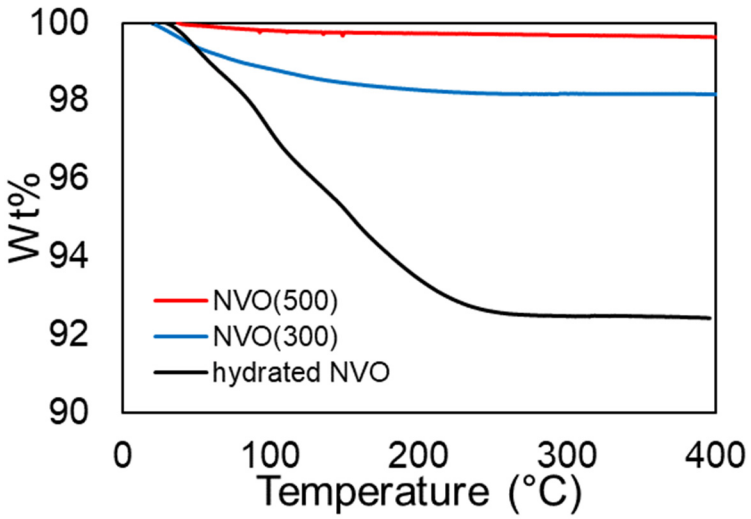

Figure S1: Thermogravimetric analysis of hydrated NVO precursor, NVO(300), and NVO(500).

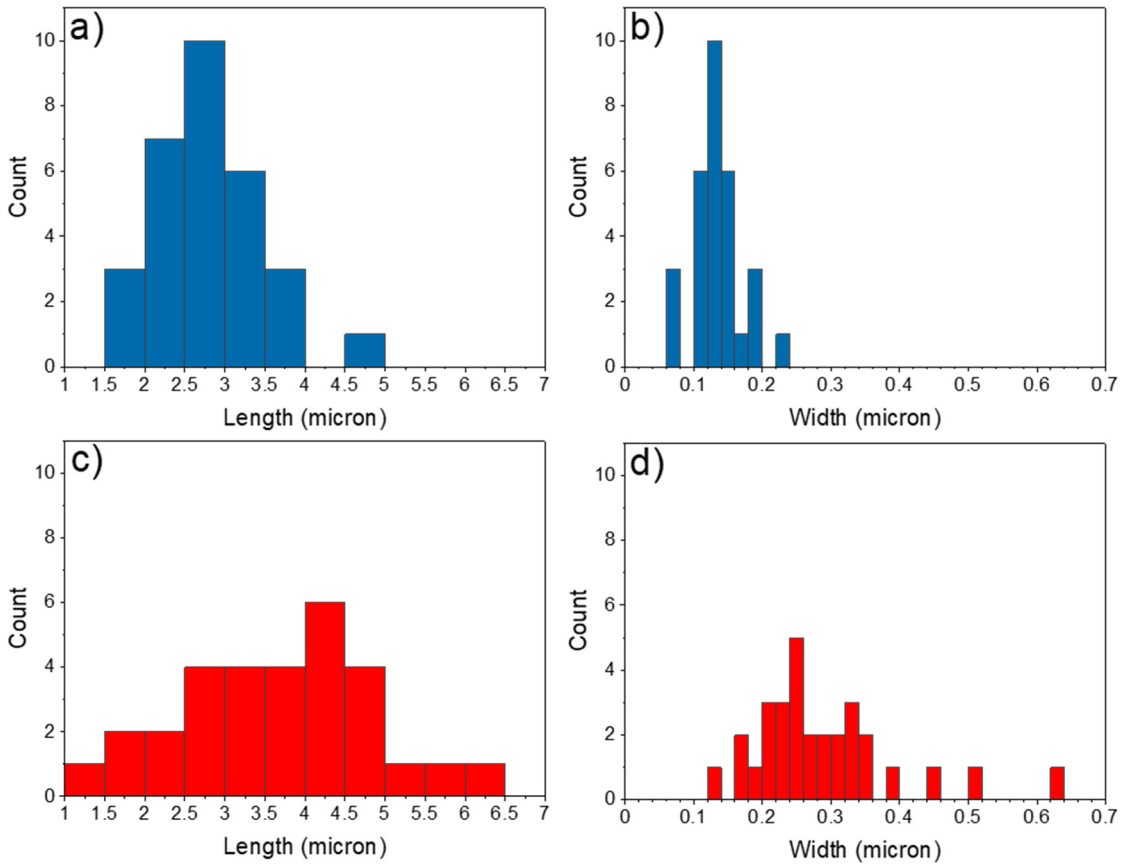

Figure S2. Particle size analysis of SEM image data for **a.** NVO(300) length **b.** NVO(300) width **c.** NVO(500) length and **d.** NVO(500) width.

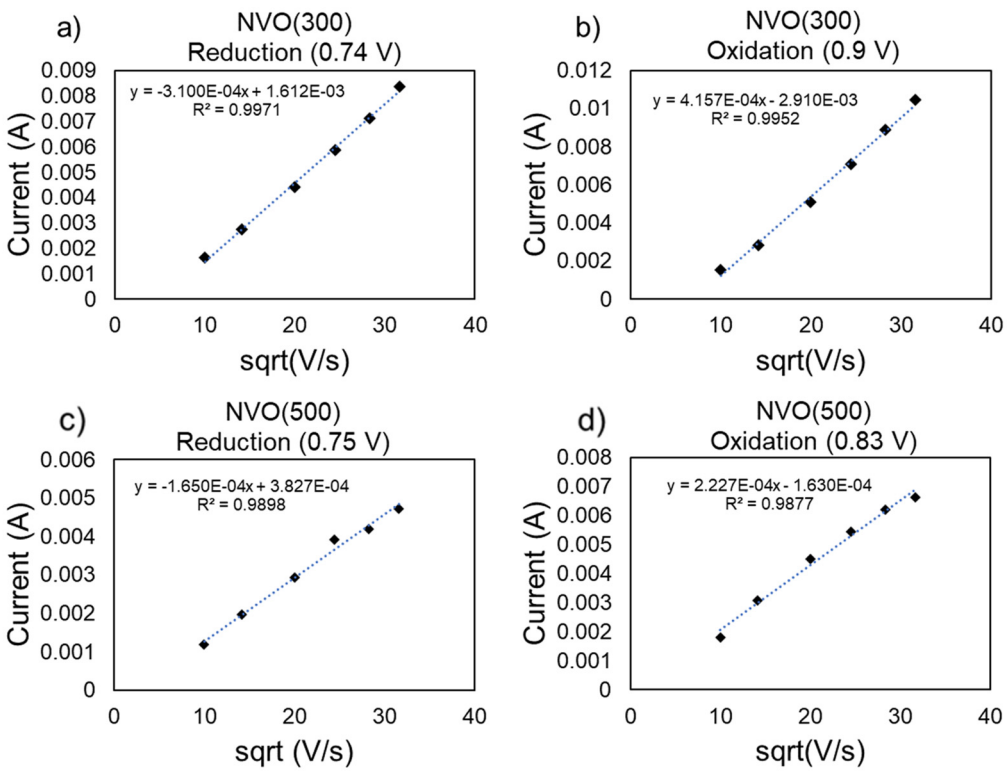

Figure S3. Peak current vs. the square root of the scan rate for **a,b** NVO(300) and NVO(500). All peak currents show linear responses to the change in scan rate, indicating free diffusion of the redox species to the electrode.

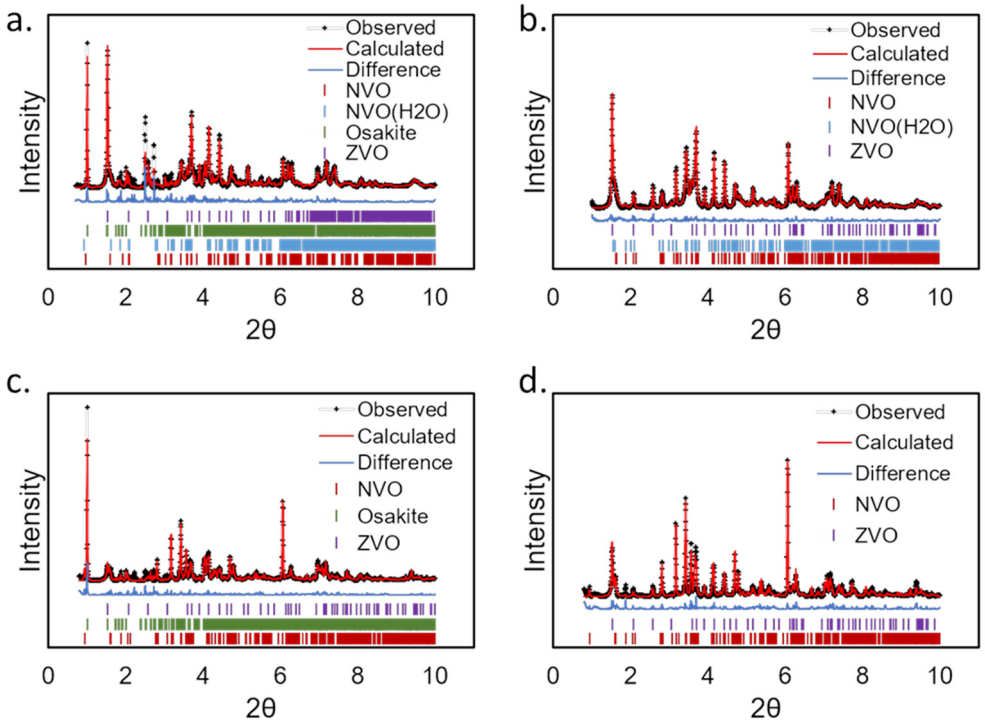

Figure S4. XRD patterns and Rietveld refinements of **a, b)** NVO(300) and **c,d)** NVO(500) electrodes after **a, c)** discharge to 0.4 V and **b, d)** charge to 1.4 V at 50 mA/g.

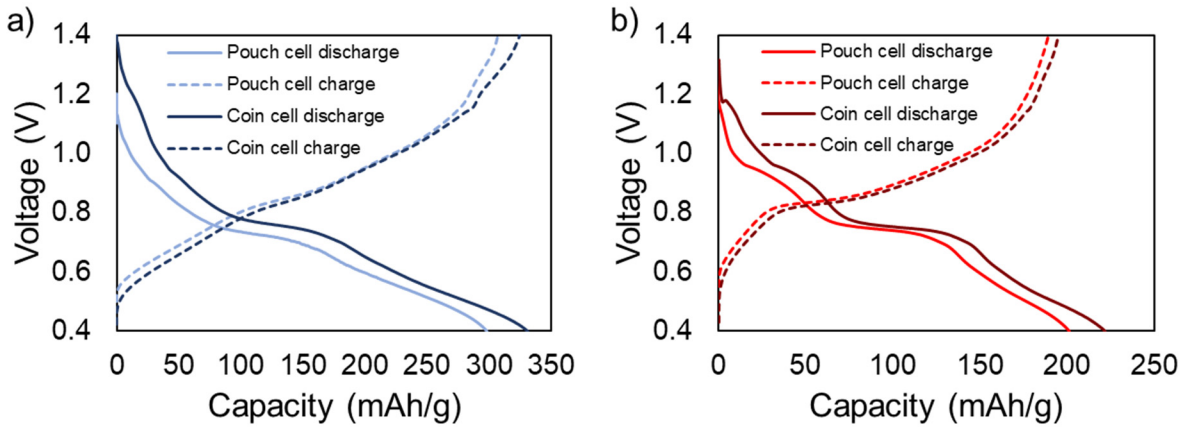

Figure S5. First cycle discharge and charge for *operando* cell and *ex situ* cell for **a)** NVO(300) and **b)** NVO(500)

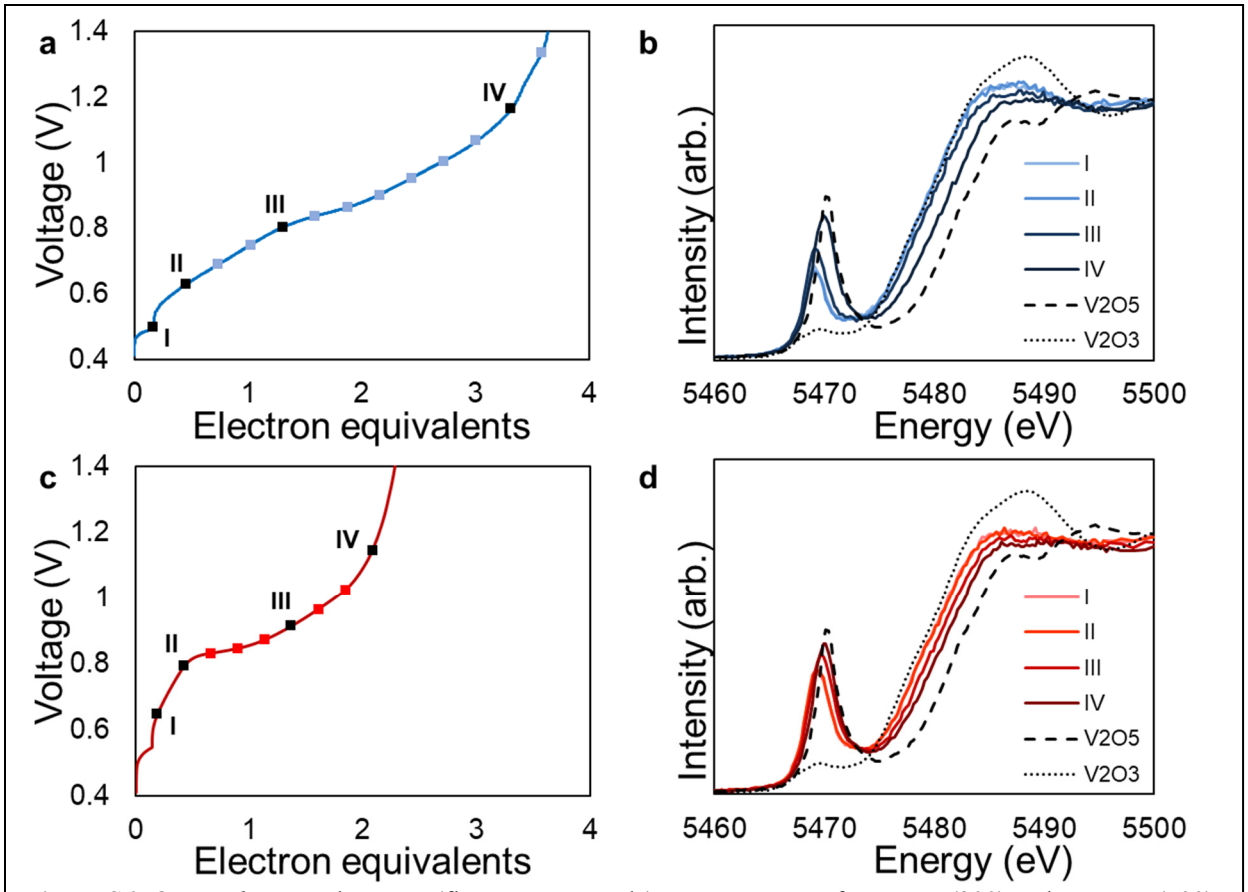

Figure S6. *Operando* V K-edge XAS (fluorescence-mode) measurements of **a,b** NVO(300) and **c,d** NVO(500) during first discharge. Voltage profiles and selected scans XANES spectra (Red dots) are presented.

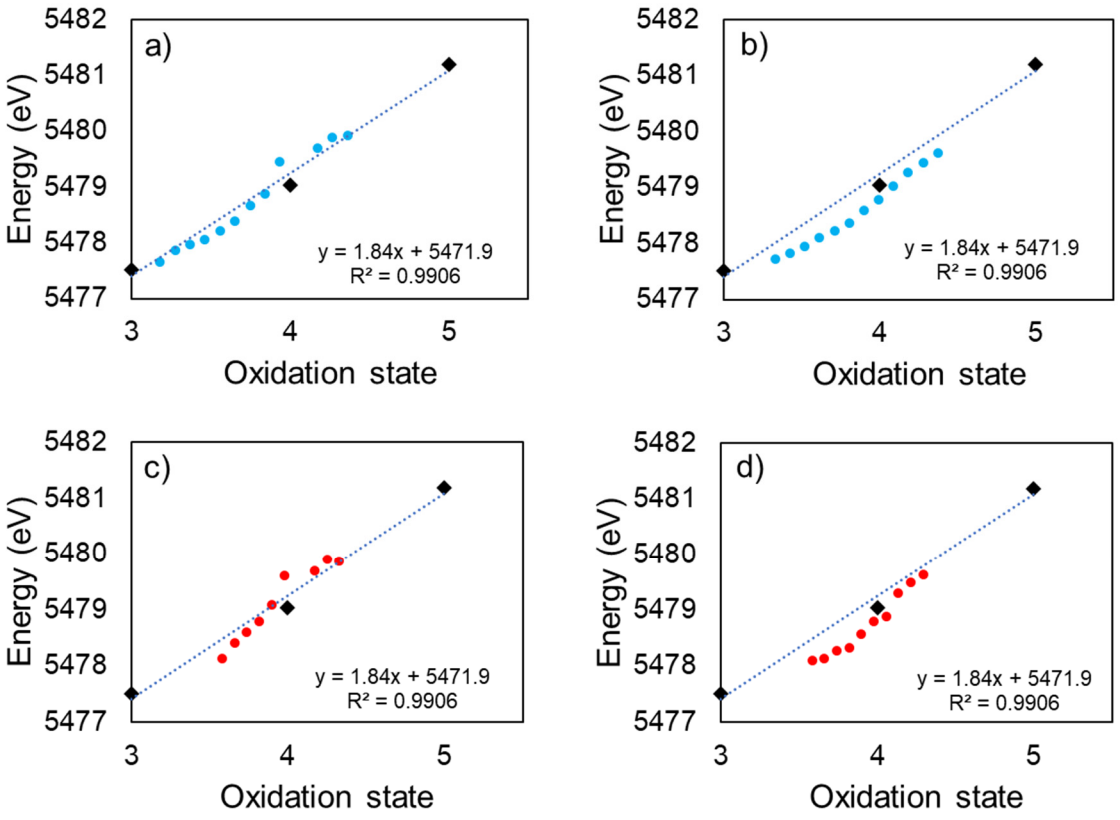

Figure S7. Change edge energy of *operando* XAS of NVO(300) cell during **a.** discharge and **b**. charge. Change edge energy of *operando* XAS of NVO(500) cell during **c.** discharge and **d**. charge. V_2O_3, VO_4, and V_2O_5 edge energies are shown as red dots for oxidation states V^{3+}, V^{4+}, and V^{5+}, respectively.

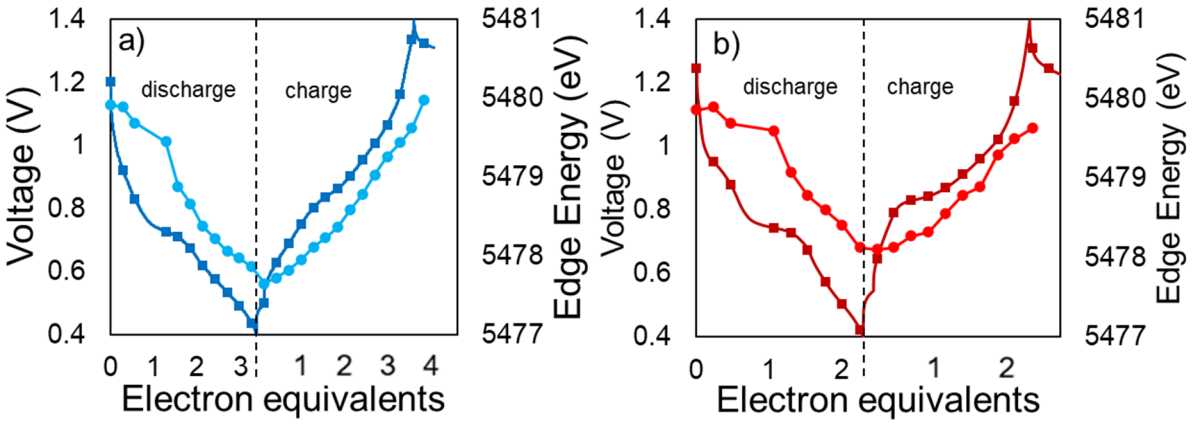

Figure S8. V K-edge position during cycle of **a.** NVO(300) and **b.** NVO(500) *operando* cells. Voltage profiles are denoted with square symbols. Edge position is denoted with circle symbols

Table S1. Rietveld refinement parameters of NVO(300) and NVO(500) powders.

Parameter	NVO(300) Anhydrous/Monohydrate	NVO(500)
Space Group	P_{21}/m	P_{21}/m
Phase Composition	23(1) %/76(1) %	100 %
a (Å)	7.43(1) Å/7.221(5) Å	7.295(1) Å
b (Å)	3.620(1) Å/3.6134(4) Å	3.6109(2) Å
c (Å)	12.10(3) Å/12.20(1) Å	12.18(1) Å
α (°)	90.0 °/90.0 °	90.0 °
β (°)	106.85(5) °/107.66(2) °	107.77(1) °
γ (°)	90.0 °/90 °	90.0 °
V ($Å^3$)	311.8(2) $Å^3$/303.4(1) $Å^3$	305.55(4) $Å^3$
Crystallite Size (Axial, nm)	0.0193(6) µm/0.0167(4) µm	0.061(1) µm
Crystallite Size (equatorial, nm)	1.0 µm/1.0 µm	1.0 µm
microstrain (%)	0.12(1) %/0.07(3) %	0.02(1) %
$\%R_{wp}$	5.99 %	8.26 %

Table S2. Refined atomic positions of NVO(300) powder.

Atom	X Anhydrous/Monohydrate	Y Anhydrous/Monohydrate	Z Anhydrous/Monohydrate
V1	0.897(4)/0.877(3)	0.250/0.250	0.545(5)/0.548(1)
V2	0.161(4)/0.204(2)	0.250/0.250	0.100(4) /0.0837(9)
V3	0.024(5)/0.075(2)	0.250/0.250	0.797(4)/0.815(1)
O1	0.01(1)/0.0213(7)	0.250/0.250	0.42(2)/0.436(6)
O2	0.82(1)/0.73(1)	0.250/0.250	0.87(2)/0.89(4)
O3	0.79(2)/0.842(7)	0.250/0.250	0.64(1)/0.669(4)
O4	0.15(1)/0.428(8)	0.250/0.250	0.26(1)/0.189(4)
O5	0.58(1)/0.624(9)	0.250/0.250	0.56(1)/0.440(4)
O6	0.24(1)/0.307(6)	0.250/0.250	0.94(1)/0.960(3)
O7	0.30(1)/0.248(8)	0.250/0.250	0.80(1)/0.739(4)
O8	1.03(1)/1.01(1)	0.250/0.250	0.19(2)/0.184(4)
Na1	0.42(1)/0.48(1)	0.250/0.250	0.66(1)/0.672(5)
Na2	0.568/0.574(4)	0.250/0.250	0.059/0.038(5)
O_{H_2O}	---/0.537(8)	---/0.250	---/0.352(3)

Table S3. Refined atomic positions of NVO(500) powder.

Atom	X	Y	Z
V1	0.857(1)	0.250	0.5453(7)
V2	0.181(1)	0.250	0.0806(6)
V3	0.075(1)	0.250	0.8132(6)
O1	0.069(3)	0.250	0.451(2)
O2	0.889(3)	0.250	0.925(2)
O3	0.816(3)	0.250	0.678(2)
O4	0.371(3)	0.250	0.191(2)
O5	0.632(4)	0.250	0.452(2)
O6	0.270(3)	0.250	0.965(2)
O7	0.229(3)	0.250	0.737(2)
O8	1.000(4)	0.250	0.169(2)
Na1	0.500(2)	0.250	0.669(1)
Na2	0.586	0.250	0.059

Table S4. Cathodic and anodic peak values, ΔE values, and $E_{1/2}$ values at the different scan rates for CV of NVO(300).

Redox Couple	Scan Rate (mV/s)	Cathodic Peak (V)	Anodic peak (V)	ΔE (V)	$E_{1/2}$ (V)
1	0.1	0.884	1.020	0.136	0.952
	0.2	0.872	1.030	0.158	0.951
	0.4	0.856	1.051	0.195	0.954
	0.6	0.838	1.082	0.244	0.96
	0.8	0.820	1.113	0.293	0.967
	1	0.810	1.142	0.332	0.976
2	0.1	0.740	0.886	0.146	0.813
	0.2	0.714	0.912	0.198	0.813
	0.4	0.682	0.957	0.275	0.8195
	0.6	0.658	0.994	0.336	0.826
	0.8	0.630	1.031	0.401	0.8305
	1	0.605	1.056	0.450	0.831

Table S5. Cathodic and anodic peak values, ΔE values, and $E_{1/2}$ values at the different scan rates for CV of NVO(500).

Redox Couple	Scan Rate (mV/s)	Cathodic Peak (V)	Anodic peak (V)	ΔE (V)	$E_{1/2}$ (V)
1	0.1	0.953	0.984	0.031	0.969
	0.2	0.940	0.998	0.058	0.969
	0.4	0.923	1.017	0.094	0.97
	0.6	0.915	1.042	0.127	0.979
	0.8	0.909	1.050	0.141	0.980
	1	0.905	1.065	0.16	0.985
2	0.1	0.731	0.885	0.150	0.81
	0.2	0.716	0.906	0.190	0.811
	0.4	0.698	0.931	0.230	0.819
	0.6	0.688	0.953	0.260	0.822
	0.8	0.676	0.967	0.291	0.8215
	1	0.670	0.980	0.306	0.827

Table S6. Rietveld refinement parameters of an NVO(300) electrode following discharge at 50 mA/g to 0.4 V.

Parameter	NVO(300) Anhydrous	NVO(300) Monohydrate	ZHS	ZVO
Space Group	$P2_1/m$	$P2_1/m$	P-1	P-3/m1
Phase Composition	26(7) %	22(5) %	16(1) %	36(1) %
a (Å)	7.26(7) Å	7.11(8) Å	8.328(9) Å	6.109(1) Å
b (Å)	3.620(1) Å	3.612(3) Å	8.323(9) Å	6.109(1) Å
c (Å)	12.0(1) Å	12.3(2) Å	10.987(6) Å	7.160(2) Å
α (°)	90.0°	90.0°	94.05(4)°	90.0°
β (°)	108.0(3)°	105.8(3)°	83.32(3)°	90.0°

Table S7. Rietveld refinement parameters of an NVO(300) electrode following discharge to 0.4 V and charge to 1.4 V at 50 mA/g.

Parameter	NVO(300) Anhydrous	NVO(300) Monohydrate	ZVO
Space Group	$P2_1/m$	$P2_1/m$	P-3/m1
Phase Composition	61(1) %	13(1) %	26.2(4) %
a (Å)	7.05(1) Å	7.328(8) Å	6.0884(9) Å
b (Å)	3.6138(2) Å	3.600(1) Å	6.0884(9) Å
c (Å)	12.32(3) Å	12.37(3) Å	7.1798(9) Å
α (°)	90.0°	90.0°	90.0°
β (°)	108.34(5)°	109.57(4)°	90.0°

Table S8. Rietveld refinement parameters of NVO(500) electrode after discharge at 50 mA/g to 0.4 V.

Parameter	NVO(500)	ZHS	ZVO
Space Group	$P2_1/m$	P-1	P-3/m1
Phase Composition	62(1) %	25.4(8) %	12.3(8) %
a (Å)	7.156(7) Å	8.355(6) Å	6.125(5) Å
b (Å)	3.6245(2) Å	8.356(6) Å	6.125(5) Å
c (Å)	12.34(1) Å	11.006(6) Å	7.151(4) Å
α (°)	90.0°	94.27(3)°	90.0°
β (°)	108.44(2)°	83.06(3)°	90.0°

Table S9. Rietveld refinement parameters of NVO(500) electrode after discharge to 0.4 V and charge to 1.4 V at 50 mA/g.

Parameter	NVO(500)	ZVO
Space Group	$P2_1/m$	P-3/m1
Phase Composition	76.6(9) %	23.4(6) %
a (Å)	7.151(6) Å	6.105(2) Å
b (Å)	3.6254(2) Å	6.105(2) Å
c (Å)	12.35(1) Å	7.187(2) Å
α (°)	90.0°	90.0°
β (°)	108.43(2)°	90.0°