

ADVANCED ENERGY MATERIALS

Supporting Information

for *Adv. Energy Mater.*, DOI: 10.1002/aenm.201702463

Sodium Ion Stabilized Vanadium Oxide Nanowire Cathode
for High-Performance Zinc-Ion Batteries

*Pan He, Guobin Zhang, Xiaobin Liao, Mengyu Yan, * Xu Xu,
Qinyou An, Jun Liu, and Liqiang Mai**

Supporting Information

Sodium Ion Stabilized Vanadium Oxide Nanowire Cathode for High-Performance Zinc-ion Batteries

*Pan He¹, Guobin Zhang¹, Xiaobin Liao¹, Mengyu Yan^{1,2}, * Xu Xu¹, Qinyou An¹, Jun Liu^{1,3}, and Liqiang Mai^{1,4}**

Experimental Section***Synthesis***

V₂O₅ nanowires were prepared via a simple hydrothermal method. Briefly, 0.364 g V₂O₅ (Xiya Reagent, GR, 99.5%) was dissolved in 30 ml deionized water in a glass jar, then 10 mL H₂O₂ (Aladdin, AR, 30.0%) was added in the solution with continuous magnetic stirring at room temperature for 2 h. After that, the mixture was transferred to a 50 mL Teflon-lined sealed autoclave and maintained at 200 °C for 96 h. Afterward, the system was cooled down to room temperature naturally and the samples were washed with distilled water and ethanol thoroughly for 3 times, respectively. The final product was dried at 60 °C for 8 h in air, and the yellow powder was obtained.

NVO nanowires were prepared via a simple hydrothermal method. Briefly, 0.1818 g V₂O₅ was dissolved in the solution of 30 ml deionized water and 0.35 mL NaOH (Aladdin, AR, 97.0%) solution (1 mol L⁻¹) in a glass jar. Then, 0.1 g PEG-4000 (Sinopharm Chemical Reagent limited corporation, CP, 3500 ~ 4500) was added in the homogeneous solution with continuous magnetic stirring at room temperature for 15 min. After that, the mixture was transferred to a 50 mL Teflon-lined sealed autoclave and maintained at 180 °C for 48 h. Afterward, the system was cooled down to room temperature naturally and the samples were washed with distilled water and ethanol thoroughly for 3 times, respectively. The final product was dried at 60 °C for 8 h in air, and the green-yellow powder was obtained.

Material characterizations

The as-prepared samples were characterized by power X-ray diffraction (XRD, D8 Discover X-ray diffractometer with Cu K_α radiation), X-ray photoelectron spectroscopy (XPS, Thermo Scientific Escalab 250Xi), Raman spectra (Renishaw INVIA), field emission scanning electron microscopy (FESEM, JSM-7100F) transmission electron microscopy (TEM, JEM-2100F) and Energy-dispersive X-ray spectra (EDX, Oxford IE250). Inductively Coupled Plasma Optical Emission Spectroscopy analysis (ICP-OES, JY/T015-1996): Na/V compositions obtained for the pristine Na_{0.33}V₂O₅ (Sample 1), and discharged

electrodes (Sample 2) in the third cycle (the weight of Sample 1 and 2 were 6.24 mg and 5.93 mg, respectively). Electrodes were discharged to 0.2 V at the current density of 200 mA g⁻¹. At this rate, a discharge capacity of 232 mA h g⁻¹ was obtained after discharged to 0.2 V in the third cycle. Both Sample 1 and 2 were washed with distilled water for three times, and dried at 40 °C for 6 h before the ICP-OES tests.

Electrochemical characterizations

The Na_{0.33}V₂O₅ electrode was prepared by mixing NVO (70 wt%), acetylene black (Super-P, 20 wt%), and polyvinylidene fluoride (PVDF, 10 wt%), then the slurry was cast onto Ti foil and dried in a vacuum oven at 60 °C for 8 h. The mass loading of active materials was 1–2 mg cm⁻². Zinc foil and glass fiber membrane were used as the anode and separator, respectively, and 3 M Zinc trifluoromethanesulfonate (Aladdin, AR, 98.0%) solution was used as the electrolyte. A CR2016-type coin cell was assembled in the air atmosphere to evaluate the electrochemical performance on a LAND battery testing system (CT2001A). Cyclic voltammograms (CV) were test on a CHI600E electrochemical workstation. All of the tests were performed at room temperature.

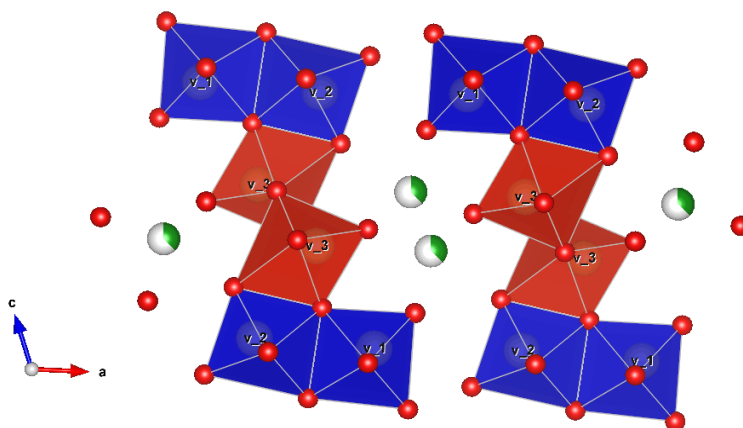


Figure S1. The crystal structure of NVO nanowire.

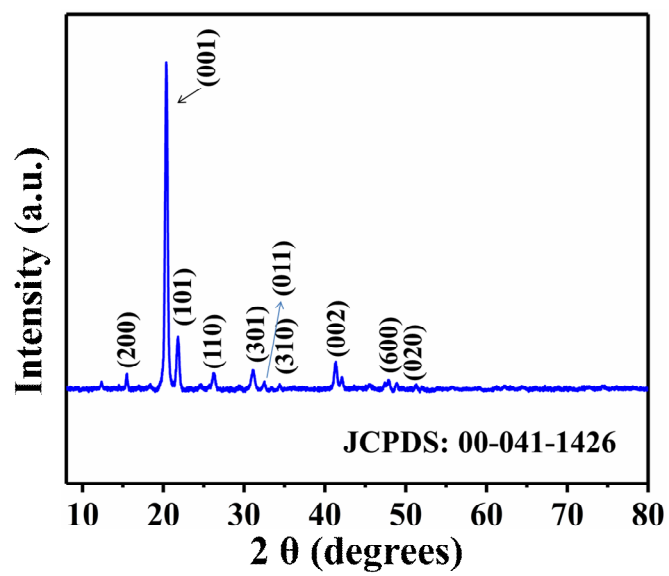


Figure S2. The XRD pattern of V₂O₅ nanowire.

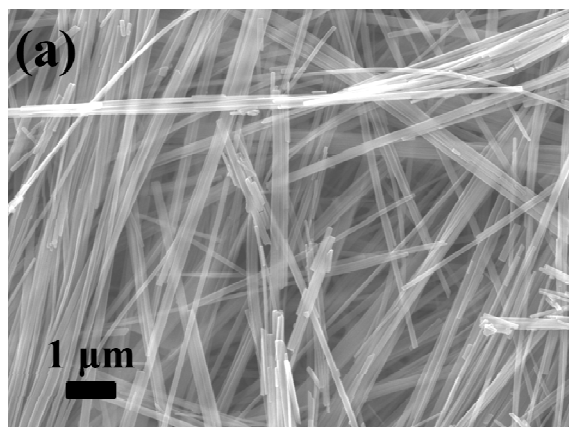


Figure S3. The SEM image of NVO nanowire.

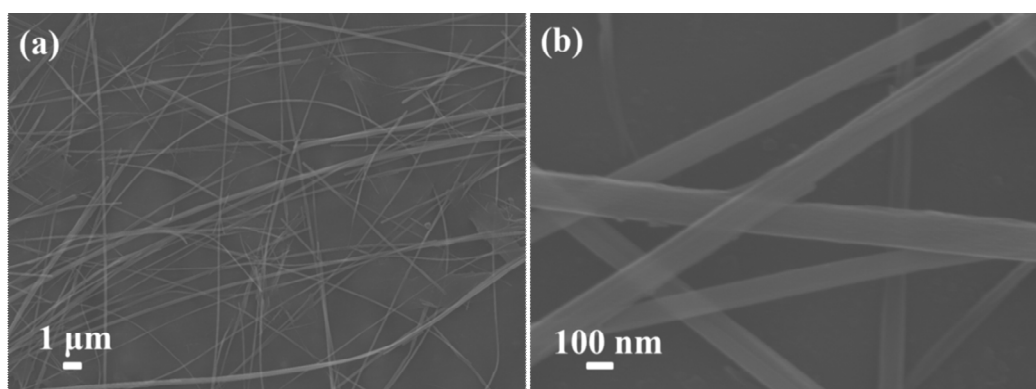


Figure S4. The SEM image of V₂O₅ nanowire.

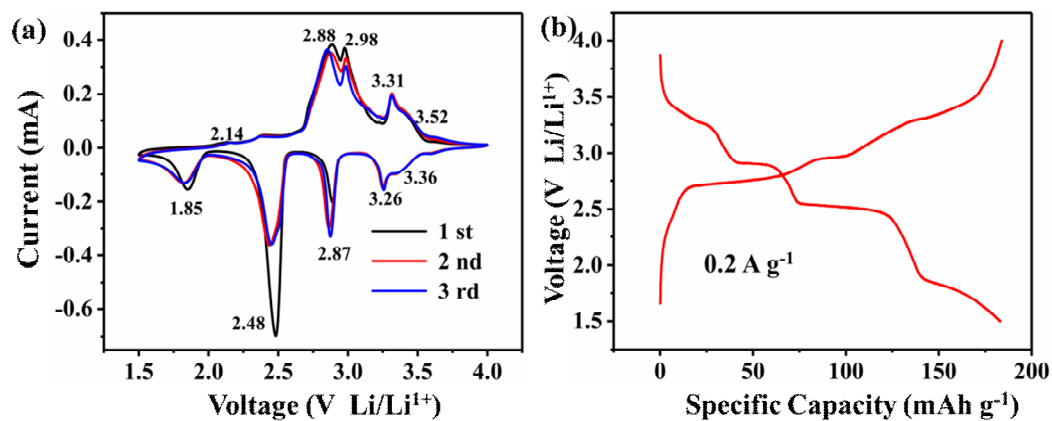


Figure S5. (a) The CV curves of NVO electrode at a scan rate of 0.2 mV s^{-1} in the voltage range of 1.5 – 4.0 V, (b) Galvanostatic charge/discharge curves of NVO at 0.2 A g^{-1} for LIBs. The electrolyte was composed of 1 M LiPF_6 dissolved in ethylene carbon (EC)/dimethyl carbonate (DMC) with a volume ratio of 1 : 1.

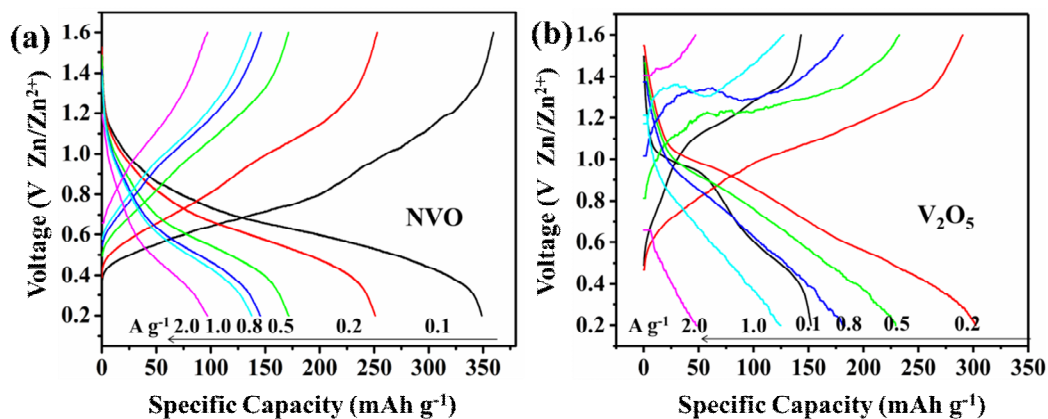


Figure S6. The galvanostatic charge/discharge curves of NVO (a), and V_2O_5 (b) at the current densities of 0.1, 0.2, 0.5, 0.8, 1.0 and 2.0 A g^{-1} .

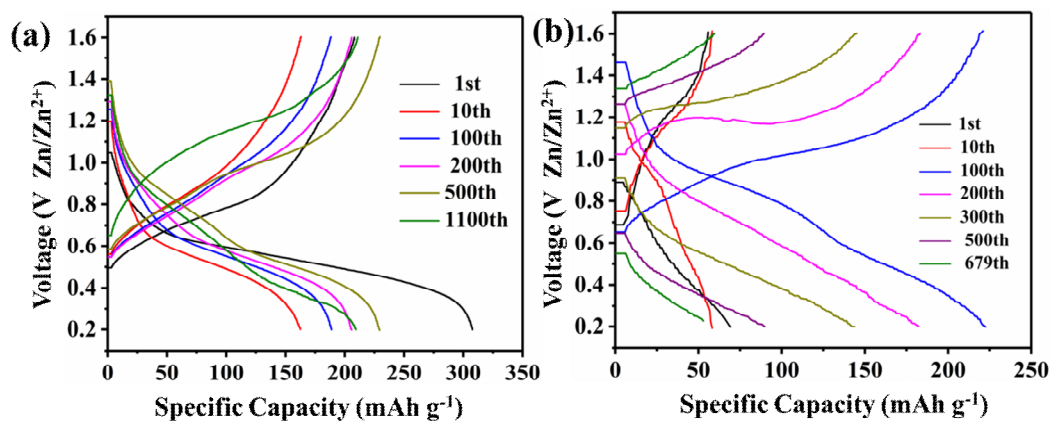


Figure S7. The galvanostatic charge/discharge curves of NVO (a), and V₂O₅ (b) at 1.0 A g⁻¹

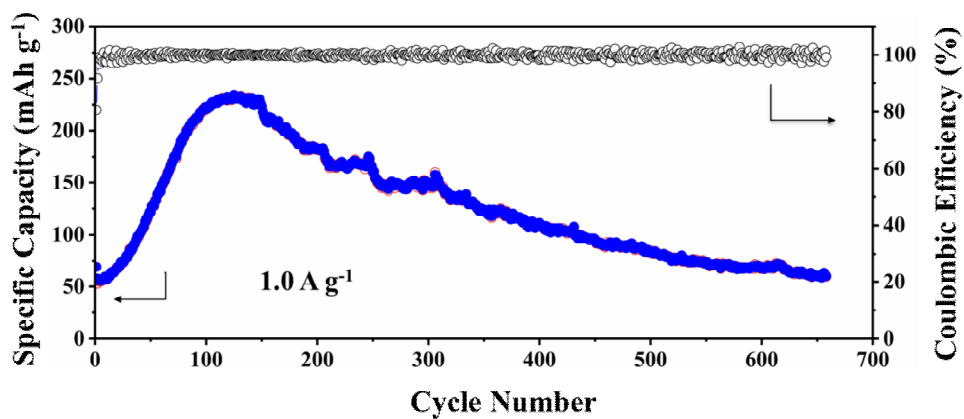


Figure S8. Cycling performance of V₂O₅ at 1.0 A g⁻¹

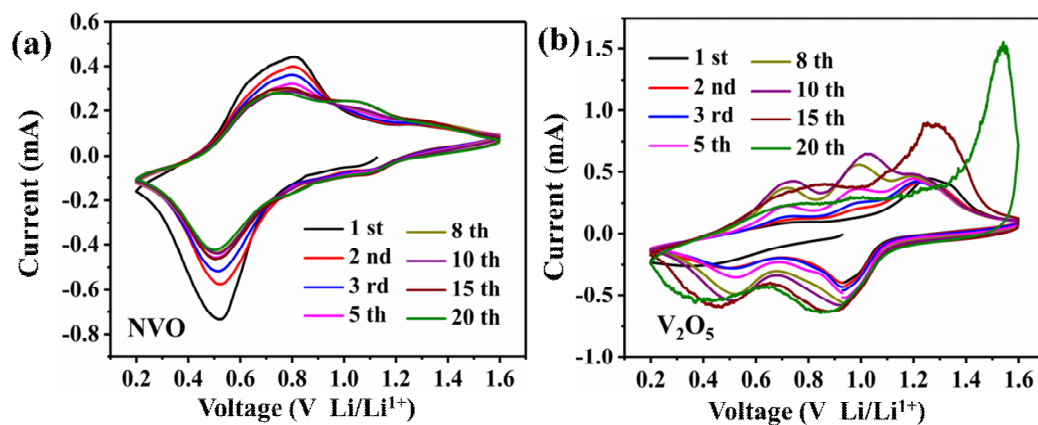


Figure S9. The CV curves of NVO (a), and V_2O_5 (b) electrode at a scan rate of 0.5 mV s^{-1} in the voltage range of $0.2 - 1.6 \text{ V}$

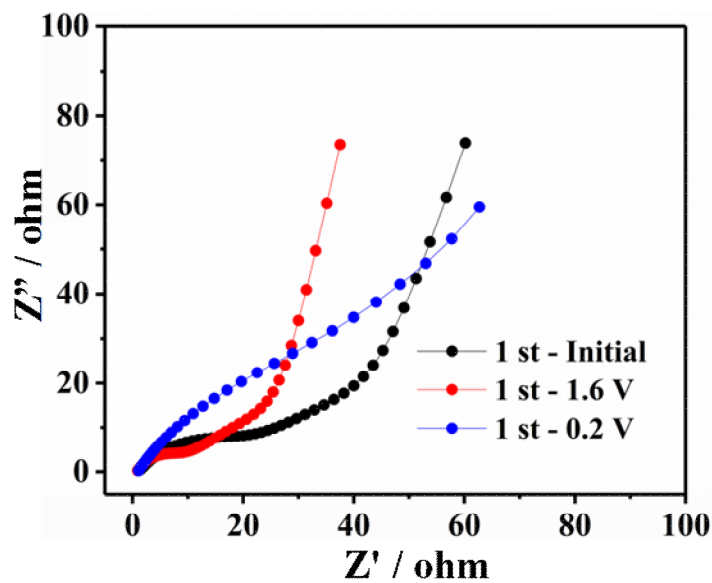


Figure S10. Alternating-current impedance plots of NVO at initial, charge to 1.6 V , and discharged to 0.2 V states.

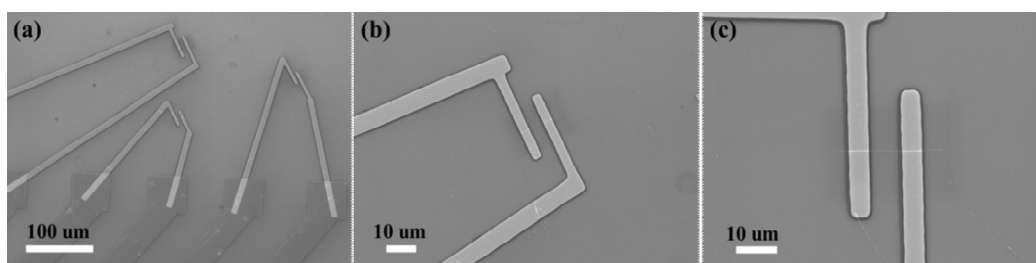


Figure S11. The SEM image of NVO (a, b), and V_2O_5 (c) single nanowire device.

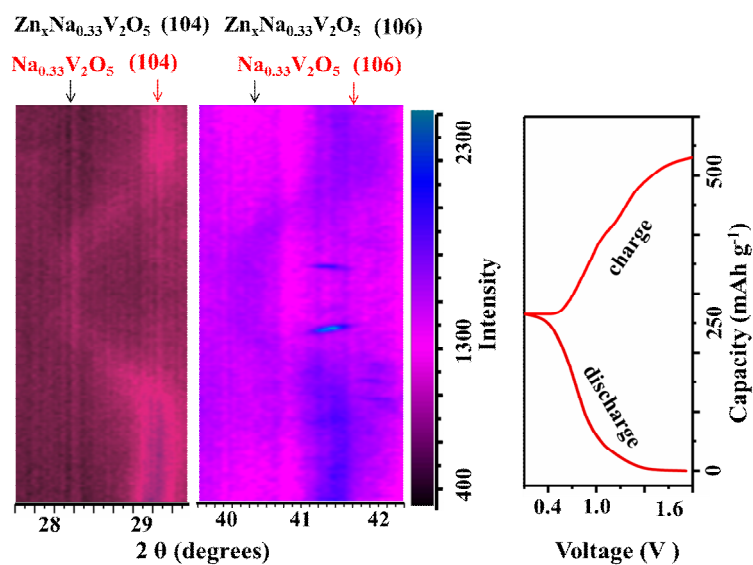


Figure S12. The *in situ* XRD patterns of NVO electrode and corresponding galvanostatic charge and discharge curves at 0.2 A g^{-1} . The 2θ are recorded from 27.6° to 29.3° , and from 39.7° to 42.3° , which can well reflect the structural changes of $Na_{0.33}V_2O_5$. The two peaks, located at 29.0° and 41.3° , shift repeatedly during the galvanostatic discharge/charge processes, which reflect the variation of (104) and (106), respectively.

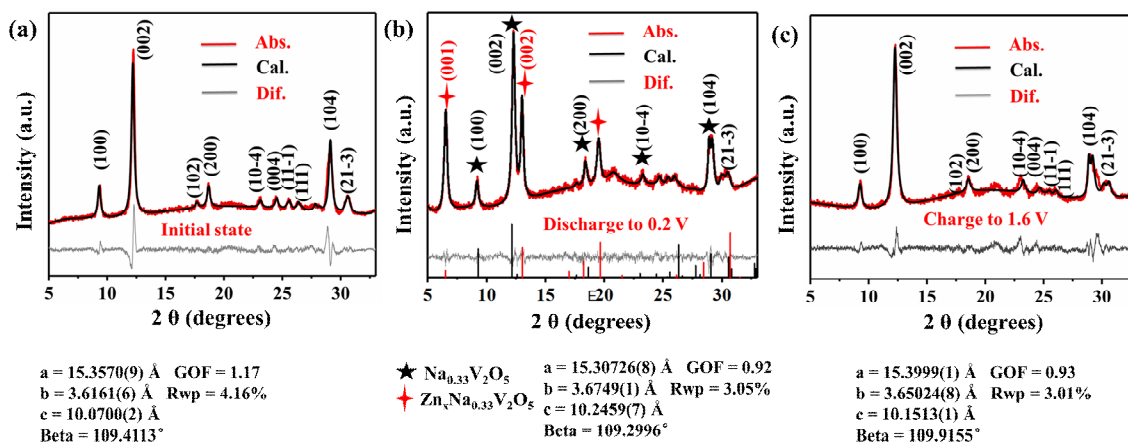


Figure S13. The Rietveld refinement XRD of NVO electrode at different states (a) initial, (b) discharged to 0.2 V, and (c) charged to 1.6 V.

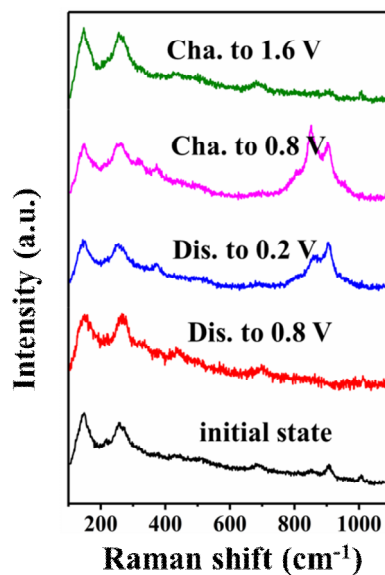


Figure S14. The *ex situ* Raman spectra of NVO electrode at different charge/discharge states.

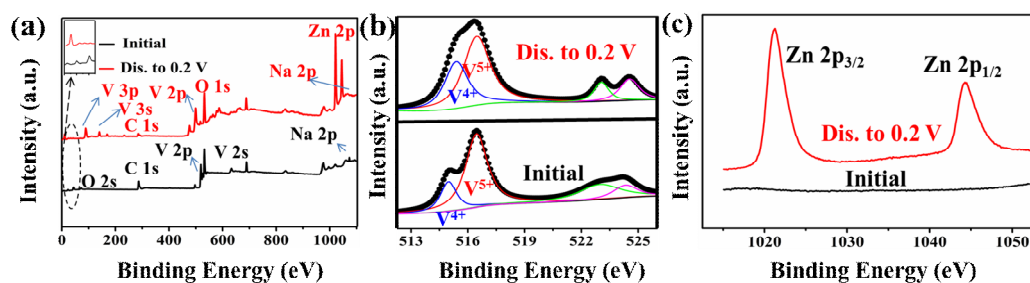


Figure S15. The XPS spectra of NVO electrode at initial and full discharge states (a) and the high-resolution XPS spectra of vanadium (b) and (c) zinc in the NVO electrode.

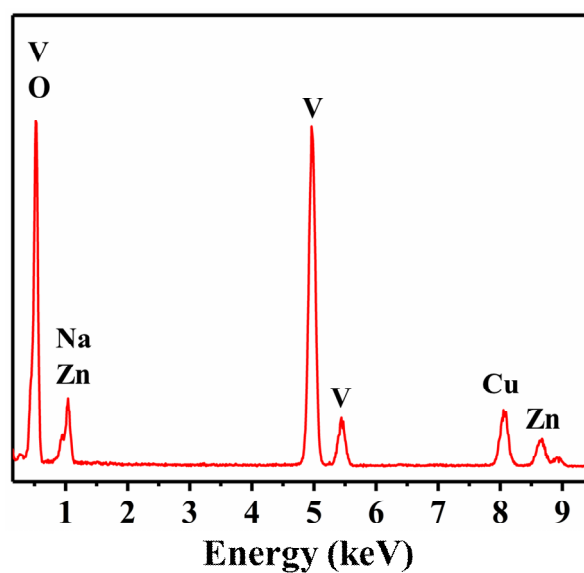


Figure S16. The EDX pattern of NVO electrode at a full discharge state after 3 cycles.

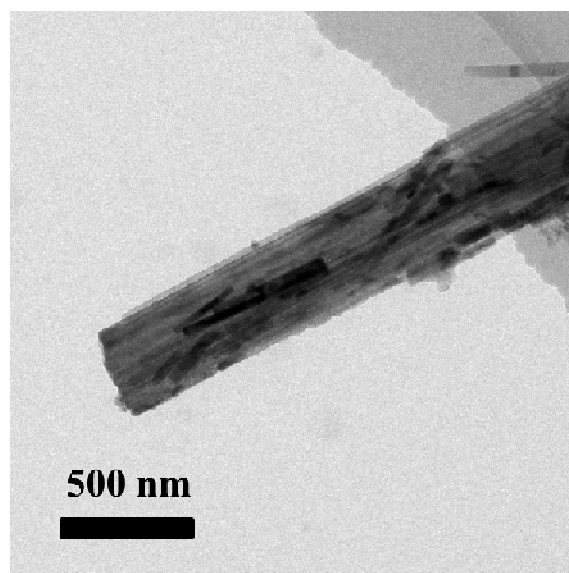


Figure S17. The TEM images of the NVO electrode after 100 cycles.

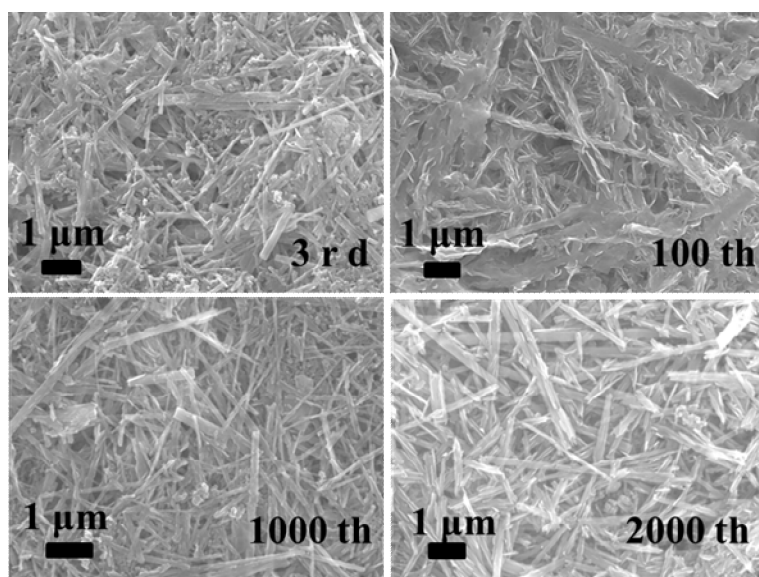


Figure S18. The SEM images of the NVO nanowires after different cycles.

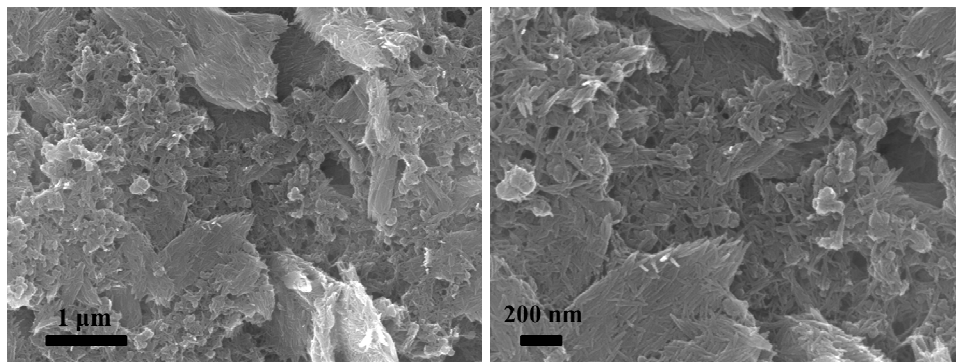


Figure S19. The SEM images of V_2O_5 nanowires after 100 cycles.

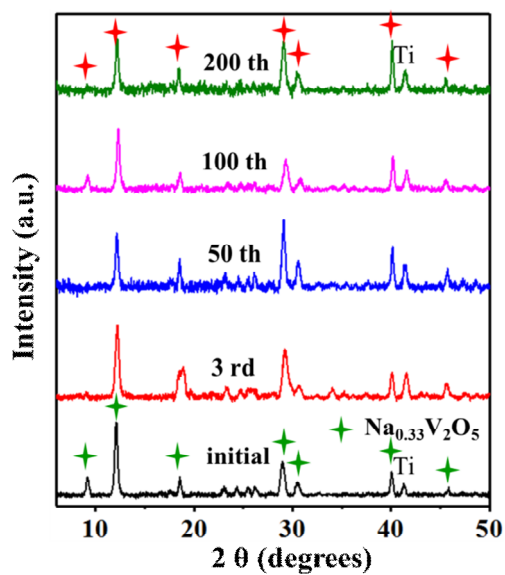


Figure S20. The XRD patterns of NVO electrode at different cycles.

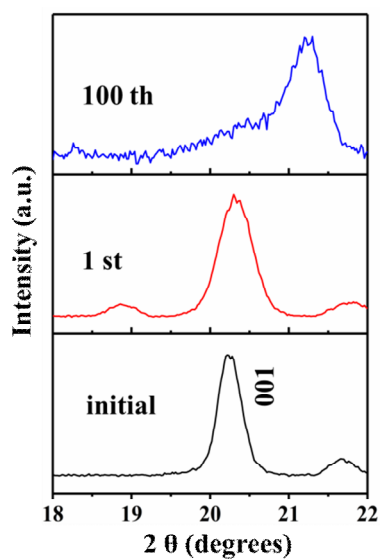


Figure S21. The XRD patterns of V_2O_5 electrode at different cycles.

Table S1. The spectra of NVO after different cycles.

NVO	Rc (Ω)	Rct (Ω)
Initial	0.99547	15.01
1st 0.2 V	0.94688	32.67
1st 1.6 V	0.69384	5.563
5th 1.6 V	0.93289	9.985
10th 1.6 V	0.85577	11.47
30th 1.6 V	0.9483	16.06
50 th 1.6 V	0.84681	13.79
80th 1.6 V	1.124	11.18
100th 1.6 V	1.186	12.96

Table S2. The spectra of NVO and V₂O₅ electrode after 1st cycle.

state	Rc (Ω)	Rct (Ω)
NVO 1st 1.6 V	0.69384	5.563
V ₂ O ₅ 1st 1.6 V	1.166	8.718

Table S3. The ICP-OES result of the electrolyte at different cycles.

Sample	Na (mg L ⁻¹)	V (mg L ⁻¹)	Zn (mg L ⁻¹)
Initial state	1.9318	Undetected	3.5916×10 ³
After 1st	1.9409	0.0054	3.3494×10 ³
After 10th	1.8682	0.0581	3.5169×10 ³
After 50th	1.9091	0.0392	3.4468×10 ³
After 100th	1.9297	0.0460	3.4122×10 ³

Table S4 The ICP result of the NVO electrode at different states.

Sample	Na (%)	V (%)	Weight ratio (m _V /m _{Na})	Molar ratio (M _V /M _{Na})
Initial state (1)	2.34	28.50	12.18	5.52
Char. to 1.6 V (2)	2.09	25.88	12.38	5.58