

Supplementary Materials for

The Importance of Electrolyte Environment during In Situ Self-transformation for Synthesizing $V_2O_5 \cdot nH_2O$

Haijia Quan, Chen Wang, Dongxu Guo, Xiaofeng Wang, Chenglin Sun* and Shenghan Wang*

*Corresponding author. Email: shenghan@jlu.edu.cn

Experimental Section

Material Preparation:

V_2O_5 (Alfa Aesar, 99.6%) and C_2H_5OH (Aladdin, 99.5%) were purchased and used without further purification. VO_2 was synthesized following a previously established protocol.[1] In a typical procedure, 3 g V_2O_5 was evenly dispersed in a combination of 83 ml C_2H_5OH and 83 ml DIW to form a suspension. This suspension was then placed in a 250 ml PTFE lining and conducted a hydrothermal reaction at 180 °C for 48 h. The resulting product was thoroughly washed with DIW and C_2H_5OH multiple times and then dried at 60 °C for further use. Subsequently, 10 mmol of the resulting product was evenly distributed in 67 ml DIW to form a suspension. This suspension was then placed in a 100 ml PPL lining and conducted to a hydrothermal reaction at 260 °C for 48 h. After the reaction, the product was washed and dried in the same way to obtain VO_2 .

Material Characterization:

X-ray diffractometer SmartLab SE (Rigaku), field emission scanning electron microscope Regulus 8100 (Hitachi) equipped with energy dispersive spectrometer Quantax 200 (Bruker) and X-ray photoelectron spectroscopy Nexsa (Thermo) were used for material and electrodes characterization. All of the above instruments were accessed through the Instrument and Equipment Sharing Platform at the College of Physics, Jilin University. Raman microscope inVia (Renishaw), field emission transmission electron microscope Talos F200S G2 (Thermo), precision balance BSA124S (Sartorius) and digimatic micrometer MDC-25PX (Sanliang) were used for material and electrodes characterization. XRD patterns were collected at a step size of 0.02 ° and a scanning speed of 3 ° per minute. Raman spectra were collected with a laser of 514.5 nm. All electrodes were washed with DIW before testing.

Electrochemical Measurements:

Super P Li (Timcal), PVDF 900 (Aekema), NMP (Canrd, 99.9%), SUS foil 304 (Canrd, 0.02 mm thickness), Zn foil (Canrd, 99.9%, 0.09 mm thickness), GF A (Whatman), CR2025 cell 316L (Canrd) with spacer (15.8*0.5 mm) and funnel vent (15.4*1.1 mm), $ZnSO_4 \cdot H_2O$ (Aladdin, 99.9%) and $Zn(OTf)_2$ (Macklin, 98.0%) were purchased and used. Sieve (Jiufeng, 100 mesh), quadruple coater SZQ (Canrd, 1000 μm), rolling machine MSK-2150 (Kejing), precision disc cutting machine MSK-T10 (Kejing) and hydraulic crimping machine MSK-110 (Kejing) were used for battery assembly. Battery test system CT2001A (Lanhe), electrochemical station CHI760E (CH) and battery testing temperature control system MJS-SP250 (MJS) were used for battery testing. Battery assembly was carried out in an open-air environment. By blending VO_2 , Super P and PVDF in NMP in a mass ratio of 7:

2: 1, a slurry was created. This slurry was then passed through a sieve and evenly spread on a SUS foil using a quadruple coater. After drying at 60 °C, VO₂ electrode was calendared to a thickness of 0.05 mm. Separator was GF including 80 μl electrolyte. Counter electrode was Zn foil. VO₂ electrode (10 mm diameter), separator (16 mm diameter) and counter electrode (12 mm diameter) were assembled in a cell, sealed under a pressure of 750 psi and conducted to in situ self-transformation. The mass of active material was calculated by weighing each piece of VO₂ electrodes, with values ranging from 1.3 to 1.7 mg cm⁻². VOH-1 and VOH-2 were assembled in the same way. Electrolyte was acquired by soaking VOH-1 and VOH-2 with GF in 2M Zn(OTf)₂ for 0.5 h. All electrochemical tests were carried out at a constant temperature of 25 °C. GCD is carried out using a battery testing system, whereas CV is carried out using an electrochemical station.

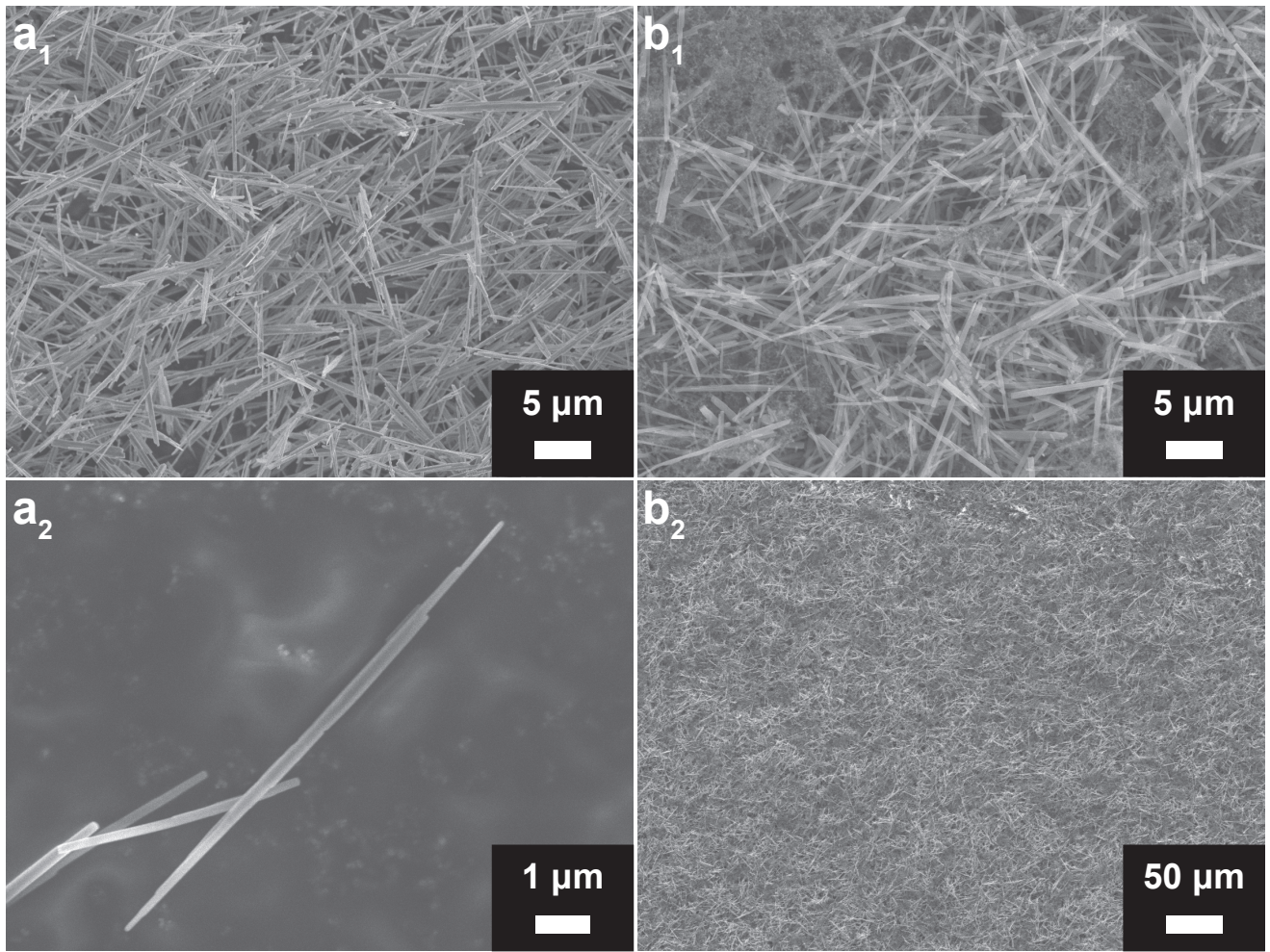


Figure S1: The morphological characterization of VO_2 . The SEM images of a_1 and a_2) powder. b_1 and b_2) electrode.

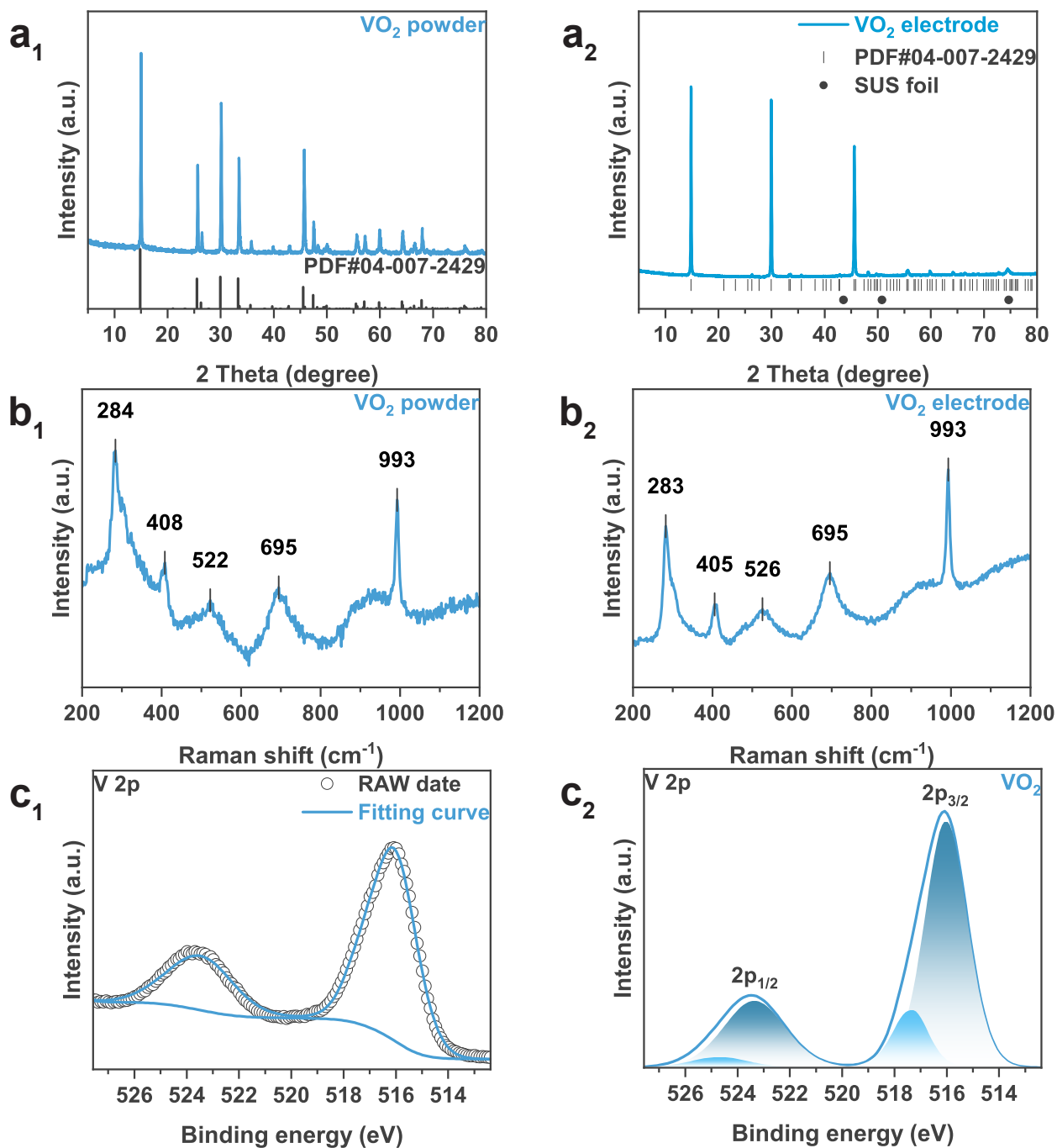


Figure S2: The structural characterization of VO₂. a₁ and a₂) XRD patterns. b₁ and b₂) Raman spectra. c₁ and c₂) XPS spectra.

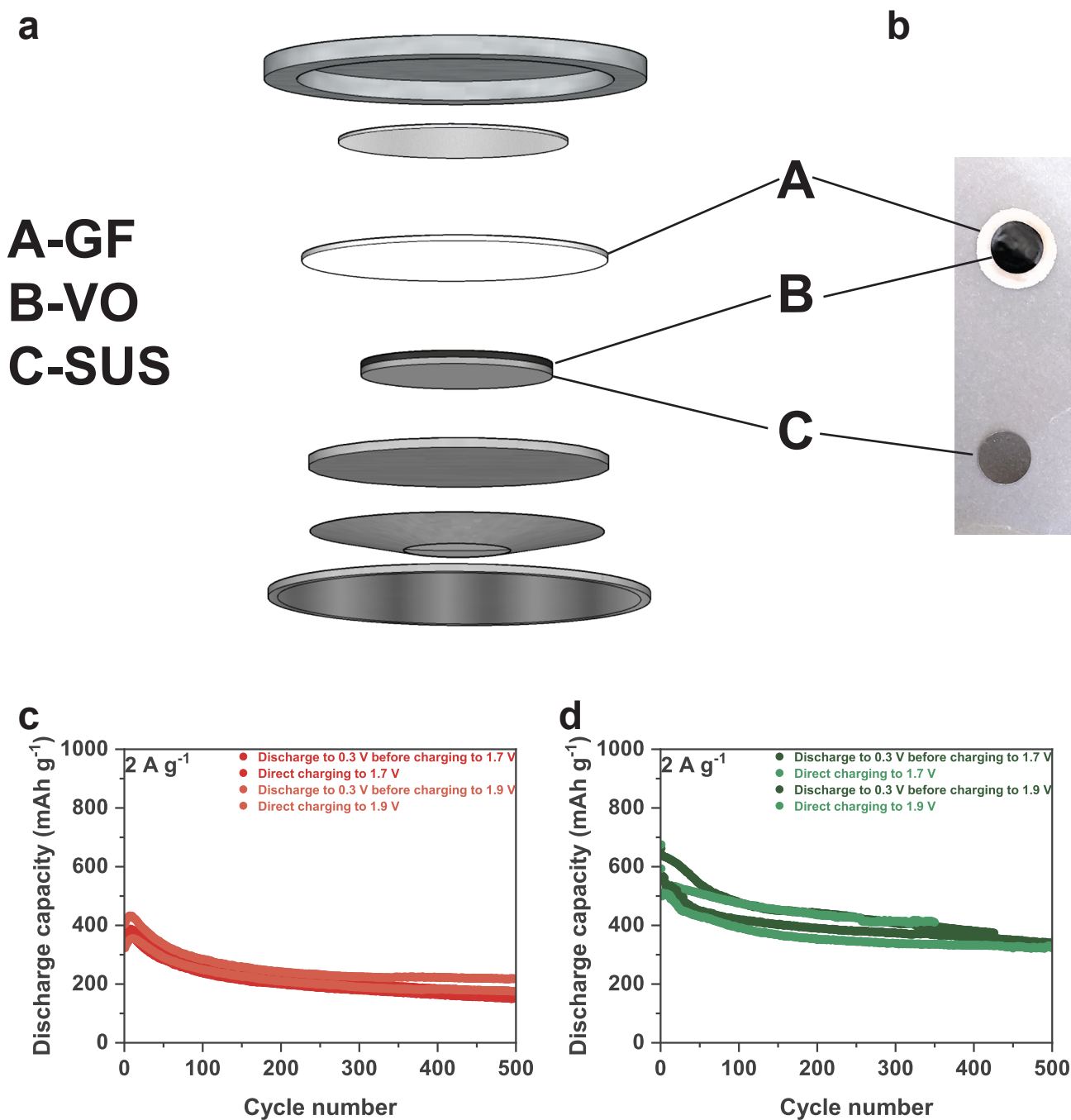


Figure S3: a) The schematic illustration of battery disassembly. b) The photo of VOH-1. The cycling performance of batteries without replacing electrolyte of c) VOH-1. d) VOH-2

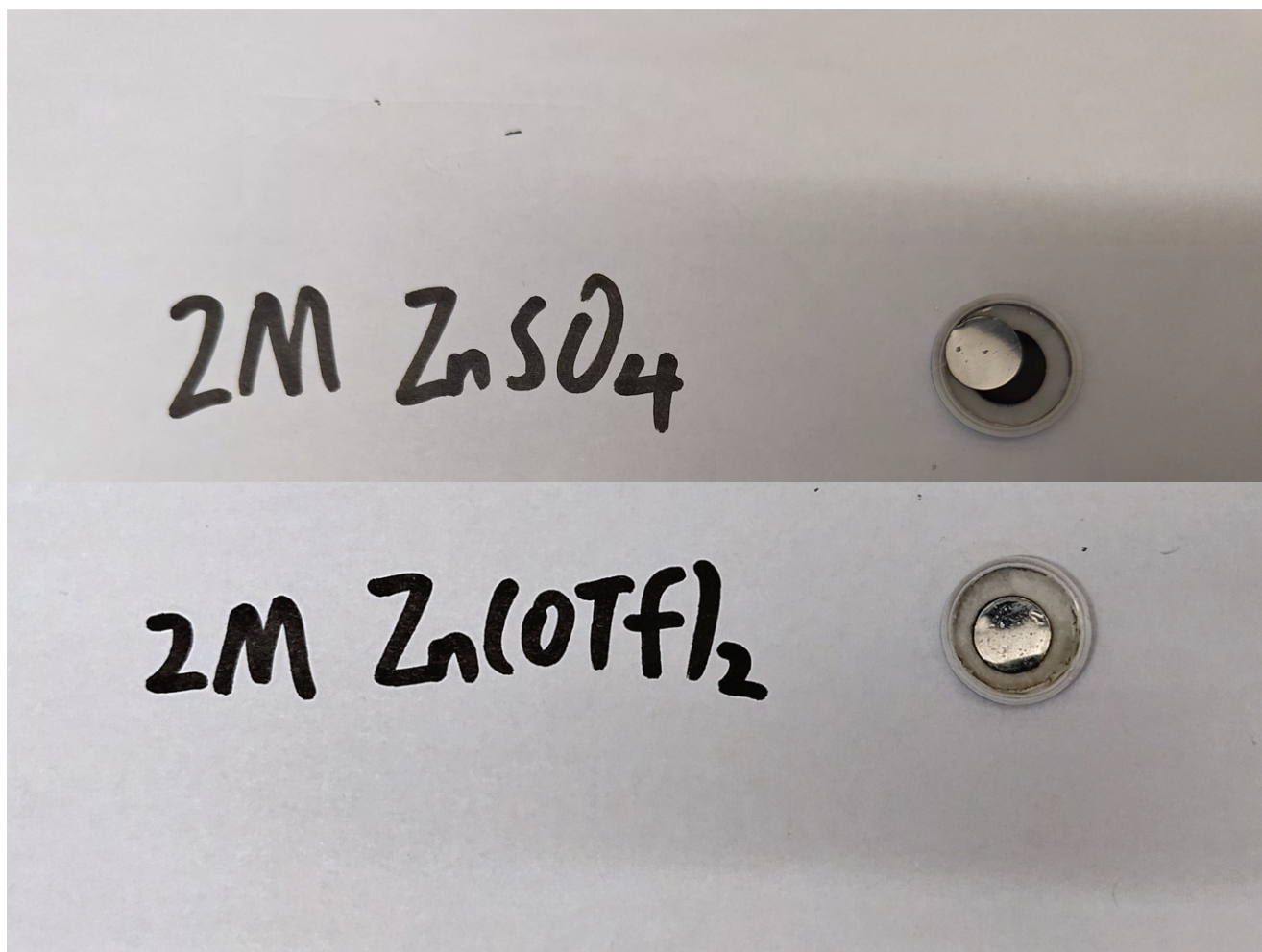


Figure S4: The photos of VO₂ electrodes, standing in cells for 24 h.

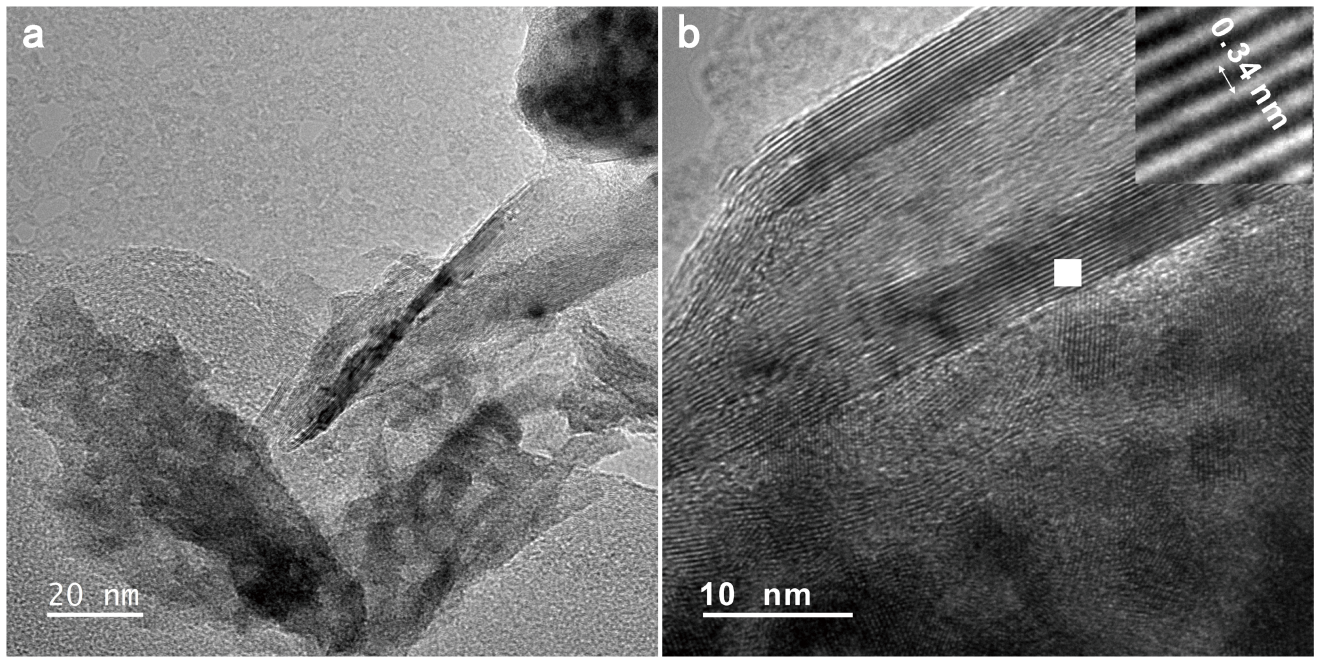


Figure S5: The TEM images of VOH-1.

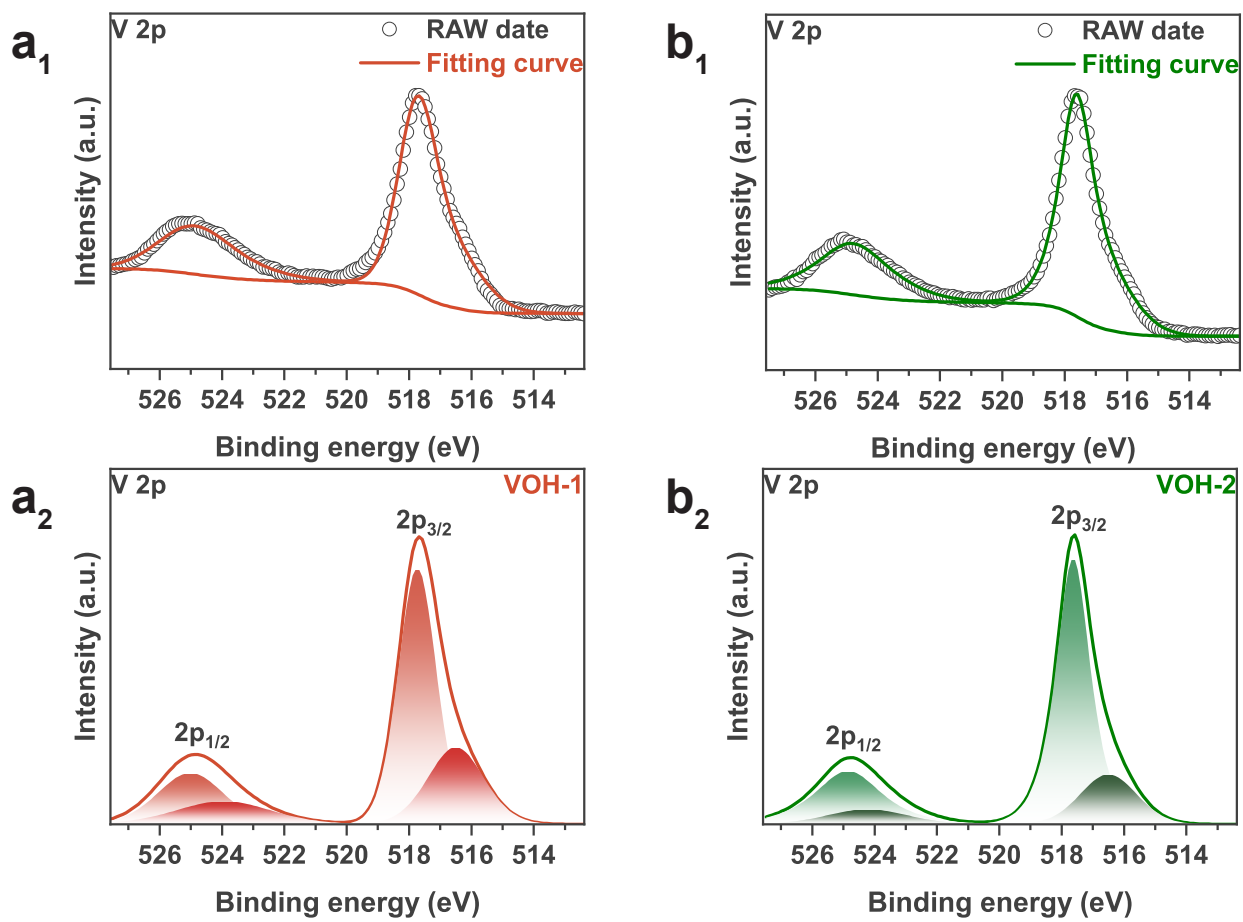
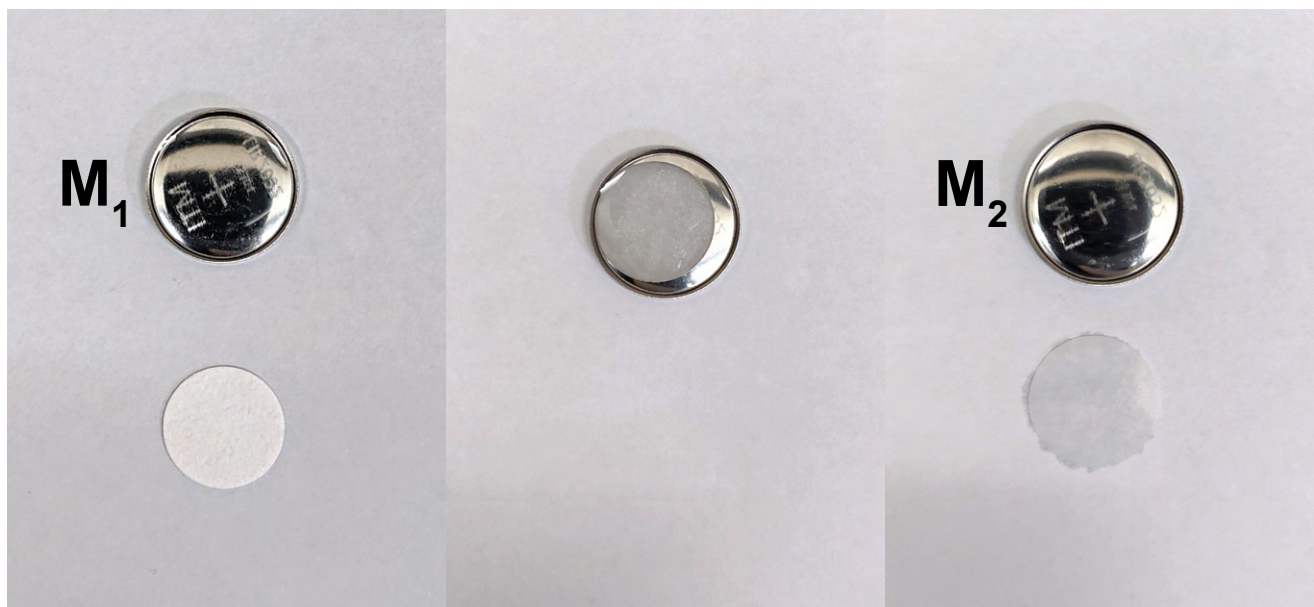


Figure S6: The XPS spectra of a_1 and a_2) VOH-1. b_1 and b_2) VOH-2.



$$M_1 - M_2 = 113 \text{ mg} \approx 90 \text{ } \mu\text{l}$$

Figure S7: The measurement of the electrolyte amount of 2M $\text{Zn}(\text{OTf})_2$ in the CR2025 cells using VOH-1 and VOH-2.

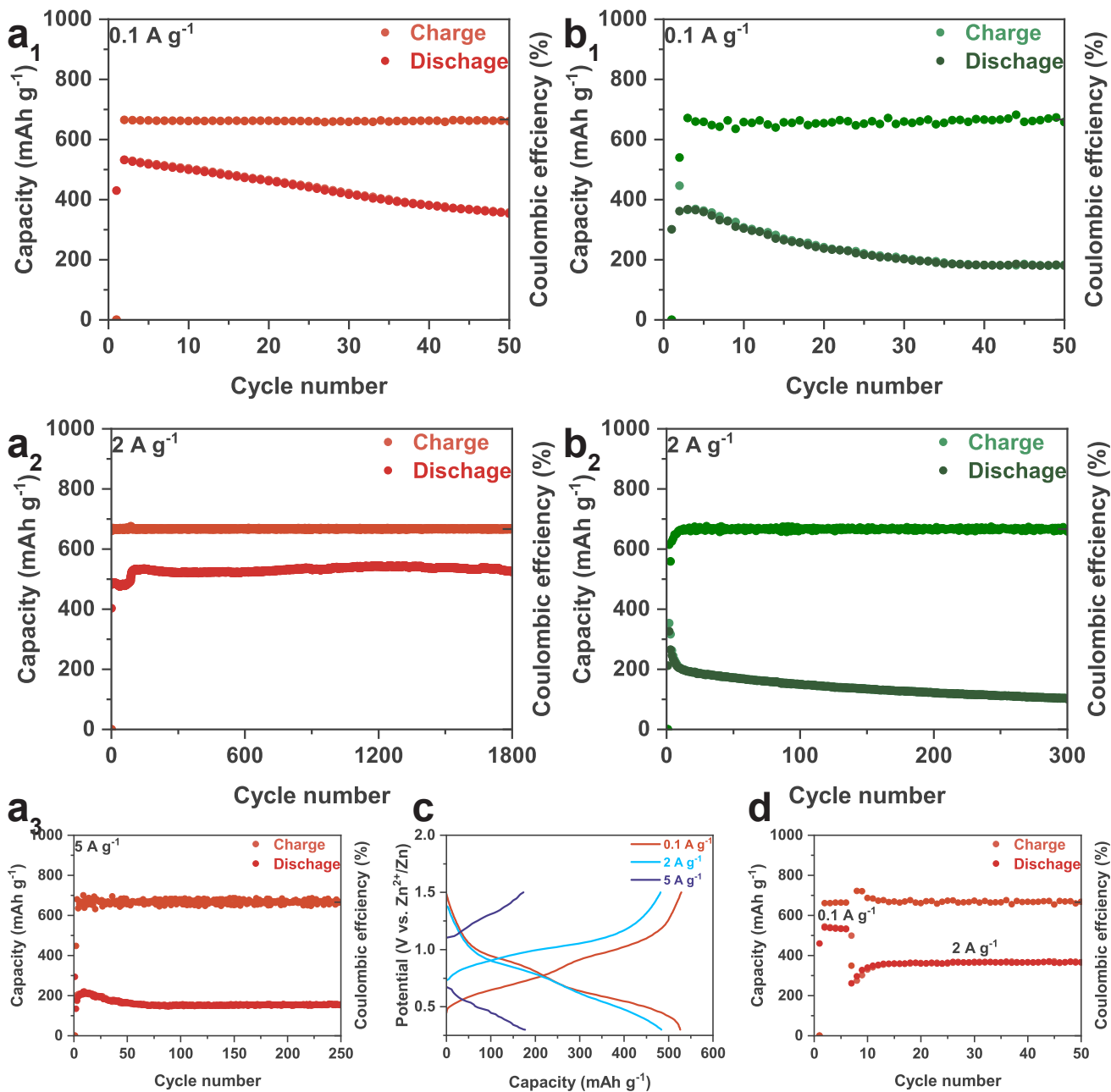


Figure S8: The electrochemical characterization. a₁ a₂ and a₃) The cycling performance of VOH-1. b₁ and b₂) The cycling performance of VOH-2. c) The capacity-potential curves of the second cycles of VOH-1. d) The cycling performance of VOH-1, underwent 5 cycles at a rate of 0.1 A g⁻¹.

References

- [1] Y. Zhang, M. Fan, X. Liu, G. Xie, H. Li and C. Huang, *Solid State Communications*, 2012, **152**, 253–256.