

Supporting Information

Metallic Vanadium Activated by In-Situ Dissolution-Deposition Process for Superior Aqueous Zinc Ion Battery Cathode

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Materials and Methods

Materials

All chemical reagents including V and $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ are analytically pure and purchased from Adamas-beta. Deionized (DI) water with a specific resistance of 18.1 $\text{M}\Omega$ cm.

Materials Characterizations

The morphology of metal vanadium and electrodes was analyzed by field emission scanning electron microscopy (TESCAN MIRA LMS) and transmission electron microscopy (JEOL JEM-F200). X-ray diffraction patterns of the samples were obtained by a Rigaku SmartLab SE X-ray diffractometer. X-ray photoelectron spectroscopy data were measured by a Thermo Scientific K-Alpha. The inductively coupled plasma-atomic emission spectrometry (ICP-OES) was conducted by PerkinElmer Optima 8300. The separators of Zn//V coin cells after charging to 1.3, 1.5 and 1.7 V were soaked in 10 mL of DI water for 5 minutes to prepare dilute electrolytes, which were analyzed by ICP-OES to detect the concentration of vanadium species. The dilute electrolyte at different charging states were also characterized by PE lambda 750 to obtain the ultraviolet (UV) spectroscopy.

Electrochemical measurements

The electrochemical measurement of samples was performed in 2032-type coin cells with 100 μL electrolyte (3M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$). The cathode was prepared by mixing 70 wt% active materials, 20 wt% acetylene black, and 10 wt% PVDF in N-methyl-2 pyrrolidinone, followed by pasting the slurry on a stainless steel mesh and drying at 80 $^\circ\text{C}$ for 12 h in a vacuum oven. The average active material loading of the cathode was approximately 1.2 mg cm^{-2} . For the fabrication of the zinc battery, a 12 mm zinc disc was used as the anode, meanwhile a 3 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ aqueous solution and glass fiber film disk (Whatman GF/D) was used as the electrolyte and separator respectively. Discharge and charge tests were performed at different current rates on a Neware CT-4008Tn battery tester in the voltage range from 0.1 V to 1.9 V at 28 $^\circ\text{C}$. Cyclic

voltammetry measurements of the batteries were collected using a CHI 660e electrochemical workstation. The galvanostatic intermittence titration technique was carried out at a current density of 0.1 A g^{-1} with a galvanostatic discharge pulse of 15 min and a relaxation of 0.5 h to reach the quasi-equilibrium potential. The electrochemical performance tests and calculations are based on the mass of pristine V metal material.

Calculations of energy density

The energy density can be obtained by the formula below:

$$\text{Energy density} = \text{battery capacity (Ah)} \times \text{average voltage (V)} / \text{battery weight (kg)}$$

The battery capacity refers to the amount of charge that the battery can release. Average voltage is the average output voltage of a battery during discharging, which can be obtained by integrating the voltage data in the battery discharge curve then dividing by the discharge time. Battery weight refers to the weight of the cathode material.

Galvanostatic intermittent titration study

The diffusion coefficient of Zn^{2+} was tested by using GITT and calculated according to the following equation:

$$D = \frac{\pi}{4} \left(\frac{m_B V_m}{M_B S} \right)^2 \left(\frac{\Delta E_S}{\Delta E_t} \right)^2$$

where τ is the duration time of the current pulse; m_B and M_B is the mass and molar mass of cathode material, respectively; V_m is the molar volume of the cathode materials; S is the total area of the contact surface between cathode and electrolyte.

Characterizations of metallic V powder

The commercial vanadium metal powder was characterized by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). The powder X-ray diffraction (XRD) pattern is shown in Figure S1, and all the diffraction peaks of the sample are consistent with the characteristic peaks of V metal (PDF No. 22-1058). The

scanning electron microscopy (SEM) image shows that the vanadium metal is in the morphology of irregular particles with a size of about 1.5-2 μm (Figure S2).

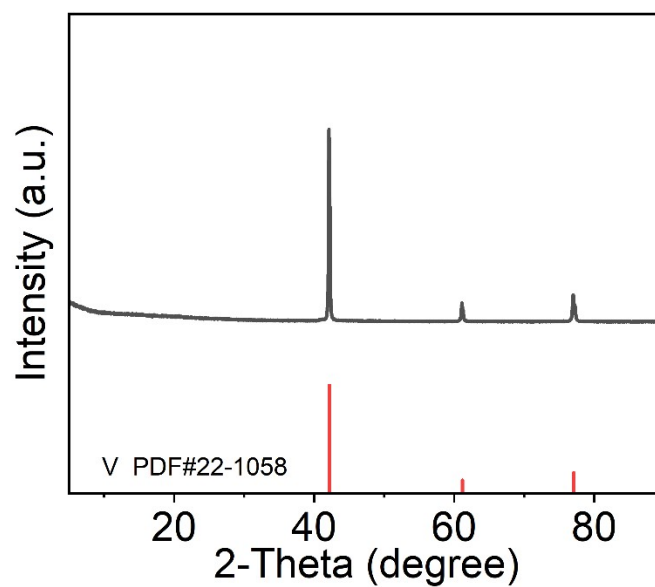


Figure S1. XRD of V metal powder.

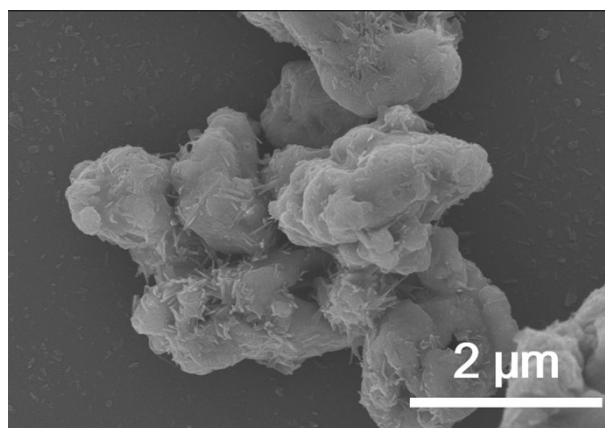


Figure S2. SEM images of V metal powder.

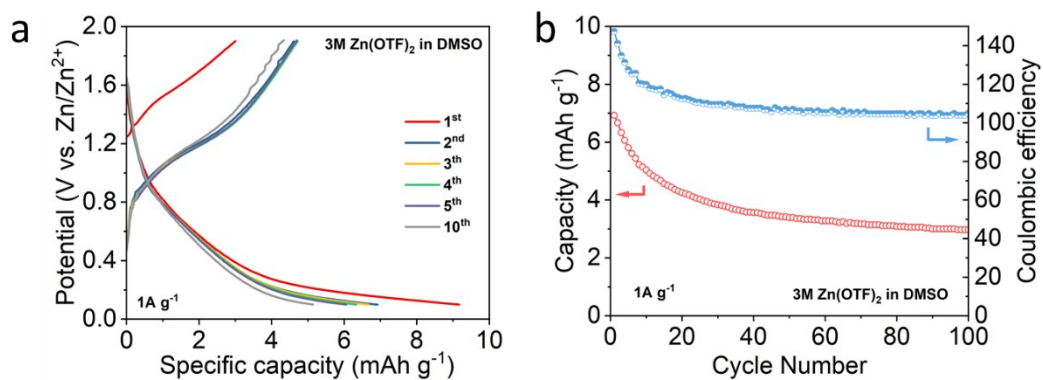


Figure S3. Electrochemical characterization of vanadium metal cathode in organic electrolyte. (a) GCD curves and (b) cycling stability at 1 A g⁻¹.

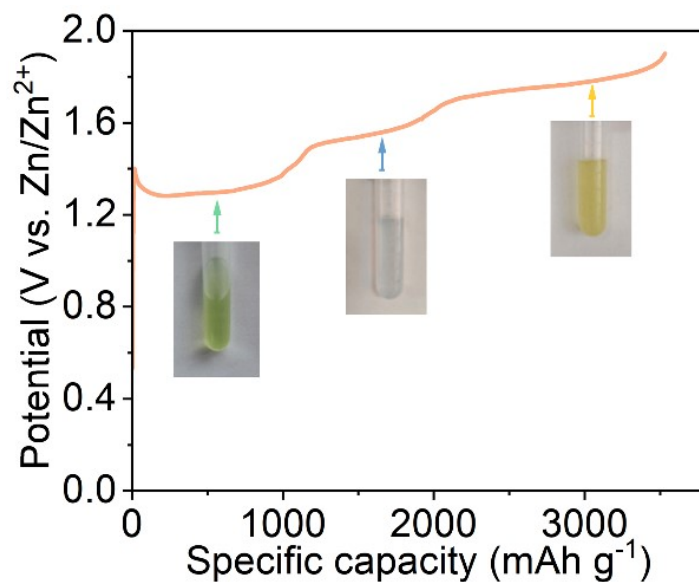


Figure S4. The electrode and diaphragm immersion solution when the battery is first charged to 1.3V, 1.5V and 1.8V.

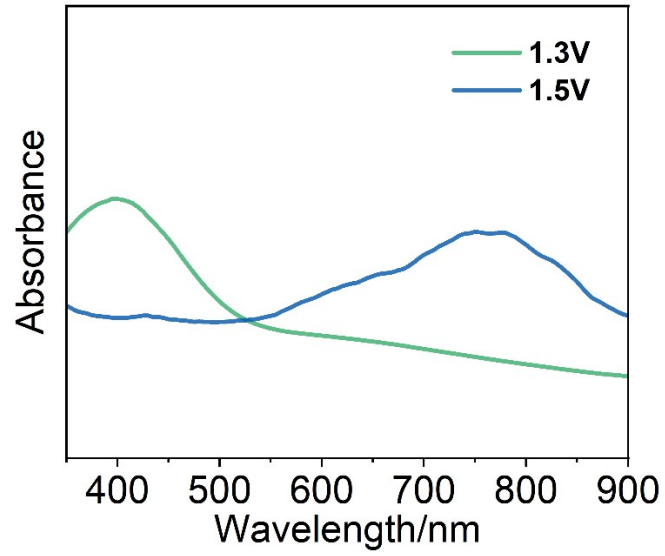


Figure S5. UV spectra of electrolytes after the first charging to 1.3 and 1.5 V.

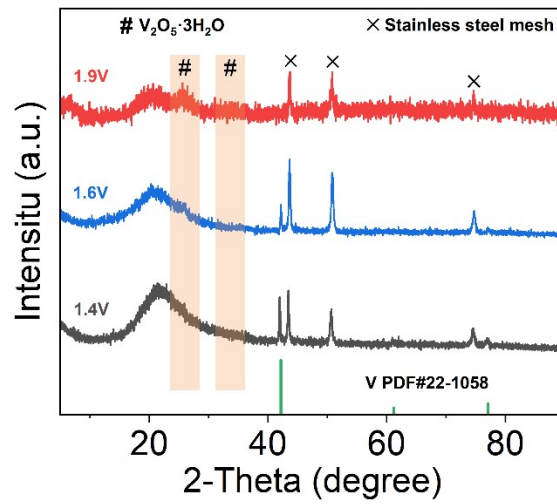


Figure S6. XRD patterns of the V cathode at different states during the first charging process.

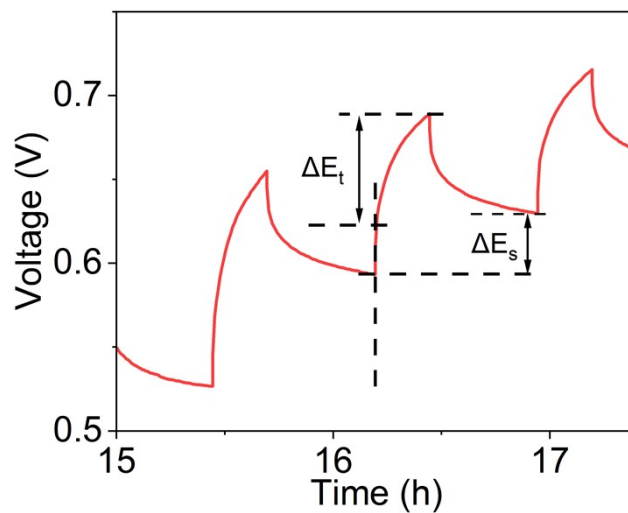


Figure S7. Time-voltage curve of the GITT measurement for V metal cathode.

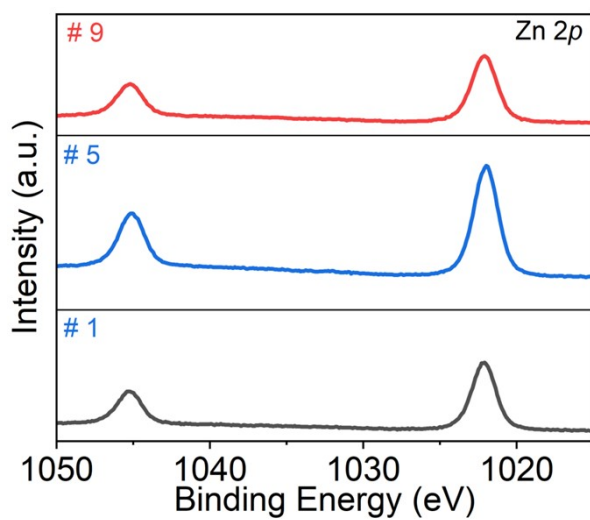


Figure S8. Ex-situ XPS spectra of Zn 2p at different charging/discharging states.

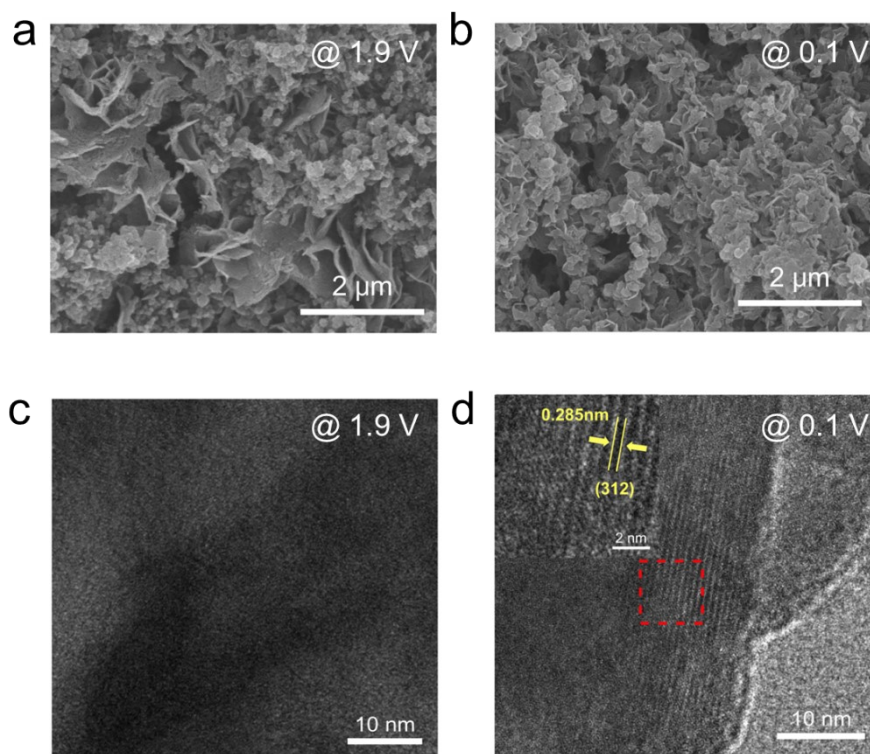


Figure S9. (a) Ex-situ TEM image at fully charged state and (b) fully discharged state, respectively. (c) High-resolution TEM image at fully charged state and (d) fully discharged state.

Table S1 Recently reported ZIB cathodes with vanadium-based materials

Materials	Electrolyte	Voltage /(V)	Max specific capacity /(mAh·g ⁻¹)	Rate performance /(mAh·g ⁻¹)	Cycle performance	Ref.
V	3M	0.1-1.9	610	340	1000, 83.9%	
	Zn(CF ₃ SO ₃) ₂		(0.1 A g ⁻¹)	(20 A g ⁻¹)	(507.4→425.72mAh g ⁻¹ , 1 A g ⁻¹)	This work
ZnO-QDs-VN	3M	0.4–1.6	384.1	125.4	1800, 54%	
	Zn(CF ₃ SO ₃) ₂		(0.1 A g ⁻¹)	(5 A g ⁻¹)	(125.4→67.7 mAh·g ⁻¹ , 5 A g ⁻¹)	[1]
VN-rGO	2M	0.2–2.0	467	467	400, 63.8%	
	Zn(CF ₃ SO ₃) ₂		(2 A g ⁻¹)	(2 A g ⁻¹)	(698→445 mAh·g ⁻¹ , 1 A g ⁻¹)	[2]
VN _x O _y	2M	0.4–1.4	240	200	2000, 75%	
	ZnSO ₄		(1 A g ⁻¹)	(30 A g ⁻¹)	(200→150 mAh·g ⁻¹ , 20 A g ⁻¹)	[3]
MXene@VO ₂	2M	0.2-1.4	363.2	169.1	5000, 76%	
	Zn(CF ₃ SO ₃) ₂		(0.06 A g ⁻¹)	(15 A g ⁻¹)	(271.8→206.6 mAh·g ⁻¹ , 6 A g ⁻¹)	[4]
MIL- 88B(V)@rGO	3M	0.2-1.4	479.6	263.6	400, 80.3%	
	Zn(CF ₃ SO ₃) ₂		(0.05 A g ⁻¹)	(5 A g ⁻¹)	(362→290 mAh·g ⁻¹ , 2 A g ⁻¹)	[5]
V ₂ O ₃ @C	3M	0.3-1.6	472.4	217	1800, 66.5%	
	Zn(CF ₃ SO ₃) ₂		(0.1 A g ⁻¹)	(10 A g ⁻¹)	(200→133 mAh·g ⁻¹ , 10 A g ⁻¹)	[6]

References

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