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Enhancing stability in zinc-ion batteries with titanium-doped VO_2 cathode materials

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Chemicals

The following reagents are used without further purification. vanadium pentoxide (Vanadium(V) oxide, AR, 99.0%), Glucose (AR), Titanium sulfate dihydrate ($Ti(SO_4)_2 \cdot 2H_2O$,AR,96.0%), Hexadecyl trimethyl ammonium bromide (Cetyl-trimethyl Ammonium Bromide(CTAB), AR, 99.0%), Hydrogen peroxide (30 wt%) and double distilled water.

Material characterization

The crystalline phase of the samples was analyzed by an X-ray powder diffractometer (Bragg-Brentano, Bruker D8 Advance). X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Scientific ESCALAB 250Xi instrument. To prepare electrodes for ex-situ XRD and XPS measurements, the cells were disassembled at specific voltages, followed by multiple washes with deionized water and dried in vacuum. The samples were imaged by field emission scanning electron microscopy (SEM) and field emission transmission electron microscopy (TEM), while imaging was performed using TEM energy dispersive X-ray spectroscopy (EDS). To characterize the pore distribution, an automatic adsorption instrument (Micromeritics ASAP 2020) was used to conduct N_2 isothermal adsorption/desorption experiments, and the specific surface area was calculated according to the Brunauer-Emmet-Teller (BET) equation. Finally, the electrode samples obtained after these steps were used for XRD and XPS measurements.

Electrochemical measurements

First, the cathode material was prepared by mixing the active material, carbon black and polytetrafluoroethylene (PVDF) in a mass ratio of 7:2:1 in n-methyl-2-

pyrrolidone (NMP) solvent and assembled into a CR2032 coin. type cells to evaluate the electrochemical performance of all samples. Subsequently, the slurry was coated on stainless steel foil and dried at 60 °C for 12 hours. At the same time, metal zinc discs, glass fibers and 3mol L^{-1} zinc trifluoromethanesulfonate ($Zn(CF_3SO_3)_2$) solution were used as anode, separator and electrolyte respectively. All batteries are assembled under natural conditions. The electrochemical properties were studied using cyclic voltammetry (CV) on an electrochemical workstation (CHI 760e) with scan rates between 0.2 and 1.6 V and a current density of 0.2 A g^{-1}. The cycling and charge-discharge behavior of the button cells were tested using a battery test system (LAND MTI-5 V 10 mA). In addition, testing was performed by galvanostatic intermittent titration technique (GITT) using a series of galvanostatic discharge pulses (100 mA g^{-1}, 10 minutes, 30 minutes rest) in the potential range of 0.2 ~ 1.6 V. All electrochemical tests were completed at room temperature.

Energy Density and Power Density

The energy density and power density were obtained by the following equations:

$$E = \int_0^{\Delta t} \frac{V \times i}{m} dt$$

$$P = \frac{E}{1000 \times \Delta t}$$

where E (Wh kg^{-1}) is the energy density, P is the power density (kW kg^{-1}), V (V), i (mA), m (g) and Δt (h) represent the working potential, discharging current, the mass loading of the cathode and the discharging time, respectively.

Diffusion Coefficient

The diffusion coefficient (D) is obtained from the following equation,

$$D = \frac{4L^2}{\pi\tau}\left(\frac{\Delta Es}{\Delta Et}\right)$$

where τ (s) is the constant current pulse time. The L is diffusion length (cm) of Zn^{2+} and H^{+} which is equal to thickness of electrode. The ΔEs is the steady-state voltage change caused by the current pulse. The ΔEt are voltage changes during the constant current pulse.

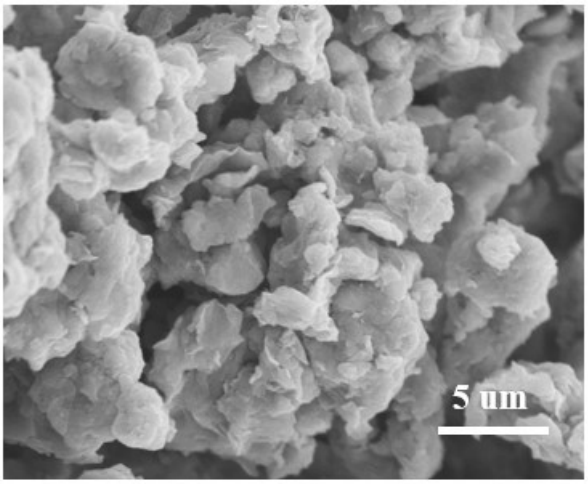

Fig. S1. SEM image of VO_2.

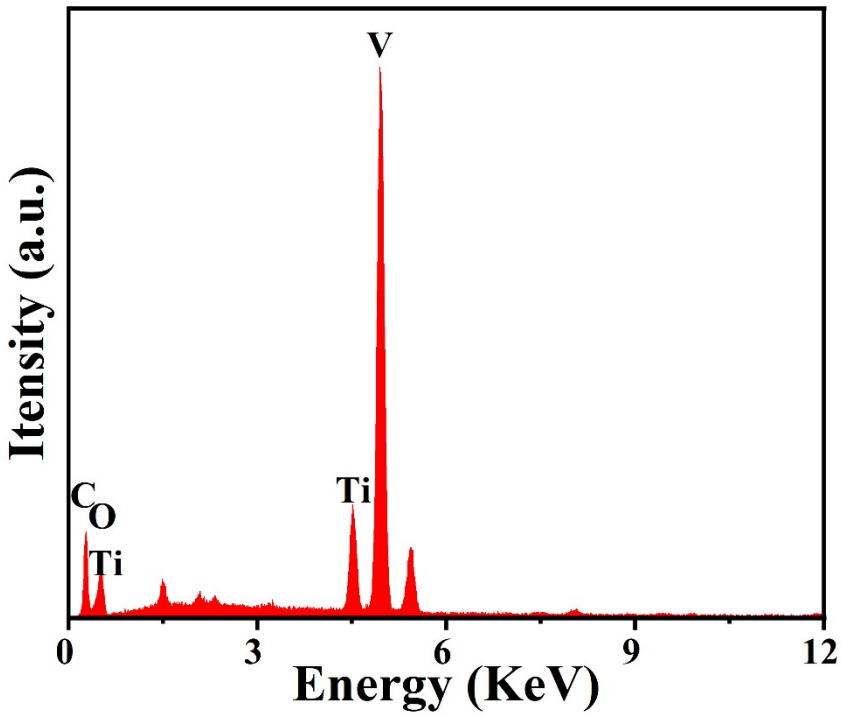

Fig. S2. EDS spectrum of the Ti-VO_2

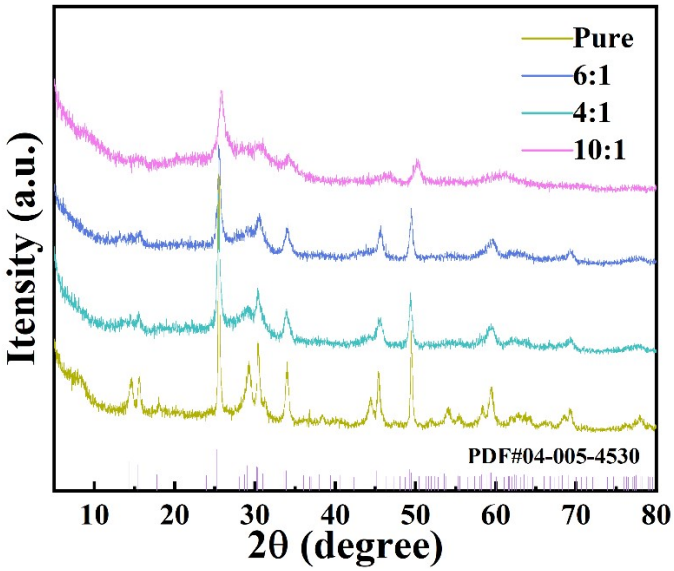

Fig. S3. XRD patterns of the Ti-doped VO_2 at varying proportions.

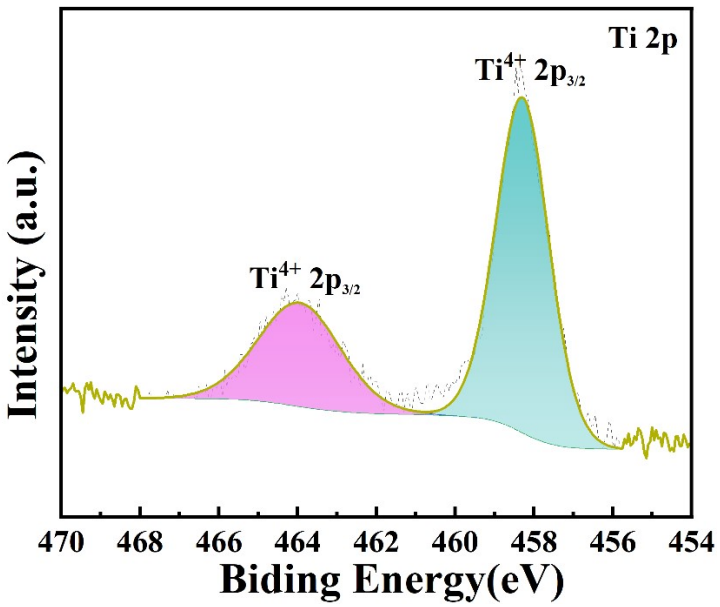

Fig. S4. Ti 2p fine spectrum of Ti-VO_2

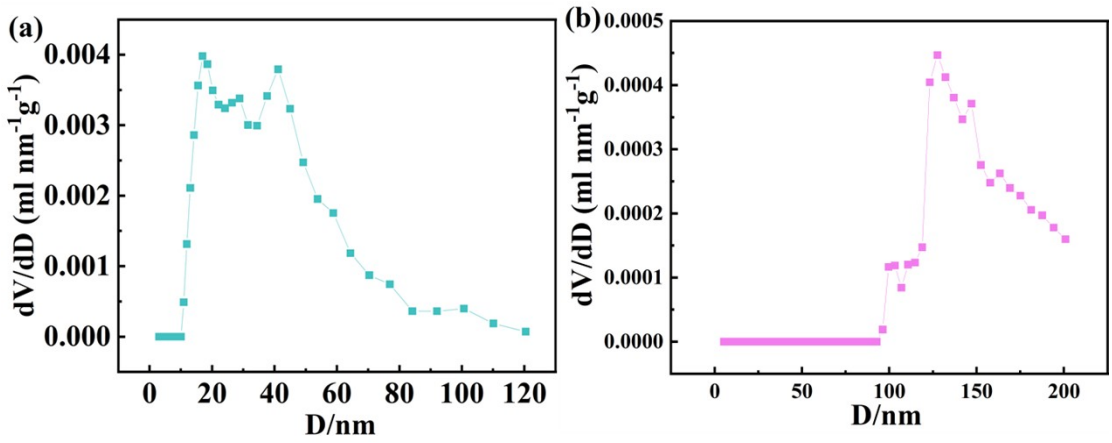

Fig. S5. (a) Ti-VO_2 pore size distribution; (b) VO_2 pore size distribution.

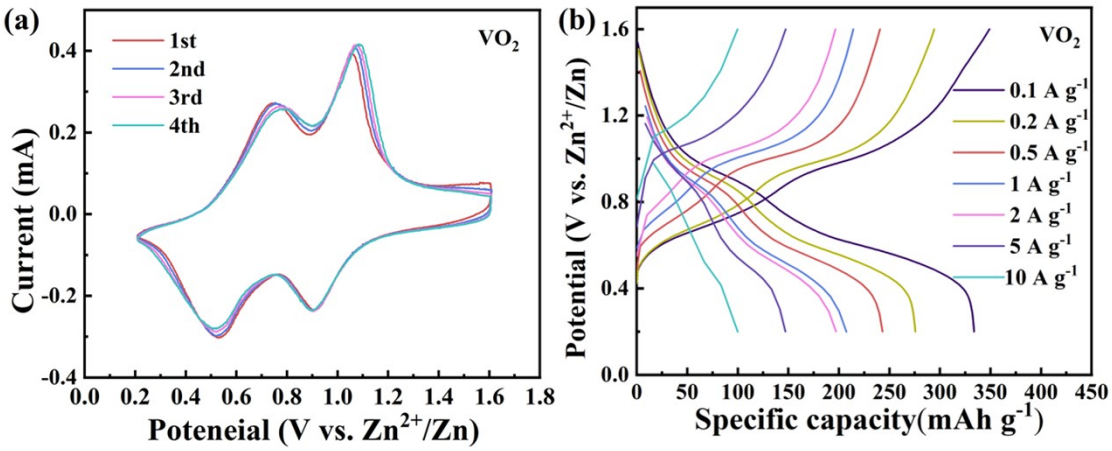

Fig. S6. (a) CV curves of VO_2 at 0.2 mV s^{-1};(b) GCD curves of VO_2 at different current densities.

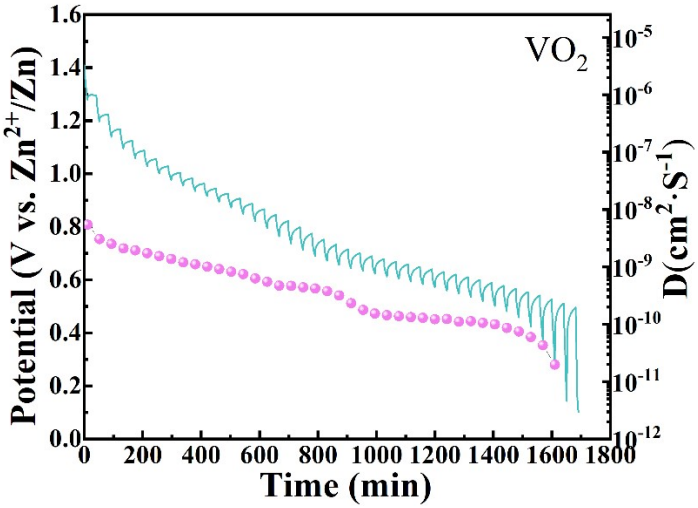

Fig. S7. GITT curve and corresponding diffusion coefficient of VO_2 for ZIBs during discharge process.

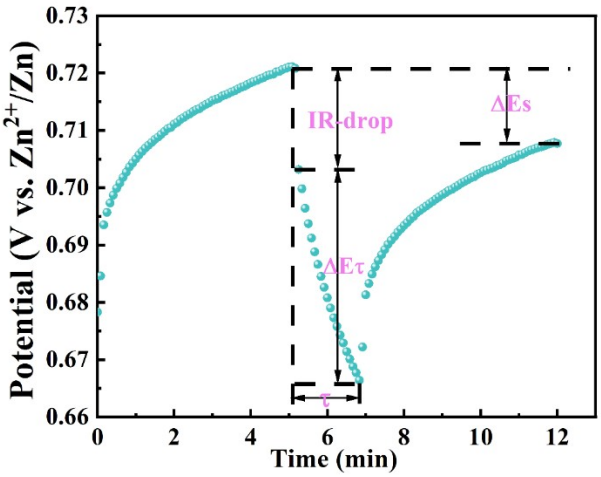

Fig. S8. Representative GITT titration curve.

Table S1. Performance comparison of aqueous ZIBs with vanadium oxide-based materials as cathodes.

Cathode material	Electrolyte	Specific capacity	Capacity retention	Ref.
Ti-VO_2	3M $Zn(CF_3SO_3)_2$	399.58 mA h g^{-1} at 0.2 A g^{-1}	89% retained after r 100 cycles at 0.2 A g^{-1}	This work
VO_2/MXene	3M $Zn(CF_3SO_3)_2$	445 mA h g^{-1} at 0.1 A g^{-1}	82 % retained after 2600 cycles at 20 A g^{-1}	[1]
$V_2O_5 \cdot nH_2O$	3M $Zn(CF_3SO_3)_2$	359 mA h g^{-1} at 0.3 A g^{-1}	90.9 % retained after 1000 cycles at 6.0 A g^{-1}	[2]
VS_2	1 M $ZnSO_4$	116 mA h g^{-1} at 2.0 A g^{-1}	98 % retained after 200 cycles at 0.5 A g^{-1}	[3]
$K_{0.5}V_2O_5$	3M $Zn(CF_3SO_3)_2$	241 mA h g^{-1} at 1 A g^{-1}	90% retained after 1900 cycles at 5 A g^{-1}	[4]
$(NH_4)_xV_2O_5 \cdot nH_2O$	3M $Zn(CF_3SO_3)_2$	374 mA h g^{-1} at 0.1 A g^{-1}	80 % retained after 2000 cycles at 5.0 A g^{-1}	[5]
$Mg_{0.23}V_2O_5 \cdot H_2O$	1M $Zn(CF_3SO_3)_2$	255 mA h g^{-1} at 0.5 A g^{-1}	210% retained after 100 cycles at 0.5 A g^{-1}	[6]
VO_2(A) hollow spheres	3M $Zn(CF_3SO_3)_2$	357 mA h g^{-1} at 0.1 A g^{-1}	76 % retained after 500 cycles at 5.0 A g^{-1}	[7]
ZnV_2O_4	2M $Zn(ClO_4)_2$	289 mA h g^{-1}at 0.46 A g^{-1}	76% retained after 1000 cycles at 4.6 A g^{-1}	[8]
MgV_2O_4	1M $Zn(CF_3SO_3)_2$	235 mA h g^{-1}at 0.5 A g^{-1}	~68% retained after 500 cycles at 4.0 A g^{-1}	[9]
VSe_2 Nanosheets	3M $Zn(CF_3SO_3)_2$	131.8 mA h g^{-1} at 0.1 A g^{-1}	80.8 % retained after 500 cycles at 2.0 A g^{-1}	[10]

References

[1] W. Kou, L. Yu, Q. Wang, Y. Yang, T. Yang, H. Geng, X. Miao, B. Gao, G. Yang, Enhanced Zn^{2+} transfer dynamics via a 3D bird nest-like VO_2/MXene heterojunction for ultrahigh-rate aqueous zinc-ion batteries, Journal of Power Sources, 520 (2022).

[2] L. Chen, Y. Ruan, G. Zhang, Q. Wei, Y. Jiang, T. Xiong, P. He, W. Yang, M. Yan, Q. An, Ultrastable and high-performance Zn/VO_2 battery based on a reversible single-phase reaction, Chemistry of Materials, 31 (2019) 699-706.

[3] P. He, M. Yan, G. Zhang, R. Sun, L. Chen, Q. An, L. Mai, Layered VS2 nanosheet-based aqueous Zn ion battery cathode, Advanced Energy Materials, 7 (2017) 1601920.

[4] G. Su, S. Chen, H. Dong, Y. Cheng, Q. Liu, H. Wei, E.H. Ang, H. Geng, C.C. Li, Tuning the electronic structure of layered vanadium pentoxide by pre-intercalation of potassium ions for superior room/low-temperature aqueous zinc-ion batteries, Nanoscale, 13 (2021) 2399-2407.

[5] L. Xu, Y. Zhang, J. Zheng, H. Jiang, T. Hu, C. Meng, Ammonium ion intercalated hydrated vanadium pentoxide for advanced aqueous rechargeable Zn-ion batteries, Materials Today Energy, 18 (2020) 100509.

[6] W. Xu, C. Liu, Q. Wu, W. Xie, W.-Y. Kim, S.-Y. Lee, J. Gwon, A stretchable solid-state zinc ion battery based on a cellulose nanofiber–polyacrylamide hydrogel electrolyte and a $Mg_{0.23}V_2O_5 \cdot 1.0H_2O$ cathode, Journal of Materials Chemistry A, 8 (2020) 18327-18337.

[7] L. Chen, Z. Yang, Y. Huang, Monoclinic VO_2(D) hollow nanospheres with super-long cycle life for aqueous zinc ion batteries, Nanoscale, 11 (2019) 13032-13039.

[8] Y. Liu, C. Li, J. Xu, M. Ou, C. Fang, S. Sun, Y. Qiu, J. Peng, G. Lu, Q. Li, Electroactivation-induced spinel ZnV_2O_4 as a high-performance cathode material for aqueous zinc-ion battery, Nano Energy, 67 (2020) 104211.

[9] W. Tang, B. Lan, C. Tang, Q. An, L. Chen, W. Zhang, C. Zuo, S. Dong, P. Luo, Urchin-like spinel MgV_2O_4 as a cathode material for aqueous zinc-ion batteries, ACS sustainable chemistry & engineering, 8 (2020) 3681-3688.

[10] Z. Wu, C. Lu, Y. Wang, L. Zhang, L. Jiang, W. Tian, C. Cai, Q. Gu, Z. Sun, L. Hu, Ultrathin VSe_2 nanosheets with fast ion diffusion and robust structural stability for rechargeable zinc-ion battery cathode, Small, 16 (2020) 2000698.