Quantifying vanadium-vacancy clusters in V₂O₃ towards ultra-long cycling aqueous zinc-ion battery

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Abstract

Defect engineering has been attracted widespread attention for promoting the stability of the electrodes. However, accurately quantifying and defining the effect of defects is extremely difficult. Here, the Rietveld analysis with combined neutron powder diffraction (NPD) and X-ray powder diffraction (XRD) patterns reveal vanadium defect (V₄) clusters in the V₂O₃ lattice up to 5.7% in aqueous zinc-ion batteries (ZIBs), further confirmed by positron annihilation spectroscopy (PAS) and synchrotron-based X-ray analysis. Benefitting from the V₄ clusters, the V₂O₃ cathode achieves excellent cycle life with 81% capacity retention at 5.0 A g⁻¹ after 30,000 cycles that is the most superb stable cathode for aqueous ZIBs at this current density. Besides, the density functional
theory (DFT) calculations strongly indicate that the $V_d$ clusters not only provide permanent sites for $\text{Zn}^{2+}$ anchormen to enhance the integrity of $\text{V}_2\text{O}_3$ after the first discharging process, but also make $\text{Zn}^{2+}$ de/intercalation in complex oxide, contributing collectively and effectively reducing the strong electrostatic interaction between host multivalent ions, resulting in the remarkable storage performance of $\text{Zn}^{2+}$. This work highlights accurately quantifying and identifying the significant effect of defects for designing cathodes with ultra-long cycle life in future intelligent devices.

Introduction

With the increase of energy crisis and environmental pollution problems, it is essential to develop green and clean energy storage devices. As a bellwether in the field of energy storage, lithium-ion batteries (LIBs) are a key technique in advanced power technologies\textsuperscript{1,2}. However, emerging worries are their limited lithium resources and security issues towards future large-scale applications\textsuperscript{3-6}. Encouragingly, rechargeable aqueous ZIBs have emerged as the most promising complements to LIBs regarding high specific capacity (819 mA h g\textsuperscript{-1}), low cost, abundant resources, and environment friendly\textsuperscript{7-9}. It has been demonstrated that aqueous ZIBs have been applied in miniaturized electronic devices, such as epidermis, implantable and wearable sensors\textsuperscript{10-12}, indicating that aqueous ZIBs have great commercial potential. But great upgrading is needed to put it into a widespread application. The most compelling issue is to seek long-cycling cathodes for aqueous ZIBs due to serious consequences of stability penalty caused by the aqueous system and bigger ionic radius of $\text{Zn}^{2+}$. Defect engineering has been regarded as an availability approach for promoting the stability of
electrodes, where the strong electrostatic interaction between the host and multivalent ions with a greater charge can be efficiently reduced, accelerate the reaction kinetics and facilitate the reversible storage of Zn ions\textsuperscript{13−16}. Particularly, the research of defects in oxide electrodes most used for ZIBs is required due to the complex composition and the dynamic process during the working process. Accurately quantification of material defects is essential to determine the metal vacancies and oxygen vacancies at the same time. However, it is extremely hard to simultaneously determine the concentration of two vacancies. For example, light oxygen is difficult to be detected by XRD owing to its small atomic radius, compared with most metal elements. Consequently, the joint application of multiple spectroscopy is essential to accurately quantify defects.

In this work, we have quantified for the first time in aqueous ZIBs that V\textsubscript{2}O\textsubscript{3} (V\textsubscript{d}-V\textsubscript{2}O\textsubscript{3}) electrode contains 5.7% V\textsubscript{d} clusters by Rietveld analysis with combined XRD and NPD patterns. It is the V\textsubscript{2}O\textsubscript{3} cathode containing V\textsubscript{d} clusters that delivers ultra-long cycling stability (81% retention after 30,000 cycles at a current density of 5 A g\textsuperscript{-1}), which is the longest cycling stability for the aqueous ZIBs cathode to date. Accurately quantifying and identifying the effect of defects provides a new path for the design of cathodes with long stability for energy storage devices.

**Structure and morphology characterization of V\textsubscript{d}-V\textsubscript{2}O\textsubscript{3}**

The V\textsubscript{d}-V\textsubscript{2}O\textsubscript{3} cathode was designed by a hydrothermal method and an ensuing annealing process (see Supplementary Information for details). Scanning electron microscopy (SEM, Supplementary Fig. 1) and Transmission electron microscope (TEM, Supplementary Fig. 2a) images show that the V\textsubscript{d}-V\textsubscript{2}O\textsubscript{3} is a uniform flower-like
hierarchical structure assembled by thin nanosheets with a size of around 100-200 nm. In the high-resolution TEM (Supplementary Fig. 2b) image of the flowerliked Vd-V2O3, a lattice fringe with a layer spacing of d = 0.27 nm was found, corresponding to the (104) lattice plane. The surface area and pore size were detected by BET (Brunauer-Emmett-Teller) characterization, the Vd-V2O3 has a high surface area of 60.34 m² g⁻¹ and a large pore size of about 22 nm (Supplementary Fig. 3). A large surface area can provide sufficient contact between the electrode and electrolyte and shorten the Zn²⁺ diffusion path time. The mesoporous structure is advantageous to the insertion and extraction of Zn²⁺, which can effectively improve the cycle life of the battery.

For detailed structure information, X-ray absorption fine structure (XAFS) was performed to investigate the local fine structure of Vd-V2O3. As illustrated in the XANES spectra of V K-edge (Fig. 1a inset), the absorption edge of the Vd-V2O3 is found to shift toward higher energy (Site B) compared with commercial V2O3 (c-V2O3), stating clearly that Vd-V2O3 possesses a higher average valence state. The high-resolution XPS of V 2p further shows that despite the valence states of V in Vd-V2O3 and c-V2O3 are +3 and +4 coexistence (Supplementary Fig. 4), the content of V⁴⁺ is larger (Supplementary Table 1). The identical result can be gotten from electron paramagnetic resonance (EPR) spectroscopy, where the EPR signal of tetravalent vanadium has a stronger response strength¹⁷,¹⁸ (Supplementary Fig. 5). It has been reported that the surface of V₂O₃ is vulnerable to be oxidized to V⁴⁺, which explains the existence of V⁴⁺ in c-V₂O₃¹⁹,²⁰. But the situation in Vd-V₂O₃ is different, the surface of Vd-V₂O₃ is proved to be uniformly coated with carbon (Supplementary Figs. 6 and 7).
Thermogravimetric analysis (TGA) shows that the carbon content is 19.36% (Supplementary Fig. 8). Surface coated with the carbon of V\textsubscript{d}-V\textsubscript{2}O\textsubscript{3} is believed to be not easily oxidized, so the higher content of V\textsuperscript{4+} in V\textsubscript{d}-V\textsubscript{2}O\textsubscript{3} may attribute to the existence of vanadium vacancies, which leads to a valence increase of V. The pre-edge peak in the XANES of V K-edge corresponds to the electronic transition from 1s to 3d\textsuperscript{21}, which can promulgate the local structure symmetry. As shown in Fig. 1a inset (Site A), the increase of pre-edge peak intensity attributes to the decrease of local symmetry of V\textsubscript{d}-V\textsubscript{2}O\textsubscript{3}. That is suggested that the structure of V\textsubscript{d}-V\textsubscript{2}O\textsubscript{3} is distorted around V atoms, owing to the absence of surrounding atoms. To further obtain the accurate coordination numbers (CN), the corresponding Fourier transformed EXAFS is fitted that is shown in Supplementary Fig. 9 and the detailed fitting results can be found in Supplementary Table 2. The results demonstrate that the CN of the V-V in V\textsubscript{d}-V\textsubscript{2}O\textsubscript{3} is significantly lower than that in c-V\textsubscript{2}O\textsubscript{3} (2.2 vs. 4), which exhibits that there are vanadium vacancies in V\textsubscript{d}-V\textsubscript{2}O\textsubscript{3}.

In order to further corroborate the defect situation in V\textsubscript{d}-V\textsubscript{2}O\textsubscript{3}, we used PAS to explore the defect type and concentration of the material\textsuperscript{22}. Table I shows the positron annihilation lifetime data of V\textsubscript{d}-V\textsubscript{2}O\textsubscript{3} and c-V\textsubscript{2}O\textsubscript{3}. There are three life components (τ\textsubscript{1}, τ\textsubscript{2}, and τ\textsubscript{3}), among which τ\textsubscript{1}, τ\textsubscript{2}, and τ\textsubscript{3} correspond to defect-free bulk region and the tiny vacancies, vacancy clusters, and interfaces (free space between nanograins) in the material, respectively\textsuperscript{23,24}. Due to the microscopic sizes of both V\textsubscript{d}-V\textsubscript{2}O\textsubscript{3} and c-V\textsubscript{2}O\textsubscript{3} are above 500 nm (Supplementary Figs. 1 and 10), there exist considerable amount of vacancy clusters in both samples. It is noteworthy that the intensity I\textsubscript{2} of τ\textsubscript{2} for V\textsubscript{d}-
V$_2$O$_3$ is 78.01%, which is much higher than that of c-V$_2$O$_3$, indicating that the concentration of vacancy clusters in V$_d$-V$_2$O$_3$ is much higher than that in c-V$_2$O$_3$. The PALS results provide reliable and valuable proof of the coexistence of vanadium vacancies with a relatively high concentration in V$_d$-V$_2$O$_3$, and the phenomenon of defect aggregation may occur, also revealed by DFT.

For accurately determine the type and concentration of defects, we combined NPD and XRD techniques. In the V$_d$-V$_2$O$_3$ cathode, the neutron scattering amplitude of V element is just -0.3438cm$^{-12}$ and the atomic radius of light oxygen element is about 0.66Å. As a result, the scattering factor of the vanadium element in the V$_d$-V$_2$O$_3$ cathode is too small to be detected by NPD, while the light oxygen element is hard to be probed by XRD. Therefore, Rietveld analysis with combined XRD and NPD patterns was conducted to reveal the crystal structure information (Fig. 1c). The refinement results (Supplementary Table 3) and show that, the V$_d$-V$_2$O$_3$ has a typical corundum-type hexagonal structure (Space group: R - 3 c) with lattice parameters to be a=b=4.9473(1) Å, c=13.9990(5) Å. The V and O atoms occupy the 12c (0, 0, 0.15437(6)) and 18e (0.3145(3), 0, 0.25) crystallographic positions, respectively. Moreover, the occupancy rate of vanadium atoms at 12c sites is about 94.3(1) %, while no oxygen vacancy was detected at 18e sites (Fig. 1b). In general, we have demonstrated the presence of coordinately unsaturated atoms of V in V$_d$-V$_2$O$_3$ and the vacancy occupancy rate of vanadium is 5.7%, and the vanadium vacancies exist in the form of vacancy clusters.

**Electrochemistry**

To investigate the Zn$^{2+}$ storage performance of the V$_d$-V$_2$O$_3$ cathode, the 2032 type
coin-cells were assembled using a zinc foil anode, a 3 M Zn(CF₃SO₃)₂ electrolyte (Supplementary Figs. 11 and 12), and a filter paper separator. As shown in Supplementary Fig. 13, the cyclic voltammetry (CV) curves of the V₃-V₂O₅ electrode are carried out at a scan rate of 0.1 mV s⁻¹ within a voltage window of 0.1-1.3 V (vs Zn/Zn²⁺). Two pairs of redox peaks located at 1.09/0.78 V and 0.93/0.53 V are observed, which attributes to a two-step (de)intercalation process of Zn²⁺. The rate performance for V₃-V₂O₅ at current densities from 0.1 to 4.0 A g⁻¹ is presented in Fig. 2a and Supplementary Fig. 14. The reversible capacities of the V₃-V₂O₅ electrode are 196, 187, 165, 147, 138, 125, 117 and 113 mA h g⁻¹ at the current densities of 0.1, 0.3, 0.5, 0.8, 1.0, 2.0, 3.0, and 4.0 A g⁻¹, respectively. When current density returns to 0.5 A g⁻¹, a specific capacity of 163 mA h g⁻¹ is restored which ulteriorly illustrates the high electrochemical reversibility of the V₃-V₂O₅ electrode. The capacity retention reaches 70.4% when the current densities increase from 0.1 to 1.0 A g⁻¹, exhibiting excellent rate capability. It is ecstatic that the V₃-V₂O₅ electrode delivers ultra-long cycling stability with a capacity retention rate of 98% after 10,000 cycles, 90% after 20,000 cycles, and 81% after 30,000 cycles at a current density of 5 A g⁻¹ (Fig. 2b). To the best of our knowledge, the cycling stability of 30,000 cycles is the longest cycle lifetime for reported ZIBs at this current density. As shown in Fig. 2c, the life span of V₃-V₂O₅ is superior to most of the other aqueous ZIBs (Supplementary Table 4) recently reported in pieces of literature²⁵-³⁰. These results certainly highlight the great potentials of V₃-V₂O₅ cathode-based Zn batteries in the field of smart energy storage devices. The longevity of this V₃-V₂O₅ cathode comes ultimately from abundant vacancy clusters.
that attenuate the strong electrostatic interaction between Zn\(^{2+}\) and the V\(_d\)-V\(_2\)O\(_3\) host.

As shown in Supplementary Fig. 15, the c-V\(_2\)O\(_3\) cathode, without vacancies, demonstrates inferior both rate and stability electrochemical performance for aqueous ZIBs, which strongly confirms the positive effects of vacancies in V\(_d\)-V\(_2\)O\(_3\) cathode.

To further understand the greatly enhanced Zn\(^{2+}\) storage performance, the electrochemical kinetics of the V\(_d\)-V\(_2\)O\(_3\) electrode was investigated. As shown in Fig. 2d, CV measurements are carried out at different scan rates. With the increase of scan rates from 0.1 to 1.0 mV s\(^{-1}\), the CV curves show a similar shape and the reduction and oxidation peaks are well preserved. Regularly, the peak currents \(i\) and their corresponding sweep rates \(v\) obey a power-law relationship that is described by

\[
i = av^b,
\]

(1)

Where \(i\) represents the peak current (A), \(v\) represents the scan rate (V s\(^{-1}\)) and \(a, b\) are constants. The \(b\) values are useful as the base for analyzing electrochemical processes, where the \(b\) value is equal to 0.5 indicates that the electrochemical process is governed by ionic diffusion, and a capacitive storage process is indicated when \(b\) value is 1.0.

From the equation of \(\log (i) = \log (v) + \log (a)\) derived from equation (1), the calculated \(b\)-values for both cathode and anode peaks from CV curves are 0.94, 0.75, 0.79, and 0.88, respectively (Fig. 2e). It is suggested that the Zn\(^{2+}\) storage behavior of V\(_d\)-V\(_2\)O\(_3\) is controlled collectively by ionic diffusion and capacitive, which leads to fast Zn\(^{2+}\) diffusion kinetics enabling the high-rate performance. In order to further quantify the contribution of diffusion-controlled and capacitive-controlled at a specific scan rate, equation (1) is divided into two halves to form formula (2):
\[ i(V) = k_1v + k_2v^{1/2} \] (2)

According to the above equation, the current \( i \) at a specific potential \( V \) can be divided into a capacitance limiting effect \( (k_1v) \) and a diffusion control effect \( (k_2v^{1/2}) \). As shown in Supplementary Fig. 16, the capacitance contribution (corresponding to the purple region) is 82.5% of the overall contribution at scan rate 0.8 mV s\(^{-1}\). With the increases of scan rates from 0.1 to 1 mV s\(^{-1}\), the capacitance contribution rates increase from 66.3% to 86.4% (Fig. 2f). This suggests a substantially greater proportion of capacitive-dominated process, which directly contributes to excellent rate performance due to the fast kinetics of \( \text{Zn}^{2+} \). Galvanostatic intermittent titration technique (GITT) is performed to analyze the diffusion coefficient of \( \text{Zn}^{2+} \) in the \( V_d-\text{V}_2\text{O}_3 \) electrode (Supplementary Fig. 17). The result shows that the diffusion coefficient of \( \text{Zn}^{2+} \) in the \( V_d-\text{V}_2\text{O}_3 \) electrode is between \( 10^{-7}-10^{-8} \text{ cm}^2 \text{ s}^{-1} \), which stays ahead of the other existing electrodes\(^6,31,32\).

**Zinc-ion storage mechanism of \( V_d-\text{V}_2\text{O}_3 \)**

DFT calculations were conducted to explore the veritable function of \( V_d-\text{V}_2\text{O}_3 \) for \( \text{Zn}^{2+} \) storage. To investigate the distribution of vanadium vacancies, based on the XRD and NPD Rietveld analysis results, diverse vanadium vacancy models at the concentration of 6.25%, in good agreement with experiments were constructed as shown in Supplementary Fig. 18. A lower formation enthalpy represents a more stable phase. Structure 1 possesses the smallest formation enthalpy, illustrating the short aggregation of \( V_d \) clusters which is consistent with Table 1. Then, the p-\( \text{V}_2\text{O}_3 \) and \( V_d-\text{V}_2\text{O}_3 \) were implemented to disclose the insertion of \( \text{Zn}^{2+} \). The frustrated insertion of \( \text{Zn}^{2+} \) into p-\( \text{V}_2\text{O}_3 \) was observed due to the enormously positive Gibbs free energy (2.69 eV)\(^33\),
illustrating no capacity or an extremely tiny capacity (Fig. 3a), consistent with the badly Zn$^{2+}$ storage performance of c-V$_2$O$_3$ (Supplementary Fig. 15). What’s more, the direct insertion of Zn$^{2+}$ into p-V$_2$O$_3$ may cause the destruction of the structure, leading to bad stability. However, for V$_d$-V$_2$O$_3$, vanadium vacancies will accept the insertion of Zn$^{2+}$ and provide high capacity than c-V$_2$O$_3$. Intriguingly, the distinguishing Gibbs free energies demonstrate the process of insertion of Zn$^{2+}$ into V$_d$-V$_2$O$_3$ is different. Firstly, the vanadium defect is occupied with Zn$^{2+}$ and a large number of heat was released (-1.34 eV) due to the strong electrostatic, improving the integrities and stabilities of V$_d$-V$_2$O$_3$. Nevertheless, due to this strong electrostatic interaction, the extraction of this kind Zn$^{2+}$ is unbearable, demonstrating the self-anchoring action of Zn$^{2+}$ in the lattice. Secondly, the feasible and sustainable insertion of Zn$^{2+}$ into V$_d$-V$_2$O$_3$ is observed, affording the capacity and voltage (Fig. 3a). This phenomenon unravels the residual of Zn in V$_d$-V$_2$O$_3$. Consequently, the dual-effect of vanadium vacancies in V$_d$-V$_2$O$_3$ is specified in Fig. 3b. When Zn$^{2+}$ initially entries into the V$_d$-V$_2$O$_3$ electrode that has many vanadium vacancies, part of Zn$^{2+}$ will be riveted on vanadium vacancies and caged inside during the whole time. In other words, the eventual structure is a Zn doped V$_d$-V$_2$O$_3$ after the first discharging self-optimized process, in which the Zn$^{2+}$ will reversibly insert or leave in the subsequent cycles.

Based on the above analysis, a series of characterizations were conducted to demonstrate the Zn$^{2+}$ storage mechanism of the V$_d$-V$_2$O$_3$ cathode and effect of vanadium vacancies. It can be seen from Figs. 4a and 4b that the characteristic (104) and (110) peaks move to a lower 20 degree during the discharging process and return
to the original position in the subsequent charge process. These reversible movements originate from the expansion and contraction of the lattice of V$_d$-V$_2$O$_3$ with the de/intercalation of Zn$^{2+}$. Besides, no other diffraction peaks were detected, indicating no phase transformations in the V$_d$-V$_2$O$_3$ electrodes during the charge/discharge process. The stability of V$_d$-V$_2$O$_3$ was further incarnated in the unchanged XRD curves after 500 cycles (Supplementary Fig. 19). It is noteworthy that the morphology of the V$_d$-V$_2$O$_3$ electrodes have transformed into particles with a diameter of about 25 nm after the first cycle and remained unchanged in the subsequent cycles, which adapts to the reversible insertion/extraction of Zn$^{2+}$ better. (Supplementary Figs. 20-22).

X-ray photoelectron spectroscopy (XPS) and soft X-ray absorption spectrum (sXAS) were performed to give insight into the chemical states of the V$_d$-V$_2$O$_3$ electrodes at different states. The reversible insertion and extraction of Zn$^{2+}$ are shown in Supplementary Fig. 23a. At a fully discharged state, the V$_d$-V$_2$O$_3$ electrode displays two Zn 2p$_{3/2}$ components located at 1022.5 eV and 1023.2 eV which belong to the intercalated Zn$^{2+}$ at different occupation sites (vanadium vacancies and tunnels nearby vanadium vacancies). At fully charged state, the Zn 2p$_{3/2}$ peak located at 1023.2 eV disappears while the peak of 1022.5 eV is reserved. That is to say that some vanadium vacancies occupied Zn$^{2+}$ is riveted in the lattice of V$_d$-V$_2$O$_3$, only enable Zn$^{2+}$ reversibly (de)intercalation in the tunnel neighboring the remaining vanadium vacancies. Precise quantification of the V and Zn contents at fully dis/charged states was carried on the inductively coupled plasma emission spectroscopy (ICP-AES) and the detailed results show in Supplementary Table 5. The identical results can be gotten from TEM
elemental mapping where the Zn, V, and O elements are uniformly distributed (Supplementary Figs. 24 and 25). The charge compensation of V in the process of Zn\textsuperscript{2+} insertion/extraction is shown in the V L-edge patterns (Figs. 4c and 4d). Two peaks located at ~518 eV and 525 eV are observed in the V L-edge pattern, corresponding to V 2p\textsubscript{3/2}→V 3d and V 2p\textsubscript{1/2}→V 3d transitions, respectively\textsuperscript{34,35}. The intensity of V 2p\textsubscript{3/2} peaks are increased with the entrance of Zn\textsuperscript{2+} and decreased with the release of Zn\textsuperscript{2+}, gradually, stating the electronic acquirement and deprivation of V in the Zn\textsuperscript{2+} electrochemistry. Notably, under the same voltage, the peak intensity remains the same revealing the high reversibility of the V\textsubscript{d}-V\textsubscript{2}O\textsubscript{3} electrode. The valence changes in the whole cycle are also shown in the high-resolution XPS of V (Supplementary Fig. 23b) where the peak of V\textsuperscript{4+} becomes dominant upon charging while releasing a sign of a let-up upon discharging. Given the local environment of vacancy, the local chemical and electronic environment of intercalated Zn\textsuperscript{2+} was investigated by Zn K-edge XAFS. Since the surrounding local environment of Zn\textsuperscript{2+} is the same during charging and discharging, the K-edge XAFS of Zn is changeless (Fig. 4e and Supplementary Fig. 26).

Conclusion

In summary, we have quantified 5.7\% V\textsubscript{d} clusters in a V\textsubscript{d}-V\textsubscript{2}O\textsubscript{3} cathode for the first time in aqueous ZIBs which shows remarkable Zn\textsuperscript{2+} storage performance. The DFT calculations indicated that the Zn\textsuperscript{2+} storage reversibility and stability will be greatly enhanced under the effects of V\textsubscript{d} clusters. Concretely, part of vanadium vacancies provides permanent sites for the preoccupation of a small amount of Zn\textsuperscript{2+} so that the
system will have a more stable structure to against collapsing during the process of Zn\(^{2+}\) insertion/extraction. Meanwhile, the other vanadium vacancies can effectively weaken the strong interaction between Zn\(^{2+}\) and V\(_2\)O\(_3\) material host to allow free insertion/extraction of Zn\(^{2+}\). Benefitting from the 5.7% V\(_d\) clusters, the V\(_d\)-V\(_2\)O\(_3\) cathode provides a capacity of 196 mA h g\(^{-1}\) at 0.1 A g\(^{-1}\) and exhibits ultra-long stability up to 30,000 cycles with a capacity retention of 81%, which is the longest aqueous ZIBs stability as far as we know. This accurately quantifying and determining the effect of defects opens a new window for designing aqueous ZIBs cathodes with ultra-long stability.

**Data availability**

The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

**References**


Acknowledgments

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**Author contributions**

L.S. and S.M.C. supervised the project. K.F.Z. and S.Q.W. designed the work and carried out most of the experiments. L.H.H. and F.R.S. measured and analyzed XRD and NPD data. H.W.S. simulated most of the calculations. P.J.Z. and C.D.W. performed XAFS and sXAS experiments. Y.Y.C. and X.G. helped to prepare most of the samples. H.J.Z., B.J.Y., and M.L. guided the PAS measurements and helped to analyze PAS results. X.J.W. helped to explain some experimental data. All the authors discussed the results and assisted during the manuscript preparation.
Figure

Fig. 1 | a, Normalized XANES spectrum of $V_d$-$V_2O_3$ and $c$-$V_2O_3$, inset: the corresponding Fourier-transformed V K-edge EXAFS spectra of $V_d$-$V_2O_3$ and $c$-$V_2O_3$. b, Schematic diagram of the structure of $V_d$-$V_2O_3$ along the c-axis. The oxygen atoms are represented by small red spheres, and the V atoms are depicted in blue. c, Observed (black circle), calculated diffraction patterns (red line), their difference (purple line) and peak position (black bar) of the NPD pattern (upper part) and XRD pattern (lower part).

Table 1 | Position lifetime parameters of $V_d$-$V_2O_3$ and $c$-$V_2O_3$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\tau_1$ (ns)</th>
<th>$\tau_2$ (ns)</th>
<th>$\tau_3$ (ns)</th>
<th>$I_1$ (%)</th>
<th>$I_2$ (%)</th>
<th>$I_3$ (%)</th>
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<tr>
<td>$V_d$-$V_2O_3$</td>
<td>0.156</td>
<td>0.373</td>
<td>1.559</td>
<td>17.023</td>
<td>78.011</td>
<td>4.966</td>
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<tr>
<td>$c$-$V_2O_3$</td>
<td>0.175</td>
<td>0.392</td>
<td>1.610</td>
<td>57.085</td>
<td>37.943</td>
<td>4.972</td>
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</table>
Fig. 2 | a, Rate performance at different current densities of $V_d$-$V_2O_3$ electrode. b, Long-term cycling performance and coulombic efficiency of $V_d$-$V_2O_3$ electrode at a current density of 5 A g$^{-1}$. c, Comparison of the cycle stability between $V_d$-$V_2O_3$ and other vanadium-based cathodes for aqueous zinc-ion batteries. d, CV curves of the $V_d$-$V_2O_3$ electrode at scan rates ranging from 0.1 to 1 mV s$^{-1}$. e, Log ($i$) versus log ($v$) plots at specific peak currents. f, Contribution ratios of capacitive and diffusion-controlled capacities at different scan rates from 0.1 mV s$^{-1}$ to 1.0 mV s$^{-1}$.

Fig. 3 | a, The Gibbs free energy of different models. b, The schematic illustration of the energy storage mechanism in the Zn/V$_2$O$_3$ battery.
Fig. 4  |  a, Ex-situ XRD patterns of V₆₋V₂O₃ electrodes at different cut-off voltages during the charge and discharge process. b, An enlarged view of the red dotted frame in Figure 4a. c, Normalized XANES spectrum of the V L-edge for V₆₋V₂O₃ electrodes at different voltages during the charging process. d, Normalized XANES spectrum of the V-edge for V₆₋V₂O₃ electrodes at different voltages during the discharging process. e, Fourier-transformed Zn K-edge EXAFS spectra of V₆₋V₂O₃ electrodes at fully charged and discharged states.