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Electrochemical performance and reaction mechanism investigation of V$_2$O$_5$ positive electrode material for aqueous rechargeable zinc batteries

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Abstract

The electrochemical performance and reaction mechanism of orthorhombic \( V_2O_5 \) in 1 M \( ZnSO_4 \) aqueous electrolyte are investigated. \( V_2O_5 \) nanowires exhibit an initial discharge and charge capacity of 277 and 432 mAh g\(^{-1}\), respectively, at a current density of 50 mA g\(^{-1}\). The material undergoes quick capacity fading during cycling under both low (50 mA g\(^{-1}\)) and high (200 mA g\(^{-1}\)) currents. \( V_2O_5 \) can deliver a higher discharge capacity at 200 mA g\(^{-1}\) than that at 50 mA g\(^{-1}\) after 10 cycles, which could be attributed to a different type of activation process under both current densities and distinct degrees of side reactions (parasitic reactions). Cyclic voltammetry shows several successive redox peaks during Zn ion insertion and deinsertion. *In operando* synchrotron diffraction reveals that \( V_2O_5 \) undergoes a solid solution and two-phase reaction during the 1\(^{st}\) cycle, accompanied by the formation/decomposition of byproducts \( Zn_3(OH)_2V_2O_7\cdot2(H_2O) \) and \( ZnSO_4Zn_3(OH)_6\cdot5H_2O \). In the 2\(^{nd}\) insertion process, \( V_2O_5 \) goes through the same two-phase reaction as that in the 1\(^{st}\) cycle, with the formation of the byproduct \( ZnSO_4Zn_3(OH)_6\cdot5H_2O \). The reduction/oxidation of vanadium is confirmed by *in operando* X-ray absorption spectroscopy. Furthermore, Raman, TEM and X-ray photoelectron spectroscopy (XPS) confirm the byproduct formation and the reversible Zn ion insertion/deinsertion in the \( V_2O_5 \).

**Keywords:** Orthorhombic \( V_2O_5 \); *In operando* synchrotron diffraction; *In operando* X-ray absorption spectroscopy; Aqueous rechargeable zinc batteries
1. Introduction

Aqueous rechargeable zinc batteries (ARZBs) have received much attention for application in large-scale energy storage because of their advantages, such as high safety, low cost, and sufficient abundance\(^1,2\). Aqueous electrolytes have higher ionic conductivity (up to 1 S cm\(^{-1}\)) than that of non-aqueous electrolytes (about 10 mS cm\(^{-1}\)), resulting in a higher rate capability\(^1\). Meanwhile, the utilization of aqueous electrolytes can lower the activation energy for charge transfer at the electrode/electrolyte interface. The manufacturing costs of ARZBs are expected to be low since water-based electrolytes are non-toxic, inflammable, and strict humidity control is not required during cell assembling\(^3,4\). Moreover, metallic Zn has a high specific capacity (820 mAh g\(^{-1}\)) and high volumetric capacity (5854 mAh cm\(^{-3}\)), making it promising as a negative electrode. It also owns sufficiently high overpotentials with respect to the hydrogen evolution, overcompensating the negative value of -0.76 V vs. SHE that makes it usable in water\(^5\) and, therefore, can be directly used as the negative electrode in aqueous-based electrolytes. However, the lack of high-performance positive electrode materials, the heavy mass, and the large polarization of divalent Zn\(^{2+}\) hinder the practical applications of ARZBs.

Many efforts have been made on the exploration of high-performance positive electrode materials for ARZBs, including the polymorphs of manganese oxide (\(\alpha-, \beta-, \gamma-, \delta\)-MnO\(_2\)), and spinel-MnO\(_2\))\(^4,6-17\), Prussian blue analogues\(^18-21\), vanadium-based oxides (\(\text{Ca}_{0.25}\text{V}_2\text{O}_5\cdot n\text{H}_2\text{O}, \text{Zn}_{0.25}\text{V}_2\text{O}_5\cdot n\text{H}_2\text{O}, \text{Na}_{0.33}\text{V}_2\text{O}_5, \text{V}_2\text{O}_5\cdot n\text{H}_2\text{O}, \text{LiV}_3\text{O}_8, \text{and H}_2\text{V}_2\text{O}_8\))\(^2,5,22-38\), organic compounds\(^39,40\), and other compounds such as \(\text{Na}_3\text{V}_2(\text{PO}_4)_3\)\(^41\), \(\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3\)\(^42\), VS\(_2\)\(^43\), and Mo\(_6\)S\(_8\)\(^44\). Among them, vanadium-based oxides are very promising due to their open framework and relatively high capacity as well as operation voltage of around 0.6–1.0 V. For example, Kundu et al.\(^5\) reported Zn\(_{0.25}\text{V}_2\text{O}_5\cdot n\text{H}_2\text{O} positive electrode, which delivers a high initial discharge/charge capacity of 282/278 mAh g\(^{-1}\) at C/6 rate, excellent rate capability, and high cycling stability with a capacity retention of 80% after 1000 cycles at 15 C rate. Xia et al.\(^29\) demonstrated that Na\(_{0.33}\text{V}_2\text{O}_5 nanowires have a high capacity of 367.1 mAh g\(^{-1}\) at 100 mA g\(^{-1}\) when used as the positive electrode in ARZBs. This material also exhibits good rate capability and high capacity retention of 93% after 1000 cycles. Pang et al.\(^34\) investigated H\(_2\)V\(_3\)O\(_8\)/graphene composite, which shows a high capacity of 394 mAh g\(^{-1}\) at C/3, high rate capability, and excellent cycling stability with a capacity retention of 87% after 2000 cycles. Despite this significant progress, it is still urgently required to deeply understand the electrochemical reaction mechanism of positive electrode materials. Because it is
more meaningful to the development of ARZBs by understanding the reaction mechanism behind good electrochemical performance than trying to improve performance empirically.

Because of its typical layered structure and relatively high capacity, V$_2$O$_5$ is considered a promising positive electrode for ARZBs$^{45-48}$. Despite its good electrochemical performance in ARZBs, the structural changes of V$_2$O$_5$ during electrochemical processes are still under debate. Three different viewpoints regarding the structural changes of V$_2$O$_5$ in ARZBs have been proposed so far:

(i) Zhou et al.$^{46}$ compared the performance of V$_2$O$_5$ in different electrolytes (i.e. Zn(NO$_3$)$_2$, Zn(CH$_3$COO)$_2$, ZnCl$_2$, and ZnSO$_4$ aqueous-based electrolytes) and with different concentrations of ZnSO$_4$-based electrolytes. In 3 M ZnSO$_4$, V$_2$O$_5$ delivers the best performance with a high capacity of 224 mAh g$^{-1}$ at 100 mA g$^{-1}$ and good cycling stability at the high current densities of 1 and 2 A g$^{-1}$, respectively. Ex situ X-ray diffraction (XRD) demonstrated the formation of a new phase of Zn$_x$V$_2$O$_5$ upon Zn insertion into V$_2$O$_5$.

(ii) Zhang et al.$^{45}$ also reported a V$_2$O$_5$ cathode material with a capacity of 470 mAh g$^{-1}$ at 0.2 A g$^{-1}$ and high capacity retention of 91.1% after 4000 cycles at 5 A g$^{-1}$ in 3 M Zn(CF$_3$SO$_3$)$_2$ electrolyte. They proved that this material can work in extreme conditions at both high (50 oC) and low (-10 oC) temperatures. The co-insertion of hydrated Zn ions into the V$_2$O$_5$ crystal structure was proposed based on ex situ XRD, X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM).

(iii) Chen et al.$^{47}$ proposed a phase transition reaction mechanism via ex situ XRD, Raman, and XPS. Orthorhombic V$_2$O$_5$ underwent a phase transition to zinc pyrovanadate during the first discharge, where the formed zinc pyrovanadate showed reversible Zn$^{2+}$ (de)insertion during subsequent cycles.

However, the electrochemical reaction mechanism of V$_2$O$_5$ in the above-reported works was investigated through ex situ techniques. The findings are in controversy with each other and a detailed investigation of the structural changes of V$_2$O$_5$ upon Zn-ion insertion/deinsertion is still missing. Moreover, non-equilibrium or intermediate species or states cannot be detected using ex situ studies, while in operando studies can provide a more reliable understanding of the structural evolution of a battery material in “real use”.

In addition, it has been frequently reported that a mass of complex byproducts was produced/decomposed during the discharge/charge cycling of vanadium oxides such as...
NaV$_3$O$_8$·1.5H$_2$O$^2$, VO$_{1.52}$(OH)$_{0.77}$$^2$, Zn$_2$V$_2$O$_{3.5}$, and NH$_4$V$_4$O$_{10.49}$. Interestingly, byproducts were not observed in the three works related to the study of V$_2$O$_5$ reported above. To better understand the electrochemical mechanism of V$_2$O$_5$ in ARZBs in operando techniques like diffraction using synchrotron radiation are required. Due to their extremely bright, high flux, and tunable also high energy, synchrotron radiation-based characterizations provide deep penetration into the sample, high-quality data, and real-time diffraction. Particularly, in operando synchrotron study can effectively avoid the unpredictable contamination and irreversible changes of highly reactive samples during material preparation, handling, and transportation, which can provide more reliable and precise data for analysis. Hence, in this work, orthorhombic V$_2$O$_5$ were prepared by a facile hydrothermal method and the detailed structure evolution and reaction mechanism of orthorhombic V$_2$O$_5$ in ARZBs are studied via in operando synchrotron diffraction and X-ray absorption spectroscopy (XAS) together with ex situ Raman and X-ray photoelectron spectroscopy (XPS).

2. Experimental

**Synthesis of V$_2$O$_5$ nanowires:** V$_2$O$_5$ nanowires were prepared via a modified hydrothermal method followed by heat treatment$^{50,51}$. Briefly, 0.18 g of commercial V$_2$O$_5$ powder (Alfa Aesar, 99.99%) was added to 30 ml of deionized water under vigorous stirring for a few minutes to form a light orange suspension. Then, 2.5 ml 30 % hydrogen peroxide (H$_2$O$_2$) was dropwise added to the above suspension and kept stirring for 30 mins to get a transparent orange solution. The obtained solution was transferred to a 50 ml Teflon-lined stainless-steel autoclave and kept at 190 °C for 4 days. The precipitate was collected and washed with deionized H$_2$O several times and dried at 80 °C for 12 h. Finally, the product was annealed at 400 °C for 2 h with a heating rate of 5 °C min$^{-1}$ in air atmosphere.

**Preparation of the electrolyte:** The 1 M ZnSO$_4$ electrolyte was prepared by dissolving a corresponding amount of ZnSO$_4$·7H$_2$O powder in distilled H$_2$O with vigorous stirring at room temperature.

**Morphological and Structural Study:** The morphology was studied with a Zeiss Supra 55 Scanning Electron Microscope (SEM) with primary energy of 15 keV. The structural characterization was performed using synchrotron radiation ($\lambda = 0.4132$ Å, 30 keV) at the Material Science and Powder Diffraction beamline (MSPD) of ALBA synchrotron (Barcelona, Spain)$^{52}$. The powder was filled in 0.5 mm Ø boro-silicate capillary, and the diffraction pattern was collected
in capillary geometry. A LabRam HR Evolution Raman microscope from Horiba Scientific equipped with HeNe laser (633 nm, 17 mW) and a CCD detector (Horiba) was used to collect the Raman scattering of the samples. Meanwhile, a 600 grating was used to split the measurement signal with a ×100 objective (NA 0.95) for all the pristine and cycled samples. The data were collected for 30 seconds with 4.25 mW of the laser and five measurements were added to reduce signal noise. Transmission electron microscopy (TEM) imaging and high angle annular dark field-scanning TEM (HAADF-STEM) electron dispersive X-Ray (EDX) mapping were acquired by Themis 300 under 300 kV with Ceta camera and Super-X EDX detector, respectively. The last measured screen current for high-resolution TEM (HRTEM) imaging was 998 pA and for EDS mapping was 93.4 pA. X-ray photoelectron spectroscopy measurements were performed using a K-Alpha XPS spectrometer (ThermoFisher Scientific, East Grinstead, UK), applying a micro-focused, monochromated Al Kα X-ray source with a spot size of 400 µm. To prevent any localized charge buildup, the K-Alpha+ charge compensation system was employed during analysis, using electrons of 8 eV energy and low-energy argon ions. The Thermo Avantage software was used for data acquisition and processing. The spectra were fitted with one or more Voigt profiles (binding energy uncertainty: ±0.2 eV). All spectra were referenced to the O 1s peak of vanadium oxide at 530.0 eV binding energy. In addition, the discharged and charged V₂O₅ and discharged and charged Zn electrodes were sealed in an in situ Raman cell with a quartz window inside a glovebox. Note the “discharged Zn” refers to the counter electrode of V₂O₅ at the discharged state of 0.3 V from the same cell, while “charged Zn” refers to the counter electrode of V₂O₅ at the charged state of 1.6 V from the same cell.

**Electrochemical Characterization:** The electrode was prepared by mixing active material V₂O₅ nanowires with Super C65 C (Timcal) and polyvinylidene difluoride (PVDF) binder in a weight ratio of 70:20:10 with N-Methyl-2-pyrrolidone solvent. The dried electrode mixture with mass loading of ~1.4 mg cm⁻² was pressed (4 tons) on a stainless steel mesh of 12 mm and dried at 120 °C overnight under vacuum. CR2032-type coin cells for electrochemical measurements were assembled in air at room temperature. The cells were built with V₂O₅ positive electrode, Zn foil as the negative electrode, 1 M ZnSO₄ as the electrolyte, and a piece of glass microfiber (Whatman) as the separator. The galvanostatic cycling with the potential limitation (GCPL) and cyclic voltammetry (CV) measurements were performed between 0.3 and 1.6 V (vs. Zn²⁺/Zn) with
a VMP3 potentiostat (BioLogic) at 25 °C. GCPL was performed at different current densities ranging from 50 to 1600 mA g\(^{-1}\) to determine the rate capability of the battery.

**In operando synchrotron diffraction and in operando X-ray absorption spectroscopy (XAS):** In operando synchrotron diffraction was performed at the Material Science and Powder Diffraction beamline (MSPD) at the ALBA synchrotron. The electrochemical cell consists of 2025-type coin cell with glass windows of 5 mm diameter for beam entrance. The positive electrode was prepared by pressing the dried electrode mixture (as described above) on a stainless steel mesh within a 5 mm hole in the center, a Zn foil with a 5 mm hole in the center was used as the negative electrode. In operando synchrotron diffraction was conducted with radiation \(\lambda = 0.4132\) Å wavelength (30 keV) and the position-sensitive detector MYTHEN. Data in steps of 0.006° over an angular range of 1.8° - 42° in 2theta were gathered with an effective exposure time of 60 s during the 1.5 cycles with a current density of 50 mA g\(^{-1}\). The coin cell was continuously oscillated +/-5° around the incoming beam direction to improve the powder averaging (i.e. increasing the number of crystallites fulfilling Bragg condition and contributing to the observed reflections). Diffraction data were analyzed by the Rietveld method using the Fullprof software package\(^{54}\). In operando XAS measurements were performed at beamline P65 at the synchrotron source PETRA III (DESY, Hamburg). XAS was carried out during the first charge/discharge process at the current of 50 mA g\(^{-1}\) in the same coin-cell configuration as above but with a Kapton window. X-ray absorption spectra of vanadium were recorded in quick-XAS (6 min/spectrum) mode in fluorescence geometry using a PIPS (passivated implanted planar silicon) diode. The V K-edge for V\(_2\)O\(_5\) was investigated, and the energy was calibrated utilizing vanadium foil as commonly applied in XAS experiments. V\(_2\)O\(_3\), VO\(_2\), and V\(_2\)O\(_5\) were used as standard materials. All data were collected at room temperature with a Si(111) double crystal monochromator, and all spectra were processed using the DEMETER software package\(^{55}\).

3. Results and discussion

3.1 Structural and morphological characterization
Figure 1 Rietveld refinement based on synchrotron diffraction data (a), SEM (b), and HRTEM image (c) of V$_2$O$_5$ nanowires, where fast fourier transform (FFT) was done from the marked orange area.

The crystal structure of the prepared V$_2$O$_5$ nanowires was investigated by synchrotron diffraction and HRTEM imaging, as displayed in Figure 1a. All reflections can be indexed to the orthorhombic V$_2$O$_5$ with space group $Pmn2_1$, and the lattice parameters are $a = 11.515(1)$ Å, $b = 4.374(1)$ Å, $c = 3.566(1)$ Å, in good agreement with the previous work. The strong intensities of the reflections confirm the high crystallinity of the obtained V$_2$O$_5$ nanowires material. The SEM image (Figure 1b) demonstrates that V$_2$O$_5$ material is composed of nanowire-like nanostructure with lengths up to several micrometers. TEM imaging further reveals the nanowire-like morphology of V$_2$O$_5$ while HRTEM image (Figure 1c) displays the highly crystalline sample on the [010] zone axis with lattice fringe of 0.58 nm and 0.34 nm corresponding to the (200) and (110) plane of V$_2$O$_5$, respectively. This fits well with the result obtained from synchrotron diffraction.

3.2 Electrochemical properties
Figure 2a displays the discharge-charge profiles of V$_2$O$_5$ nanowires at the specific currents of 50 mA g$^{-1}$ in the potential range of 0.30 - 1.60 V vs. Zn$^{2+}$/Zn. The open-circuit voltage (OCV) of the cell is 1.23 V. During the 1$^{	ext{st}}$ discharge (Zn ions insertion), V$_2$O$_5$ nanowires electrode displays a flat plateau at around 1.00 V, followed by a sloping-like plateau at about 0.50 V. During the 1$^{	ext{st}}$ charge process (Zn ions de-insertion), a slope and a flat plateau at 1.20 V together with a slope up to 1.6 V can be observed. Compared with the 1$^{	ext{st}}$ discharge, the 2$^{	ext{nd}}$ discharge profile shows a shorter plateau at around 1.00 V and similar sloping-like plateau at 0.50 V. In the 2$^{	ext{nd}}$ charge process, a slope similar to that for the 1$^{	ext{st}}$ charge is observed, but no clear plateau at 1.20 V can be seen. During cycling, the voltage profiles significantly change: the plateau at 1.20 V completely disappears, and only one slope and a sloping-like plateau at 0.50 V can be observed (see the 5$^{	ext{th}}$ discharge profile). On the 5$^{	ext{th}}$ charge profile, two sloping-like plateaus at 0.70 V and 1.0 V are observed. The V$_2$O$_5$ nanowires electrode delivers an initial discharge and charge capacity of 277 and 432 mAh g$^{-1}$, respectively, at a current density of 50 mA g$^{-1}$. The discharge capacity of 277 mAh/g almost reaches the theoretical one based on the insertion of 1 mol of Zn$^{2+}$ in V$_2$O$_5$ (294 mAh g$^{-1}$). The huge extra charge capacity might be attributed to side reactions such as O$_2$ evolution from the aqueous-based electrolyte. The electrode delivers a discharge capacity of 302 mAh g$^{-1}$ at the 2$^{	ext{nd}}$ cycle, a value higher than that for the first cycle, which might be due to an activation of the active material (theoretical capacity of 442 mAh g$^{-1}$ by considering insertion of 1.5 mol of Zn$^{2+}$ into V$_2$O$_5$), accompanied by Zn insertion, as also reported by other previous studies$^{6,57}$. The V$_2$O$_5$
positive electrode exhibits a dramatic decrease of capacity during the following 20 cycles at 50 mA g\(^{-1}\) (94 mAh g\(^{-1}\) at the 22\(^{\text{nd}}\) cycle) and delivers a discharge capacity of only 21 mAh g\(^{-1}\) after 100 cycles. Moreover, the cycling stability of V\(_2\)O\(_5\) positive electrode was studied at a higher specific current of 200 mA g\(^{-1}\), as presented in Figure 2b. An initial discharge capacity of 278 mAh g\(^{-1}\) is obtained, followed by a sudden capacity decline down to 180 mAh g\(^{-1}\) at the 2\(^{\text{nd}}\) cycle. In the following four cycles, the behavior differs from the one of the electrode cycled at 50 mA g\(^{-1}\): it displays a capacity increase, indicating a long activation process of the active material, which is often observed in positive electrode materials for ARZBs\(^6\) \(^{,57}\). However, this activation phenomenon takes more cycles under high current density, demonstrating its possible correlation with the involved chemical ion kinetics during cycling\(^{22}\). After 100 cycles, the capacity at 200 mA g\(^{-1}\) is higher (45 mAh g\(^{-1}\)) than that delivered at 50 mA g\(^{-1}\). This could be attributed to a different type of activation process under different current densities. The side reactions (parasitic reactions) under low current have more relevance than at high current and, consequently, the degradation is faster. Moreover, a significant difference is observed between the two first charge profiles recorded at both current densities: the charge profile recorded at 200 mA g\(^{-1}\) displays a slope-like plateau (Figure S1); a clear flat plateau in the voltage profile is observed at the low current of 50 mA g\(^{-1}\). The difference of voltage profiles suggests a different mechanism reaction and therefore results in a type of activation process under high and low current.

3.3 Electrochemical mechanism
In order to clarify the Zn-ion storage mechanism in the V$_2$O$_5$ material, CV was performed at a scan rate of 0.1 mV s$^{-1}$ in the voltage range of 0.30 - 1.60 V (vs. Zn$^{2+}$/Zn). Figure 3 displays two peaks centered at 0.92 and 0.50 V during the 1$\text{st}$ reduction process and a broad peak at 1.20 V with a shoulder at 1.05 V during the 1$\text{st}$ oxidation process. In the following scans, three features are observed for both reduction and oxidation processes, respectively. The reduction peak at 0.92 V gradually shifts to higher potential, becomes weaker, and finally disappears. However, a new reduction peak at 0.88 V emerges and grows up and the reduction peak at 0.50 V gradually shifts to 0.57 V, indicating polarization (and resistance) decrease of this process. At the same time, a new oxidation peak appears at 0.74 V. The oxidation peak at 1.05 V shifts to 1.00 V after the first cycle and increases upon cycling. The oxidation peak at 1.20 V shifts to 1.12 V in the 3$\text{rd}$ cycle; this shift is accompanied by decreasing in current intensity, indicating the decrease of polarization.

To investigate the structural evolution of V$_2$O$_5$ upon Zn-ion insertion/deinsertion, in operando synchrotron diffraction was performed during the initial 1.5 cycles. The contour maps of selected diffraction patterns and corresponding voltage-time profiles are provided in Figure 4. Note that an electrochemical activation is observed at the high current of 200 mA g$^{-1}$ during the first 5 cycles, with very interesting changes. Here we go deeper on understanding the very initial changes at low...
current and in the future, it would be interesting and necessary to study what is happening during
the further cycles at higher current density.

![Contour maps of in operando synchrotron diffraction of V$_2$O$_5$ during the first one and half
cycles and the corresponding voltage profile at a current density of 50 mA g$^{-1}$](image)

**Figure 4** Contour maps of *in operando* synchrotron diffraction of V$_2$O$_5$ during the first one and half
cycles and the corresponding voltage profile at a current density of 50 mA g$^{-1}$

Before the discharge (at 1.2 V), all reflections of the parent material can be indexed on the
orthorhombic V$_2$O$_5$ in the space group $Pmn2_1$ (see **Figure S2a** for the Rietveld refinement of
pristine V$_2$O$_5$). At the beginning of the 1$^{\text{st}}$ discharge (**Region I**), most of the characteristic
reflections of V$_2$O$_5$, such as ones at 200 (4.12°), 101 (6.96°), 400 (8.24°), 011 (8.58°), 301 (9.08°),
411 (11.90°), 600 (12.37°), 002 (13.31°), 012 (14.38°), 402 (15.67°), and 701 (15.91°),
continuously shift towards lower 2$\theta$, accompanied by a slight reduction of their intensity.
Therefore, a solid solution reaction upon Zn ions insertion into the V$_2$O$_5$ structure can be proposed
up to the stoichiometry Zn$_x$V$_2$O$_5$ ($x=0.22$, 65 mAh g$^{-1}$, black line at the end of **Region I, Figure
S3**), where lattice parameters $a$ and $c$ increase and $b$ decreases. At the same time, few reflections
at 010 (5.42°), 020 (10.85°), and 120 (11.04°) slightly shift to high angles; few other reflections at
110 (5.80°), 320 (12.49°), 021 (12.73°), and 620 (16.46°) keep in the same positions. Upon total
discharge capacity of 44 mAh g$^{-1}$ from OCV (1.02 V, $x=0.15$, cyan line in the middle of **Region
I, Figure S3**), two small reflections at 3.29° and 13.23° emerge, which belong to a new phase of
zinc pyrovanadate of 1.2 % (wt/wt), Zn$_{3+\delta}$(OH)$_2$V$_2$O$_7$·2H$_2$O (see **Figure S2b** for the Rietveld
refinement based on the 10$^{\text{th}}$ pattern recorded during discharge of V$_2$O$_5$). Other reflections related
to this phase become visible at 4.49°, 7.78°, 7.99°, 8.46°, 9.57°, 10.20°, 11.16°, 15.97°, and 17.54°
along with further Zn ions insertion. At the same time, other reflections at 3.81°, 5.67°, 7.01°,
7.61°, 11.42°, and 11.66° appear and grow (Region II). These reflections are attributed to the formation of the new Zn-rich phase Zn$_x$V$_2$O$_5$ (x=0.44) through a 2-phase reaction, corresponding to the capacity of 129 mAh g$^{-1}$. Meanwhile, the reflections of the new Zn-rich phase Zn$_{0.44}$V$_2$O$_5$ remain in their positions, together with the decrease of the intensities of the Zn$_{0.22}$V$_2$O$_5$ phase. At the end of Region II (gray line in Figure S3), most of the reflections of Zn$_{0.22}$V$_2$O$_5$ phase disappear, and the Zn-rich Zn$_{0.44}$V$_2$O$_5$ phase grows up. It implies the 2-phase coexistence transition between Zn$_{0.22}$V$_2$O$_5$ and Zn$_{0.44}$V$_2$O$_5$ in Region II during the Zn ions insertion. The formation of Zn$_{0.44}$V$_2$O$_5$ is accompanied by the formation of the byproduct Zn$_3$(OH)$_2$V$_2$O$_7$·2H$_2$O. Note that the $x$ value is determined without the consideration of the consumption of V$_2$O$_5$ to form the byproduct Zn$_{3+\delta}$(OH)$_2$V$_2$O$_7$·2H$_2$O and the possible dissolution of V$_2$O$_5$, where the dissolution and phase transformation mechanisms of V$_2$O$_5$ in ARZBs were newly reported\textsuperscript{58}. Therefore, the value of $x=0.44$ is an estimate for the lower limit of the inserted Zn content. Upon further Zn ions insertion (Region III), some new reflections begin to appear at 2.16°, 4.34°, 9.26°, 9.35°, which are assigned to the byproduct of ZnSO$_4$Zn$_3$(OH)$_6$·5H$_2$O with space group $P$-$1$. Once the byproduct is formed, all its Bragg reflections remain at the same 2$\theta$-positions throughout the discharge process, but their intensities increase. Meanwhile, most of the reflections maintain their positions along with the increase of their intensities (Region III), while only two reflections of Zn$_{0.44}$V$_2$O$_5$ at 3.81° and 7.01° shift to high and low angles, respectively. It indicates that a solid solution process happens in Region III to form a final phase Zn$_{0.94}$V$_2$O$_5$ together with the above-mentioned two byproducts with a total discharge capacity of 277 mAh g$^{-1}$ (see Figure S2c for the Rietveld refinement of 36\textsuperscript{th} pattern at first fully discharged V$_2$O$_5$). During the 1\textsuperscript{st} charge, the reflections do not evolve in a symmetric reverse backway, as indicated by the appearance and disappearance of a small reflection at 7.17°, where two 2-phase regions are observed (Region II). The reflections return back to their initial 2$\theta$-positions for the pristine V$_2$O$_5$ state, but with much lower intensities (see Figure S2d for the Rietveld refinement, based on the 69\textsuperscript{th} pattern at fully charged V$_2$O$_5$). This is possibly caused by the amorphization of the crystalline active material or by the vanadium dissolution in the electrolyte\textsuperscript{32, 36} (See Figure S4). Interestingly, both byproducts disappear again along with the 1\textsuperscript{st} charging process. The evolution of the reflections in the 2\textsuperscript{nd} discharge is analogous to that during the 1\textsuperscript{st} cycle. In Region I, the reflections show the same behavior as those for the first discharge process, suggesting a solid solution reaction. In Region II and III, the electrode undergoes the same process: a shorter two-phase transition and solid solution than in the first discharge, but
without the appearance of the reflections related to the byproduct Zn$_{3+\delta}$(OH)$_2$V$_2$O$_7$·2H$_2$O (see Figure S2e for the Rietveld refinement, based on the 97th pattern at the 2nd fully discharged V$_2$O$_5$). The formation of the other byproduct ZnSO$_4$Zn$_3$(OH)$_6$·5H$_2$O is also detected again during the second discharge process. The Zn$_{3+\delta}$(OH)$_2$V$_2$O$_7$·2H$_2$O has an open layered structure and has been reported by Alshareef et al.$^{26}$ as positive electrode material in ARZBs. The material has a capacity of 213 mAh g$^{-1}$ at 50 mA g$^{-1}$ and shows a shift of the reflection 001 during Zn-ions insertion and deinsertion$^{26}$. This means that the Zn$_{3+\delta}$(OH)$_2$V$_2$O$_7$·2H$_2$O byproduct, generated during cycling, still contributes to the overall capacity of the electrode. Recently, Chen et al.$^{47}$ reported that Zn$_3$(OH)$_2$V$_2$O$_7$·2H$_2$O is also formed via the 2-phase coexistence transition in an aqueous Zn-V$_2$O$_5$ battery, and then it functions as a host structure in the following cycles, where it shows a shift of reflection 001 during Zn ions insertion. However, in our case, the shift of the 001 reflection is not observed, which might suggest that Zn$_{3+\delta}$(OH)$_2$V$_2$O$_7$·2H$_2$O is not active or just the c-axis parameter does not change. Furthermore, our results directly show for the first time the formation and decomposition of both byproducts Zn$_{3+\delta}$(OH)$_2$V$_2$O$_7$·2H$_2$O and ZnSO$_4$Zn$_3$(OH)$_6$·5H$_2$O during cycling.

In order to investigate the variation of the oxidation state and the local electron environment of vanadium during the discharge/charge (i.e. Zn insertion/deinsertion) process, in operando XAS was performed on the V$_2$O$_5$ nanowires as positive electrode within an in operando coin cell. Figure 5 shows the normalized V K-edge spectra collected during the initial discharging and charging processes and reference spectra of standard vanadium oxides, where V$_2$O$_5$, VO$_2$, and V$_2$O$_3$ have the oxidation state of +5, +4, and +3, respectively. The edge position of the V K-edge in the pristine V$_2$O$_5$ positive electrode overlaps with that of the standard V$_2$O$_5$ reference, indicating that the oxidation state of V in V$_2$O$_5$ is +5. Moreover, an intense pre-edge peak for the V K-edge of pristine V$_2$O$_5$ is observed, which is ascribed to the transitions between the 1s and bound p-hybridized d-states$^{59,60}$. Along with progressive discharging, the main absorption edge shifts towards lower binding energies, confirming the reduction of the oxidation state of vanadium upon the Zn-ion insertion. Meanwhile, the pre-peak (A in Figure 5a) also shifts gradually to lower binding energy with the simultaneous decrease of intensity, confirming the reduction of V and the deformation of the local V environments during Zn-ions insertion. This is due to the co-existence of a distorted tetragonal pyramid and VO$_6$ octahedra. The edge resonance (B in Figure 5a) displays distinct changes in both intensity and shape, which is caused by the absorption of photons accompanied
by core-electron excitations\textsuperscript{60, 61}. During the discharge process, two broad peaks centered at 5494 eV and 5507 eV shift to lower energy and with a decrease of their intensities, before they converge into one very broad peak centered at 5500 eV from the initial stage to 0.99 V (peak B in Figure 5\textit{a}). After that, the formed broad peak centered at 5500 eV and the peak at 5486.5 eV continuously shift to lower energy accompanied by an increases of both intensities (from 0.99 V to 0.3 V). Two distinct isosbestic points\textsuperscript{62} at \textasciitilde{} 5474 eV and \textasciitilde{} 5502 eV (red arrows in Figure 5\textit{a} and \textit{b}) are observed during both discharge (from 0.99 V to 0.3 V) and charge (from 0.3 V to 1.32 V) processes. This confirms the 2-phase coexistence transitions upon Zn-ions insertion/deinsertion into/from V\textsubscript{2}O\textsubscript{5} structure, as already proposed from \textit{in operando} synchrotron diffraction. At the fully discharged state at 0.30 V, the observed energy of the V K-edge lies almost in the middle of those of the V\textsubscript{2}O\textsubscript{5} and V\textsubscript{2}O\textsubscript{3} reference spectra. This means that the oxidation state of V is very close to V\textsuperscript{4+}, in good agreement with the electrochemical data (see Figure S5). However, the energy of the edge does not completely overlap with the spectrum of VO\textsubscript{2}, reflecting structural differences between the discharged state with x=1.00 in Zn\textsubscript{x}V\textsubscript{2}O\textsubscript{5} and the reference material VO\textsubscript{2}. During the charging process (Zn-ion deinsertion), a completely reversible behavior can be observed. Pre-peak and edge resonance (A’ and B’ in Figure 5\textit{a} and \textit{b}) prove a reversible process. At the fully charged state of \textasciitilde{} 1.6 V, the V spectrum returns back to its initial state, indicating that the V ions are fully oxidized to the oxidation state of +5. The evolution of V K-edge spectra reveals that the V ions are reduced and reversibly oxidized during the Zn-ion insertion and deinsertion, respectively, accompanied by the local structural changes around the V ions and in full agreement with \textit{in operando} synchrotron diffraction.

![V_{2}O_{5} in ZnSO_{4} 1st discharge](image1)

![V_{2}O_{3} in ZnSO_{4} 1st charge](image2)
**Figure 5** *In operando* V K-edge XANES spectra during the 1st cycle in 1 M ZnSO$_4$; the isosbestic points are pointed out by red arrows.

Raman spectra were collected to investigate vibration modes as fingerprints of the short-range structure of the samples during Zn-ions insertion/deinsertion, as displayed in **Figure 6** and **Table S1**. In the pristine V$_2$O$_5$, oxygen atoms lie in four distinct sites in a [VO$_5$] pyramid unit, denoted as O(1)–O(4). The stretching mode of V–O(1) bond is located at 994 cm$^{-1}$ and its bending vibrations are located at 405 and 284 cm$^{-1}$. Raman peaks at 482 cm$^{-1}$ and 701 cm$^{-1}$ are ascribed to the bending vibration of the V–O(3) and the stretching vibration of the V–O(2), respectively. The peaks at 527 and 304 cm$^{-1}$ are attributed to the stretching and bending vibrations of the V–O(4) bond, respectively. The peaks at lower wavenumbers, 145 and 197 cm$^{-1}$ are assigned to weak Van der Waals interaction between adjacent [VO$_5$] slabs. These results are consistent with previous works.$^{63, 64}$ After Zn-ions insertion, significant changes are observed and some peaks related to V$_2$O$_5$ at 994, 701, 405, 304, and 284 cm$^{-1}$ become weak and broad, while those at 527, 482, and 197 cm$^{-1}$ completely disappear. Meanwhile, some broad and distinct new peaks appear at 1129, 967, 876, 610, and 450 cm$^{-1}$ for discharged V$_2$O$_5$, where peaks at 1129, 967, and 610 cm$^{-1}$ are attributed to the $v_3$, $v_1$, $v_4$ of SO$_4^{2-}$ vibration bands of ZnSO$_4$Zn$_3$(OH)$_6$·nH$_2$O$^{65, 66}$ and peaks at 876 and 450 cm$^{-1}$ are related to the V-O and Zn-O bonds in Zn$_x$V$_2$O$_5$ and Zn$_3$(OH)$_2$V$_2$O$_7$·2H$_2$O$^{67}$. Therefore, the coexistence of Zn$_x$V$_2$O$_5$ and byproducts, ZnSO$_4$Zn$_3$(OH)$_6$·5H$_2$O and Zn$_3$(OH)$_2$V$_2$O$_7$·2H$_2$O, is concluded in the discharged V$_2$O$_5$ electrode. On the other hand, for the Zn counter electrode in a discharged cell, several peaks at 1129, 967, 566, 440, and 398 cm$^{-1}$ are observed. The peaks appearing at 440 and 566 cm$^{-1}$ are assigned to the Zn-O vibration of Zn$_{1+x}$O on the surface of Zn metal$^{65, 68}$, while 1129, 967, and 398 are assigned to the $v_3$, $v_1$, $v_4$ of SO$_4^{2-}$-vibration in the ZnSO$_4$Zn$_3$(OH)$_6$·nH$_2$O$^{65, 66}$. Upon charging, the spectrum of fully charged V$_2$O$_5$ at 1.6 V returns back to its main original features with less intensity, indicating the disappearance of Zn$_x$V$_2$O$_5$ and the byproducts, ZnSO$_4$Zn$_3$(OH)$_6$·5H$_2$O and Zn$_{3+δ}$(OH)$_2$V$_2$O$_7$·2H$_2$O. This demonstrates the reversible reaction during Zn-ions insertion and deinsertion as identified by *in operando* synchrotron diffraction and XAS. Moreover, an additional broad peak at 875 cm$^{-1}$ related to Zn$_x$V$_2$O$_5$ is observed for the counter electrode Zn from a charged cell, compared with that from a discharged one. This indicates that the byproduct ZnSO$_4$Zn$_3$(OH)$_6$·5H$_2$O does not completely disappear on the surface of Zn metal. Dissolved Zn$_x$V$_2$O$_5$ can pass through the separator and
reaches the surface of Zn metal. This contributes to ongoing degradation and limits the cycling stability.

![Raman spectra of pristine V$_2$O$_5$, the 1st discharged and charged state of V$_2$O$_5$ and of the Zn counter electrode from a discharged and charged cell](image)

**Figure 6** Raman spectra of pristine V$_2$O$_5$, the 1st discharged and charged state of V$_2$O$_5$ and of the Zn counter electrode from a discharged and charged cell

TEM and elemental mapping were carried out to further study the structural and morphology evolution of V$_2$O$_5$ during cycling. It is unable to observe the nanowire-like feature of Zn$_x$V$_2$O$_5$ on the fully discharged electrode, whereas a sheet-like morphology can be clearly seen (Figure 7a). Figure S6 shows that the O, S, V, and Zn elements are uniformly distributed in the sheet-like material. The sheet-like material is probably attributed to the byproducts of ZnSO$_4$Zn$_3$(OH)$_6$·5H$_2$O, as demonstrated by synchrotron diffraction. Figure 7b confirms the disappearance of sheet-like morphology and the recovery of nanowire-like feature of V$_2$O$_5$ after the charge process, demonstrating the decomposition of byproducts.
XPS was applied to investigate the surface chemistry and surface elemental composition of pristine V$_2$O$_5$, first discharged V$_2$O$_5$, and first recharged V$_2$O$_5$. As displayed in Figure 8, the V 2p spectrum of pristine V$_2$O$_5$ can be fitted with two doublets: a main one with V 2p3/2 at 517.6 eV and a second one with weak intensity at 516.3 eV, which demonstrates that V exists mainly in the oxidation state +5 with a minor contribution of vanadium +4. It can be seen that the O 1s spectrum of pristine V$_2$O$_5$ can be fitted with one peak at 530.3 eV, corresponding to V−O group. The V 2p spectrum in the discharged state is not visible anymore due to the formation of the byproduct ZnSO$_4$Zn$_3$(OH)$_6$·5H$_2$O on the surface of the electrode, which blocks photoelectrons. While the V 2p spectrum of the charged state exhibits two V 2p3/2 components at 517.7 and 516.4 eV, the spectrum returns back to the one of pristine V$_2$O$_5$ after charge. For the discharged state of V$_2$O$_5$, a symmetric O 1s spectrum at 532.0 eV is obtained, assigning to the OH$^-$ and SO$_4^{2-}$ group of the byproduct ZnSO$_4$Zn$_3$(OH)$_6$·5H$_2$O, which was formed on the surface of the electrode and makes the O 1s spectrum from buried V-O groups invisible. After charging, the O 1s spectrum of the V-O group is visible again, accompanied by a minor contribution of OH$^-$ on the surface of the electrode.
Figure 8 V 2p and O 1s X-ray photoelectron spectra of pristine V$_2$O$_5$, together with the 1$^{\text{st}}$ discharged and the 1$^{\text{st}}$ charged state.

4. Conclusion

In summary, orthorhombic V$_2$O$_5$ nanowires were prepared via a facile hydrothermal approach. In the 1 M ZnSO$_4$ electrolyte, V$_2$O$_5$ nanowires deliver an initial discharge/charge capacity up to 277 and 432 mAh g$^{-1}$, respectively, at a current density of 50 mA g$^{-1}$, which almost reaches the theoretical capacity based on 1 Zn$^{2+}$ insertion with two electrons per formula unit V$_2$O$_5$ (294 mAh g$^{-1}$). The V$_2$O$_5$ positive electrode exhibits a dramatic decrease of capacity during the following 20 cycles at 50 mA g$^{-1}$ (94 mAh g$^{-1}$ for 22$^{\text{nd}}$) and delivers a very low discharge capacity of 21 mAh g$^{-1}$ after 100 cycles. Moreover, it delivers an initial discharge capacity of 278 mAh g$^{-1}$ at 200 mA g$^{-1}$, followed by an activation process of the material. The capacity is higher for 200 mA g$^{-1}$ than for 50 mA g$^{-1}$, which could be attributed to a different type of activation process under both current densities and different resulting degrees of side reactions (parasitic reactions). CV displays in the first scan two reduction peaks, centered at 0.92 and 0.50 V, and a broad oxidation peak at 1.20 V with a shoulder at 1.05 V. In the following four scans, the CV curves indicate significant changes in both reduction and oxidation peaks. In operando synchrotron diffraction focused on the first 1.5
cycles, reveals that V$_2$O$_5$ first undergoes a solid solution and 2-phase coexistence transitions upon Zn-ions insertion. It also confirms the formation of two byproducts, Zn$_{3+\delta}$OH$_2$V$_2$O$_7$$\cdot$2(H$_2$O) and ZnSO$_4$Zn$_3$(OH)$_6$$\cdot$5H$_2$O during the Zn-ions insertion. The electrode undergoes a reversible process upon Zn-ions deinsertion with the decomposition of both byproducts. The V$_2$O$_5$ electrode goes in the 2nd discharge process through the same two-phase reaction as that in the 1st discharge without the formation of the byproduct Zn$_{3+\delta}$OH$_2$V$_2$O$_7$$\cdot$2(H$_2$O). In operando XAS confirms the reduction/oxidation of vanadium during the Zn insertion/deinsertion. Moreover, ex situ Raman and XPS also prove the reversibility of the reactions during cycling. The electrochemical performance of V$_2$O$_5$ can be improved by electrode engineering such as surface coating with carbon/graphene oxide and electrolyte optimization with more concentrated salt and water-organic solvent.

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Author contributions

analyzed the data. X.L. performed XPS measurements and analyzed the XPS data. Z.D. carried out TEM and analyzed the data. Q.F. wrote the preliminary draft with input from J.W.; Q.F., J.W., M.K., H.E., and S.D., discussed the results and revised the manuscript. All authors contributed to interpreting the findings, reviewing, and commenting on the manuscript.

**Additional information**

Supplementary information is available.

**Competing interests**

The authors declare no competing financial interests.

**Reference**


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