Robust synthesis of a composite phase of copper vanadium oxide with enhanced performance for durable aqueous Zn-ion batteries

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Abstract: Rechargeable aqueous Zn-ion batteries (AZIBs) have attracted much interest as next-generation power sources due to their economical, safe, and capacity superiorities. However, the cathodes used in AZIBs always suffer from sluggish kinetics, inducing inadequate rate performance and poor cycle ability. Pre-intercalating transition metal element in the cathode materials offers an effective strategy for improving diffusion kinetics of Zn$^{2+}$ and thus the electrochemical activity. In this work, different proportions of Cu pre-intercalated V$_2$O$_5$ were synthesized to form a composite phase of Cu$_{0.4}$V$_2$O$_5$ and VO$_2$·nH$_2$O nanosheets through the hydrothermal method. The reversible redox reaction of Cu$^{2+}$ and Cu$^{0}$, accompanied by the phase changes of copper vanadate and zinc vanadate, contributes to an excellent battery performance. When the molar ratio between Cu precursor and commercial V$_2$O$_5$ in the reaction solution is 1:2, the obtained material presents an outstanding electrochemical performance with the initial discharge capacity of 332 mAh g$^{-1}$ at 0.2 A g$^{-1}$. The enlarged lattice distance together with the high conductivity leads to a high Zn ions diffusion rate of 10$^{-5}$ cm$^2$s$^{-1}$. Even after 1,000 cycles at a current density of 2 A g$^{-1}$, the capacity attenuation is only 0.035% per cycle, exhibiting distinctive activities toward AZIBs.

Keywords: aqueous Zn-ion batteries, vanadium-based cathodes, energy storage

1 Introduction

The energy storage device used for the collection of other green energies, such as solar and wind, is becoming increasingly urgent [1–6]. Rechargeable aqueous Zn-ion batteries (AZIBs) have captured a lot of attention because of their natural abundance, low price, high safety, environment-friendliness, and good conductivity [7–10], which also possess super high theoretical energy capacity (5,851 mA h cm$^{-3}$), low redox potential, and impressive electrochemical stability in water [11–14].

Exploring appropriate cathode materials with favorable capacity and stable structure during the insertion/extraction of Zn$^{2+}$ is becoming urgent for aqueous ZIBs. Layered V$_n$O$_m$ is generally recognized as preferable cathodes for ZIBs due to comparable electrochemical activity and ultralow cost [15–19]. However, the interlayer distance in the original V$_n$O$_m$ framework is confined for Zn$^{2+}$, which sterically hinders the ion diffusion kinetics during cycling, and eventually leads to deteriorative performance and poor commercial applications [20].
Thus, the structure and compositions of \( \text{V}_2\text{O}_5 \)-based materials should be carefully designed for enlarging the interlayer spacing and accelerating the insertion and extraction of \( \text{Zn}^{2+} \). Among the reported construction strategies, surface modification of \( \text{V}_2\text{O}_5 \) is considered one of the valid methods to boost ion diffusion by providing a larger contact area and shortening the ion diffusion path [16,21]. In addition, the introduction of interlayer structural water or metal ions (such as Li\(^+\) [22], Na\(^+\) [23], K\(^+\) [24], Ca\(^2+\) [25]) as pillars is also beneficial for the enlargement of interlayer spacing of \( \text{V}_2\text{O}_5 \) and accelerating the diffusion of \( \text{Zn}^{2+} \) [17]. For example, co-intercalation of water molecules and zinc in vanadium oxide bronze (\( \text{Zn}_{0.25}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O} \)) could decrease the activation energy for charge transfer and reversibly enlarge/shrink the layered structure of \( \text{Zn}_{0.25}\text{V}_2\text{O}_5 \) during \( \text{Zn}^{2+} \) (de)intercalation, leading to good kinetics, outstanding rate performance, and long-term cycle life [26]. In addition, hydroxyl copper was introduced to \( \text{V}_2\text{O}_5 \) to achieve copper pyrovanadate (\( \text{Cu}_x\text{V}_2\text{O}_5\text{(OH)}_x \cdot 2\text{H}_2\text{O} \)) cathode for aqueous zinc ion batteries to improve the electrochemical performance [27]. Although the intercalation of \( \text{Zn}^{2+} \) would give rise to the reduction of Cu ions to metallic Cu\(^0\), allowing for an increased conductivity of \( \text{Cu}_x\text{V}_2\text{O}_5\text{(OH)}_x \cdot 2\text{H}_2\text{O} \), the \( \text{Cu}_x\text{(OH)}_x \text{V}_2\text{O}_5 \cdot 2\text{H}_2\text{O} \) presented fast fading in the initial cycles due to the phase change [28]. It is still a challenge to directly introduce copper in vanadium oxide bronze to obtain layered cathode materials with satisfactory electrochemical properties.

Herein, we demonstrated the robust synthesis of Cu pre-intercalated \( \text{V}_2\text{O}_5 \) to obtain cathode materials with a composite phase of \( \text{Cu}_x\text{V}_2\text{O}_5 \) and \( \text{VO}_2\cdot n\text{H}_2\text{O} \) for AZIBs through a simple one-step hydrothermal reaction (Figure 1), which was marked as \( \text{(Cu}_x\text{V}_2\text{O}_5\)\(_x\)\(_y\)\(_{n\text{H}_2\text{O}}\text{)} \). The influence of the different ratios of Cu on the structure and electrochemical performance of the final product was discussed in detail. The activity of the \( \text{(Cu}_x\text{V}_2\text{O}_5\)\(_x\)\(_y\)\(_{n\text{H}_2\text{O}}\text{)} \) was found to be highly dependent on its composition. When the molar ratio between Cu precursor and \( \text{c-V}_2\text{O}_5 \) in the reaction solution was 1:2, the obtained material exhibits a superior reversible capacity of 332 mAh g\(^{-1}\) at 0.2 A g\(^{-1}\) within the voltage window of 0.3–1.6 V. And, the material displayed good long-term performance during 1,000 cycles with the capacity attenuation of 0.035% per cycle at 2 A g\(^{-1}\). We also elucidated that the charge storage chemistry is the multi-step \( \text{Zn}^{2+} \) insertion/extraction reaction with the replacement reaction. We hope this work can draw more attention to cathodes in AZIBs and drive the applications of AZIBs in massive-scale energy storage devices in the future.

2 Experimental

2.1 Chemicals and materials

\( \text{Cu}_4\text{H}_6\text{CuO}_4\cdot\text{H}_2\text{O} \) (Guangfu Chemical Reagent, AR, 99%), \( \text{Cu}_4\text{H}_6\text{O}_6 \) (Damao Reagent, AR, 99%), \( \text{V}_2\text{O}_5 \) (Shanpu Reagent, AR, 99%), and \( \text{H}_2\text{O}_2 \) (Beijing Chemical works, AR, 30%) were used.

2.2 Materials preparation

The composite phase of copper vanadium oxide nanosheets with different proportions of Cu was synthesized by a one-step hydrothermal method. First, 10 mL of commercial \( \text{V}_2\text{O}_5 \) (c-\( \text{V}_2\text{O}_5 \)) with different concentrations (0.09, 0.135, 0.18, 0.36 mmol mL\(^{-1}\)) was, respectively, added into deionized water (10 mL), followed by decanting of 30 wt\% \( \text{H}_2\text{O}_2 \) (3 mL). The above-mixed solution was heated at 50°C for 20 min under magnetic stirring. Second, \( \text{Cu}_4\text{H}_6\text{CuO}_4\cdot\text{H}_2\text{O} \) (0.9 mmol) and \( \text{Cu}_4\text{H}_6\text{O}_6 \) (0.1 mmol) were subsequently dissolved in another 10 mL of deionized water and stirred for 10 min. Then, the mixture solution of \( \text{Cu}_4\text{H}_6\text{CuO}_4\cdot\text{H}_2\text{O} \) and \( \text{Cu}_4\text{H}_6\text{O}_6 \) was pulled into the above solution containing c-\( \text{V}_2\text{O}_5 \) and \( \text{H}_2\text{O}_2 \), followed by heating at 50°C for another 10 min. In the final reaction solution, the molar ratios between \( \text{Cu}_4\text{H}_6\text{CuO}_4\cdot\text{H}_2\text{O} \) and \( \text{c-V}_2\text{O}_5 \) were 1:1, 1:1.5, 1:2, and 1:4. The mixture reaction solution was hydrothermally reacted at 180°C for 12 h and then collected after washing with DI water and ethanol. After drying at 80°C for 12 h, the materials were heat-treated at 200°C for 2 h under argon ambience. The obtained \( \text{(Cu}_x\text{V}_2\text{O}_5\)\(_x\)\(_y\)\(_{n\text{H}_2\text{O}}\text{)} \) materials were...
2.3 Materials characterizations

The crystallographic characterization of the products was tested by the D8 Advanced X-ray diffraction (XRD) with Cu Kα radiation. Scanning electron microscopy (SEM) and EDS mapping images were taken by the JSM-IT100 microscope. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were collected on the JEM-2100 electron microscope.

2.4 Electrochemical measurement

The working electrode material was consisted of a mixture of the active materials (70%), super P (20%), and polyvinylidene fluoride (PVDF) binder (10%) with N-Methyl pyrrolidone (NMP). All materials were dispersed to form a homogeneous slurry. The slurry was then uniformly coated on a stainless-steel foil (200 mesh, Canrd) as a current collector, and dried for 12 h at 60°C. Finally, the stainless-steel foil with active materials was cut into a circular disc (12 mm) with an active material of 2 mg cm$^{-2}$. CR2032-type coin cells were fabricated with Zn foil as the anode (0.1 mm thick), Zn(CFSO$_3$)$_2$ solution (1.8 M) as electrolyte, and glass microfiber as the separators. The electrochemical performance was evaluated with a Neware battery testing system in the potential range of 0.3–1.6 V. The cycle voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were tested from 0.3 to 1.6 V vs Zn/Zn$^{2+}$ by an electrochemical workstation (CHI760E) at the room temperature.

3 Results and discussion

Figure 2: (a) The XRD patterns and (b) CV curves of CVO-1, CVO-1.5, CVO-2, CVO-4, and c-V$_2$O$_5$. (c) Rate performance and (d) cycle performance of CVO-1, CVO-1.5, CVO-2, and CVO-4.
with the least Cu intercalated V$_2$O$_5$, the characteristic peaks located at 25.4°, 30.3° and 49.5° can be assigned to the peaks of VO$_2$·$x$H$_2$O (JCPDS No. 18-1445) (Figure 2a). The formed VO$_2$·$x$H$_2$O probably results from the reduction of c-V$_2$O$_5$ by glucose during the hydrothermal process. For CVO-2, CVO-1.5, and CVO-1 with the increased Cu content, the characteristic peaks at 26.43°, 28.59°, 31.41°, and 33.2° can be well indexed to the (−111), (104), (−304), and (−213) planes of Cu$_{0.4}$V$_2$O$_5$ (JCPDS No. 18-0464), indicating Cu$^{2+}$ has been successfully inserted into the interlayer of V$_2$O$_5$ as pillars. All the obtained materials are the mixed phases of copper vanadate and zinc vanadate, with the chemical formula of (Cu$_{0.4}$V$_2$O$_5$)$_x$·VO$_2$·$n$H$_2$O. It can be speculated that the (Cu$_{0.4}$V$_2$O$_5$)$_x$·VO$_2$·$n$H$_2$O materials are composed of V-O polyhedrons and Cu-O polyhedrons as shown in Figure 1. And, the peak intensity of the Cu$_{0.4}$V$_2$O$_5$ phase improved with the increase of Cu content, which means that more Cu-O polyhedrons arrange in the rows of V-O polyhedrons. Figure 2b exhibits the cyclic voltammogram (CV) of the samples with different Cu contents between 0.3 and 1.6 V at the rate of 1 mV s$^{-1}$. The CV plot of c-V$_2$O$_5$ shows two pairs of redox peaks located at 0.99/0.95 V and 0.74/0.49 V, respectively. All the curves of CVO materials show similar shapes with three pairs of redox peaks, indicating the multi-step reaction during the ingress/egress of Zn$^{2+}$. In general, CVO-2 displays the best electrochemical performance among all the groups, with the largest peak area, indicating the most (de)intercalation and the fast diffusion of Zn$^{2+}$ during the charge and discharge processes. The CVO-2 electrode presents much better rate performance than other Cu$^{2+}$ pre-intercalated V$_2$O$_5$ cathodes, with an average-discharged capacity of 321, 317, 294, 249, and 225 mAh g$^{-1}$ at the rates of 0.3, 0.5, 1, 3, 5 A g$^{-1}$, respectively (Figure 2c), which may be caused by proper Cu-O polyhedrons arranged in the rows of V-O polyhedrons. When the current density turns back to 0.3 A g$^{-1}$, the capacity of CVO-2 recovers to 292 mAh g$^{-1}$, with 91% retention of the initial discharge capacity, suggesting the highly reversible of the electrodes. The cycling performances of the CVO electrodes with different Cu contents are conducted at 0.1 A g$^{-1}$. CVO-2 exhibits a more stable cycling performance than other cathodes over 100 cycles.
with a high-capacity retention of 77% (Figure 2d), suggesting that suitable Cu content can efficiently improve the cycling performance by expanding the interlayer spacing. Even the active materials in each cell increased to 4 mg, the cathode of CVO-2 still shows the highest initial capacity of 331 mAh g⁻¹ and the most stable cycling performance (Figure S1).

We employed the SEM to observe the morphology of CVO-2 in Figure S2. Most of them present nanosheet structure with a width of 70–160 nm, length of 200–500 nm, and average thickness of 22 nm. The transmission electron microscopy (TEM) images of the CVO-2 are shown in Figure 3a–c. The lattice fringe with a d-spacing of 0.368 nm corresponds to the (−111) face of CVO-2 (Figure 3b). Figure 3c demonstrates that the obtained material was indeed a typical layered structure with an interlayer distance of 9.125 Å, much larger than the lattice spacing of previously reported vanadium-based cathodes, such as K₀.₅V₂O₅ (3.62 Å) [24], Zn₀.₂₅V₂O₅·nH₂O (5.37 Å) [26], Na₃V₆O₁₆·3H₂O (7.1 Å) [29], and CaV₆O₁₆·3H₂O (8.08 Å) [30]. The larger lattice spacing can provide more accommodation for the (de)intercalation of Zn²⁺, resulting in excellent electrochemical performance [31]. As shown in Figure 3d, energy-dispersive X-ray spectroscopy (EDS) mapping clearly shows that Cu, V, and O were uniformly distributed through the rectangular plate.

The electrochemical performance of CVO-2 nanosheets for the zinc ion storage was tested using a CR2032-type coin cell, in which zinc metal was utilized as the anode and CVO-2 as the cathode. All the cells were tested in the voltage window of 0.3–1.6 V vs Zn²⁺/Zn. Figure 4a displays the galvanostatic charge/discharge (GCD) curves of CVO-2, which matches well with the CV result shown in Figure 2b. The GCD curves show similar charge–discharge capacities in the first three cycles, indicating the high reversibility of CVO-2. Compared with the c-V₂O₅ cathode shown in Figure S3, CVO-2 displays higher coulombic efficiency (∼100%) and an initial capacity of 332 mAh g⁻¹ at 0.2 A g⁻¹, with an attenuation of 14% after 100 cycles, indicating the high cycling stability (Figure 4b). The compared SEM images of the CVO-2 electrode before and after cycling are shown in Figure S4a and b. Only a slight difference can be observed after cycling, evidencing excellent structural stability. When the electrolyte of Zn(CFSO₃)₂ solution (1.8 M) was replaced by ZnSO₄ solution (1 M), the CVO-2 electrode still presented a high discharge capacity of 324 mAh g⁻¹ at 0.2 A g⁻¹ (Figure S5). Furthermore, even at the rate of 2 A g⁻¹, the CVO-2 electrode exhibits excellent long-term performance with the capacity attenuation of 0.035% per cycle (Figure 4c). In the meantime, the CVO-2 electrode shows the highest capacity at different current densities, which is shown in Figure 4d by comparing

**Figure 4:** (a) Galvanostatic charge/discharge (GCD) curves of CVO-2 in the initial three cycles at 0.2 A g⁻¹. (b) The discharge/charge profiles of CVO-2 at 0.2 A g⁻¹. (c) The cycling performance of CVO-2 at 2 A g⁻¹. (d) Comparison of the CVO-2 electrode with previously reported vanadium oxide cathode materials for ZIBs.
with the reported K$_2$V$_6$O$_{16}$·2.7H$_2$O [32], Cu$_3$V$_4$O$_7$(OH)$_2$·2H$_2$O [28], K$_3$V$_3$O$_8$ [33], V$_2$O$_5$@CNTs [15], (NH$_4$)$_2$V$_6$O$_{16}$ [34], and K$_2$V$_8$O$_{21}$ [35] cathodes for AZIBs.

To clearly explain the electrochemical kinetics of the CVO-2 electrode, the CV measurement at the rates of 0.1–1 mV s$^{-1}$ was carried out (Figure 5a). It can be observed that the CV curves maintain similar shapes and the reduction peaks move to the left and oxidation peaks move to the right with the increased scan rates, indicating good rate performance. As shown in Figure 5b, a relevant analysis is executed to reveal the relationship between scan rate and peak current, based on equation (1) [36–38].

$$i = av^b.$$  

When the $b$ is close to 0.5, it demonstrates that the electrochemical process is mainly controlled by diffusion; while the $b$ is close to 1, it implies a capacitive controlled charge storage mechanism. If $0.5 < b < 1$, it indicates the combination of diffusion-limited and capacitive-limited processes. The $b$ values of peak 1 to peak 4 can be calculated to be 0.89, 0.78, 0.81, and 0.8, indicating that the corresponding redox reactions are dominated by the diffusion-controlled progress and capacitive-controlled progress. In addition, the corresponding current at different scanning rates can be declared by equation (2) [39,40]:

$$i(V) = kV + kV^{1/2}. \quad (2)$$

Figure 5c illustrates that the calculation results of capacitive contribution are 67.6, 75.6, 85.3, 94.7, and 96.5% at the sweep rates of 0.1, 0.3, 0.5, 0.8, and 1 mV s$^{-1}$, respectively. When the scan rate is relatively low, the response currents are mainly attributed to the diffusion-controlled process. The capacitive-controlled process plays a crucial role in the electrochemical reactions with the increased scan rates. The red region in Figure 5d corresponding to the capacitive mechanism is accounted for 85.3% at 0.5 mV s$^{-1}$.

Furthermore, we employed the galvanostatic intermittent titration technique (GITT) to analyze the electrochemical behaviors in Zn/CVO-2 batteries. As shown in Figure 6a, the zigzag curve is generated by the relaxation rest after the discharge/charge progress. According to the
following equation (3) [41], the $D_{Zn}$ values can be calculated by the voltage recovery.

$$D_{Zn} = \frac{4}{\Pi} \left( \frac{m_{B}V_{m}}{M_{B}S} \right)^{2} \left( \frac{\Delta E_{S}}{\Delta E_{r}} \right)^{2}. \quad (3)$$

In the equation, the molar volume of the materials, molecular mass, electrode/electrolyte contact area, and duration of the current pulse is denoted as $V_{m}$, $m_{B}$, $M_{B}$, $S$, and $\tau$, respectively. The transient potential change and the steady-state voltage change are denoted as $E_{r}$ and $E_{S}$.

The $D_{Zn}$ value of CVO-2 is in the order of $10^{-5}$ to $10^{-7}$ cm$^2$ s$^{-1}$, which is much higher than that of c-V$_2$O$_5$. CVO-1, CVO-1.5, and CVO-4 (Figure 6c and d, Figures S6–8), revealing super-fast kinetics could improve the diffusion of Zn$^{2+}$ and promote the rate ability. To further illustrate the electrochemical behavior of the CVO-2 electrode, the electrochemical impedance spectroscopy (EIS) measurement is applied, and the results are shown in Figure S59. The semicircle (high-frequency region) is referred to as the charge transfer resistance ($R_{ct}$) and relative capacitance [42,43]. The $R_{ct}$ of the CVO-2 electrode after 1 cycle and after 3 cycles were 71 and 77.5 $\Omega$, respectively, which was much smaller than 113 and 118 $\Omega$ for the c-V$_2$O$_5$ electrode, indicating fast electrons charge transfers during cycling.

To deeply elucidate the Zn$^{2+}$ storage mechanism, ex-situ XRD was employed in recording the structural evolution during different states. After totally discharging to 0.3 V, several new peaks located at around 24.7° and 33.1° can be observed (Figure 7a), which can be referred to as the formation of ZnV$_3$O$_8$. The peaks of copper located at 43.8°, 50.3° indicate that the insertion of zinc ions leads to the reduction of Cu$^{2+}$ to Cu$^{0}$. According to the results of Figure 7b, the redox peak at 1.07 V in the CV curves corresponds to the oxidation of Cu$^{0}$ to Cu$^{2+}$. The redox peaks at 1.32/1.3 V, 0.98/0.97 V, and 0.65/0.5 V portray the V$^{5+}$/V$^{4+}$ and V$^{4+}$/V$^{3+}$ redox couple in the CVO-2 electrode. Combining the results of ex-situ XRD and CV curves, it can be reasonably hypothesized that the Zn$^{2+}$ storage mechanism is based on the displacement reaction (Figure 7c). During discharging, the insertion of Zn$^{2+}$ drives the reductive reaction of Cu$^{2+}$ to Cu$^{0}$ with the phase evolution from (Cu$_{0.4}$V$_{0.5}$O$_{3}$)$_{m}$·(VO$_2$·nH$_2$O)$_{y}$ to ZnV$_3$O$_8$. On the
charging process, the mixture of ZnV₃O₈ and Cu⁰ reversibly converts to \((\text{Cu}_{0.4}\text{V}_2\text{O}_5)\times(\text{VO}_2\cdot n\text{H}_2\text{O})\_y\). The replacement of divalent cations between Zn²⁺ and Cu²⁺ provides multiple electrons charge transfers and less structural destructiveness, indicating high capacity and cyclic stability. Meanwhile, the appearance of Cu⁰ tremendously enhances the conductivity of the CVO electrode.

**4 Conclusion**

We have successfully synthesized the composite phase of copper vanadium oxide materials as the cathodes of AZIBs. When the molar ratios of Cu precursor and c-V₂O₅ are 1:2, the Cu pre-intercalated V₂O₅ nanosheets (CVO-2) express the best electrochemical performance, showing the initial discharge capacity of 332 mAh g⁻¹ at the rate of 0.2 A g⁻¹. The super high diffusion of Zn²⁺ demonstrates the good conductivity of the material. The replacement mechanism provides excellent electrochemical performance. The achievement results clearly indicate that the appropriate intercalation of Cu is able to improve the properties of vanadium oxide materials, which serves as a promising candidate for high-performance AZIBs.

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