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Preparation and Performance of Highly Stable Cathode Material $\text{Ag}_2\text{V}_4\text{O}_{11}$ for Aqueous Zinc-Ion Battery

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Abstract: One of the hottest research topics at present is the construction of environmentally friendly and secure aqueous zinc-ion batteries (AZIBs) using an aqueous electrolyte instead of an organic electrolyte. As a result of their diverse structure, valence state, high theoretical specific capacity, and other benefits, vanadium-based materials, which are frequently employed as the cathode of AZIBs, have drawn the attention of many researchers. The low cycle stability of zinc ion batteries (ZIBs) is mostly caused by the disintegration of the vanadium-based cathode materials during continuous charge and discharge. In this work, using 3M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ as the electrolyte and hydrothermally synthesized $\text{Ag}_2\text{V}_4\text{O}_{11}$ as the cathode material, the high-rate performance and extended cycle life of ZIBs were evaluated. The effects of different hydrothermal temperatures on the microstructure, capacity, and cycle stability of the $\text{Ag}_2\text{V}_4\text{O}_{11}$ cathode material were examined. The experimental results show that $\text{Ag}_2\text{V}_4\text{O}_{11}$ exhibits a typical intercalation-displacement process when used as the cathode material. The multiplicative performance and cycle stability of the cathode material were significantly enhanced at a hydrothermal temperature of 180 °C. $\text{Ag}_2\text{V}_4\text{O}_{11}$ -180 has a high discharge specific capacity of $251.5 \text{ mAh}\cdot\text{g}^{-1}$ at a current density of $0.5 \text{ A}\cdot\text{g}^{-1}$ and a long cycle life ($117.6 \text{ mAh}\cdot\text{g}^{-1}$ after 1000 cycles at a current density of $3 \text{ A}\cdot\text{g}^{-1}$). According to the electrochemical kinetic investigation, the cathode material has a high pseudocapacitive charge storage and Zn^{2+} diffusion coefficient. This is attributed to the large layer spacing and the Ag^+ anchored interlayer structure.



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Keywords: aqueous zinc-ion batteries; cathode material; vanadium-based materials; $\text{Ag}_2\text{V}_4\text{O}_{11}$; hydrothermal method

1. Introduction

With more and more successful applications in electric vehicles and related facilities, lithium-ion batteries are now the most extensively used batteries, recyclable green energy storage, and conversion technologies. Nevertheless, throughout the use and development of lithium-ion batteries, the numerous benefits of their high energy density, long life, and steady cycling performance cannot disguise their disadvantages, such as the high cost and hazardous and harsh preparation methods [1–7]. With substantial raw material reserves, low cost, and easy process conditions, Aqueous zinc ion batteries (AZIBs) have the potential to replace lithium-ion batteries as a superior partner for energy storage devices in the future. AZIBs possess a high theoretical specific capacity ($820 \text{ mAh}\cdot\text{g}^{-1}$) and an acceptable negative electrode potential (-0.76 V vs. SHE), but still lack a corresponding cathode material [8,9].

Vanadium-based materials outperform manganese-based materials, cobalt-based materials, and Prussian blue counterparts in the classification of cathode materials for ZIBs [8–11]. Vanadium, for example, is plentiful and has various elemental valence states, and the laminar/tunneling structure of vanadium oxides allows the intercalation/de-intercalation of Zn^{2+} , resulting in a high theoretical capacity and structural stability [12,13]. For instance, irregular bulk V_2O_3 has a discharge specific capacity of $207 \text{ mAh}\cdot\text{g}^{-1}$ ($0.1 \text{ A}\cdot\text{g}^{-1}$) [14]. Muhammad Sufyan Javed et al. fabricated a lamellar V_2O_5 layer on

the surface of a Ti substrate. After 700 cycles at $0.5 \text{ A}\cdot\text{g}^{-1}$, this cathode material retained 86% of its original capacity, indicating that it has long-term stability [15]. Shougang Wu et al. compared the electrochemical performance of amorphous $\alpha\text{-V}_2\text{O}_5$ with that of crystalline $\text{c-V}_2\text{O}_5$ cathode materials. They concluded that nano-sheeted $\alpha\text{-V}_2\text{O}_5$ exhibited better cycling stability and Zn^{2+} diffusion kinetics after 2200 cycles at $5 \text{ A}\cdot\text{g}^{-1}$ [16]. Moreover, cathode materials such as V_6O_{13} [17], $\text{V}_{10}\text{O}_{24}\cdot 12\text{H}_2\text{O}$ [18,19], and VO_2 [20] have also been reported previously.

In practical applications, researchers have found that the inherent low electronic conductivity of vanadium-based materials and the strong electrostatic interactions between Zn^{2+} and the crystalline lattice will lead to a slower transfer kinetics of zinc ion and worse cycling stability. It is therefore particularly crucial to improve the electrochemical behavior of vanadium-based materials through different strategies. Previous works include the shielding of the electrostatic effects by crystalline water, the intercalation of metal ions, the formation of special nanostructures, or compounding with conductive materials [8–11]. The utilization of pre-intercalated Zn^{2+} and H_2O to expand the layer spacing of V_2O_3 materials has been reported to enhance the structural stability and the diffusion rate of Zn^{2+} . The specific capacity of such a V_2O_3 cathode material was as high as $435 \text{ mAh}\cdot\text{g}^{-1}$ at $0.5 \text{ A}\cdot\text{g}^{-1}$, showing considerable capacity and cycling stability [21]. Min Du et al. prepared stable Ca doped vanadium oxide cathode materials with large layer spacing by controlling the amount of Ca^{2+} addition. After 3000 cycles at $10 \text{ A}\cdot\text{g}^{-1}$, this cathode material had a high specific capacity of $187.2 \text{ mAh}\cdot\text{g}^{-1}$ with no capacity degradation. This can be attributed to the backbone effect of Ca^{2+} on the layer structure during the intercalation/de-intercalation process of Zn^{2+} [22]. In the case of $\text{Zn}/\text{Cu}_3(\text{OH})_2\text{V}_2\text{O}_7\cdot 2\text{H}_2\text{O}$ batteries, the high electrochemical performance is mainly based on a highly reversible combination of the replacement/intercalation mechanism. The Cu^0 matrix is produced during the intercalation process of Zn^{2+} , which is oxidized to Cu^{2+} during the deintercalation process. The reversible redox reaction between Cu^{2+} and Cu^0 and the reversible conversion of $\text{Zn}_{0.25}\text{V}_2\text{O}_5\cdot \text{H}_2\text{O}$ effectively promote electron transport in the system [23]. In addition, a similar conclusion was reached in a study by Shan Guo et al. The tunnel structure of $\text{Ag}_{0.33}\text{V}_2\text{O}_5$ is relatively stable, and the reversible replacement of Ag^0 and Zn^{2+} can be realized. Therefore, it has a higher cycle stability and rate performance than $\text{Ag}_{1.2}\text{V}_3\text{O}_8$ [24]. Jing Zeng et al. developed a cathode material composed of electron-conductive phase $\text{Ag}_{0.333}\text{V}_2\text{O}_5$ and ionically conductive phase $\text{V}_2\text{O}_5\cdot n\text{H}_2\text{O}$, which has a significantly higher capacity ($312.1 \text{ mAh}\cdot\text{g}^{-1}$) at $0.5 \text{ A}\cdot\text{g}^{-1}$ than that of pure $\text{Ag}_{0.333}\text{V}_2\text{O}_5$ ($244.3 \text{ mAh}\cdot\text{g}^{-1}$) [25]. The formation of a network structure between the base phases facilitates electron/ion transport, which in turn enhances the ion/electron conductivity. In summary, metal ion (such as Ag^+)-doped vanadium-based materials show promise in maintaining the stability of the main structure during charge and discharge and improving the low Zn^{2+} diffusion rate and energy density of the matrix.

In this work, high-performance $\text{Ag}_2\text{V}_4\text{O}_{11}$ nanoribbons were prepared by hydrothermal synthesis and applied to ZIB systems. The composition and morphology of the material were characterized by XRD, TEM, and SEM. The capacity performance and cycling stability of the material as a cathode material for ZIBs were investigated by a series of electrochemical tests. During the discharge and charge processes, there exists a reversible conversion of Ag^+ to Ag^0 and a rapid replacement reaction of Zn^{2+} in $\text{Ag}_2\text{V}_4\text{O}_{11}$. The unique layered structure not only facilitates an increase in active sites for high energy storage, but also provides fast diffusion channels for ion transport. The simple synthesis method and excellent electrochemical performance of $\text{Ag}_2\text{V}_4\text{O}_{11}$ composites provide a feasible solution for further research on ZIB cathode materials.

2. Experimental Procedure

2.1. Process and Materials

All of the chemical reagents used in the experiments are of analytical grade. The $\text{Ag}_2\text{V}_4\text{O}_{11}$ nanoribbons were prepared through the simple hydrothermal method. The

synthesis process mainly includes three steps: (1) first, 0.182 g of V_2O_5 (Aladdin, $\geq 99.0\%$) and 0.170 g of $AgNO_3$ (Aladdin, $\geq 99.0\%$) were dissolved in 25 mL deionized water and vigorously stirred at room temperature for 30 min; (2) After stirring, the mixed solution was transferred into a 50 mL Teflon autoclave and then placed in an oven at $180\text{ }^\circ\text{C}$ for 24 h. (3) The products obtained were cleaned with deionized water and alcohol several times, and finally placed overnight in a vacuum oven at $70\text{ }^\circ\text{C}$ to obtain nano-ribbon $Ag_2V_4O_{11}$ composites. In addition, $Ag_2V_4O_{11}$ -200 and $Ag_2V_4O_{11}$ -160 composites were prepared at 200 and $160\text{ }^\circ\text{C}$ by the same method as the comparison groups.

2.2. Materials Characterization

The crystal structure of the samples was studied by X-ray diffraction (XRD, Rigaku Ultimate IV, Cu $K\alpha$ source) with a range between 10° and 80° at a scan rate of $5^\circ \cdot \text{min}^{-1}$. The chemical valence and bonding of the elements were analyzed using X-ray photoelectron spectrometry (XPS, Thermo Scientific K-Alpha, Al $K\alpha$ source). The microscopic morphologies, microstructures, and elemental distribution of the synthesized samples were characterized by scanning electron microscopy (SEM, Phenom LE) and transmission electron microscopy (TEM, FEI talos F200x G2).

2.3. Electrochemical Measurements

The prepared active material, acetylene black, and polyvinylidene difluoride (PVDF) are ground thoroughly in N-Methylpyrrolidone (NMP) with a weight ratio of 7:2:1 to obtain a black slurry. The slurry was then evenly coated on the surface of stainless steel foil and dried under vacuum at $80\text{ }^\circ\text{C}$ for 12 h to produce the cathode material. The CR2032 battery was assembled in air, with zinc metal foil as the anode, 3M $Zn(CF_3SO_3)_2$ as the electrolyte, and glass fiber as the separator. The galvanostatic charge-discharge curve (GCD), rate performance, and galvanostatic intermittent titration technique (GITT) test of newly assembled batteries were tested by the Battery Testing System (NEWARE) at room temperature. The test voltage range was set as 0.3–1.3 V (vs. Zn^{2+}/Zn) and the test current density range was $0.1\text{--}3\text{ A}\cdot\text{g}^{-1}$. The GITT test was performed with a resting time of 1 h, a charge and discharge time of 20 min, and a current density of $0.1\text{ A}\cdot\text{g}^{-1}$. The cyclic voltammetric curves (CV) were tested using an electrochemical workstation (CHI7600E) over a set range (0.3 to 1.3V) and at different scan rates (0.1 to $1.0\text{ mV}\cdot\text{s}^{-1}$). Electrochemical impedance spectroscopy (EIS) was performed by using an electrochemical workstation (CS310H) in the frequency range of 0.01 Hz and 100 kHz.

3. Results and Discussions

Figure 1a shows the XRD patterns of the $Ag_2V_4O_{11}$ cathode materials. It can be seen from Figure 1a that the $Ag_2V_4O_{11}$ synthesized by the one-step hydrothermal method has good crystallinity. The positions of the individual characteristic peaks are in better match with the No.49-0166 PDF card ($Ag_2V_4O_{11}$ standard card). This suggests that the synthesis of $Ag_2V_4O_{11}$ by a simple hydrothermal method is feasible [26]. The space group of this laminated monoclinic phase is $C12/m1$ [27]. The lattice parameters are as follows: $a = 15.55\text{ \AA}$, $b = 3.61\text{ \AA}$, $c = 9.61\text{ \AA}$, $\alpha = 90.00^\circ$, $\beta = 127.07^\circ$, $\gamma = 90.00^\circ$. The crystalline size of the $Ag_2V_4O_{11}$ -160/180/200 samples are close to 77, 70, and $71\text{ \AA}$, respectively. As can be seen from the schematic crystal structure in Figure 1a, the continuous $[V_4O_{11}]_n$ layer formed by the Ag^+ is pre-embedded in a distorted VO_6 polyhedron. In this case, V^{5+} has two different sites. Ag^+ is bonded to five O^{2-} atoms in a 5-coordinate geometrical configuration, and two different V^{5+} are bonded to six O^{2-} atoms in a 6-coordinate geometrical configuration, respectively. Following the comparison, it was found that the width and intensity of the diffraction peaks for the $Ag_2V_4O_{11}$ -180 sample were significantly larger than those of the 160 and $200\text{ }^\circ\text{C}$ samples. This suggests that the hydrothermal temperature has an influence on the crystalline properties of the material and may have an influence on the electrochemical properties [24,26,28].

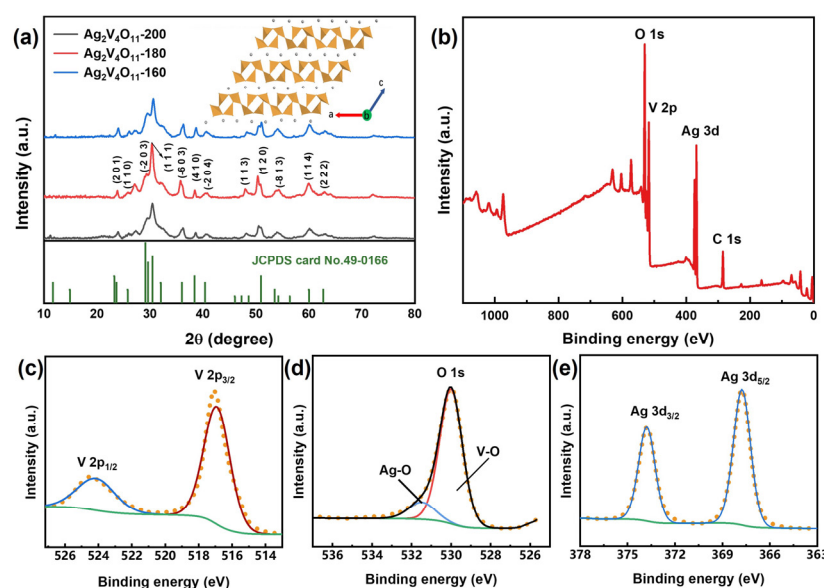


Figure 1. XRD patterns (a), XPS spectra (b), V 2p spectrum (c), O 1s spectrum (d) and Ag 3d spectrum (e) of $\text{Ag}_2\text{V}_4\text{O}_{11}$.

In order to investigate the valence states of the elements in $\text{Ag}_2\text{V}_4\text{O}_{11}$, X-ray photoelectron spectroscopy (XPS) characterization was also performed. Clear peaks for the elements Ag, V, and O can be seen in Figure 1b. Among them, the binding energy peaks of the spin-orbit dual state at 516.91 and 524.14 eV correspond to V 2p_{3/2} and V 2p_{1/2} (Figure 1c). Two fitted signal peaks can be seen in the O 1s region at 529.98 and 531.48 eV, corresponding to the bonding of V-O and Ag-O (Figure 1d). The two binding energy peaks located at 367.78 and 373.78 eV correspond to Ag 3d_{5/2} and Ag 3d_{3/2} of Ag, respectively (Figure 1e) [24,26].

Figure 2a–c shows that the SEM morphologies of $\text{Ag}_2\text{V}_4\text{O}_{11}$ resemble multiple overlapped “feathers”. The “feather rods” are broad, flat, and flaky, and around 1–2 μm in width. The “feather branches” are located on either side of the “feather rods” and appear as parallel bands (Figure 2a–c). They are approximately 0.2–0.5 μm in width and 0.5–10 μm in length. The SEM images also demonstrate that the microstructure of $\text{Ag}_2\text{V}_4\text{O}_{11}$ is influenced by the different hydrothermal temperatures. The whole size of $\text{Ag}_2\text{V}_4\text{O}_{11}$ increases gradually as the temperature increases from 160 $^{\circ}\text{C}$ to 200 $^{\circ}\text{C}$. The width of the “feather rod” gradually increases, and the size and number of “feather branches” also show an increasing trend. The elemental mappings of the $\text{Ag}_2\text{V}_4\text{O}_{11}$ samples are shown in Figure 2d–f. The results show that the O, Ag, and V elements are uniformly distributed in all three samples. This indicates that Ag was successfully introduced into the $\text{Ag}_2\text{V}_4\text{O}_{11}$ nanoribbon using the hydrothermal method and that the hydrothermal temperature did not affect the elemental distribution characteristics. The TEM images (Figure 2g–h) demonstrate that $\text{Ag}_2\text{V}_4\text{O}_{11}$ -180 is a nanoribbon composite with a width of approximately 300 nm, which is consistent with the microscopic morphology of the SEM images. Figure 2i shows the HRTEM images of $\text{Ag}_2\text{V}_4\text{O}_{11}$ -180, from which lattice stripes of width can be observed. The lattice spacing is 0.3337 nm, corresponding to the (1 1 0) crystal planes of the $\text{Ag}_2\text{V}_4\text{O}_{11}$ -180 nm band. This compares favorably with $\text{Sn}_{1.5}\text{V}_2\text{O}_7(\text{OH})_2 \cdot 3.3\text{H}_2\text{O}$ [29] (0.326 nm), $\text{KV}_{12}\text{O}_{30-y} \cdot n\text{H}_2\text{O}$ [30] (0.19 nm), V-MOF derived porous V_2O_5 [31] (0.35 nm), and $\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ [32] (0.256 nm), with a moderate advantage. This indicates that the products obtained by hydrothermal treatment at 180 $^{\circ}\text{C}$ have a good crystallinity and a large layer spacing. This nanoribbon structure is beneficial for increasing the interaction between the material and the electrolyte, which in turn increases the transport rate of Zn^{2+} .

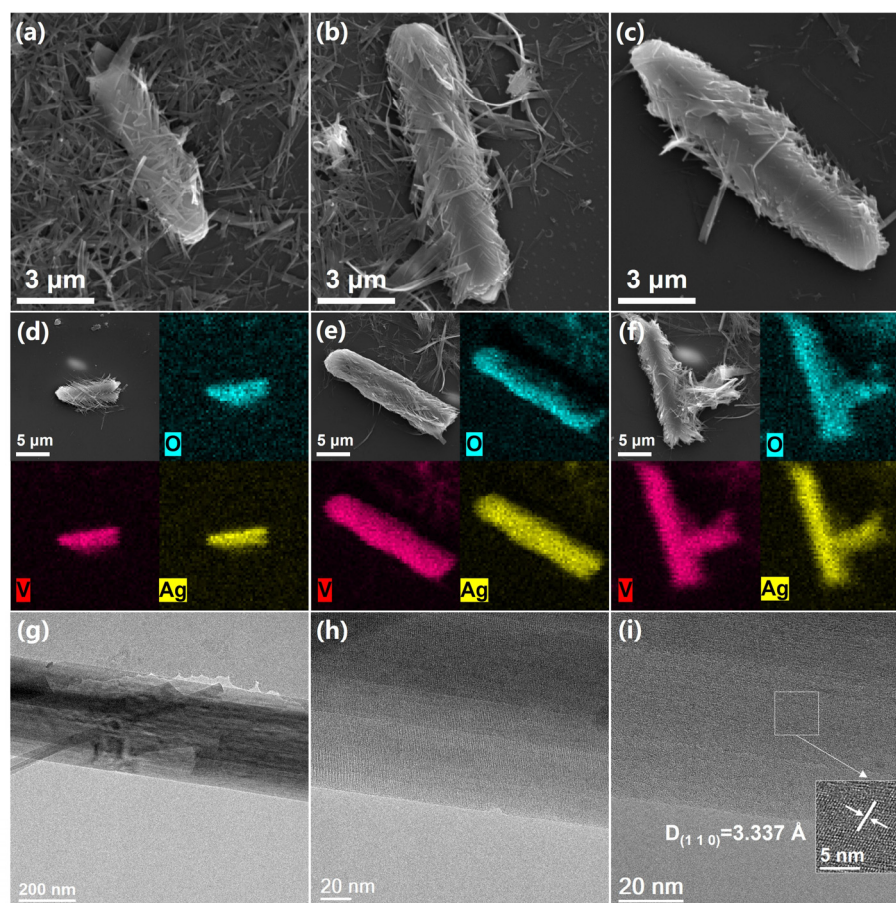


Figure 2. SEM images of $\text{Ag}_2\text{V}_4\text{O}_{11}$ -160 (a), $\text{Ag}_2\text{V}_4\text{O}_{11}$ -180 (b) and $\text{Ag}_2\text{V}_4\text{O}_{11}$ -200 (c); elemental mapping images for $\text{Ag}_2\text{V}_4\text{O}_{11}$ -160 (d), $\text{Ag}_2\text{V}_4\text{O}_{11}$ -180 (e) and $\text{Ag}_2\text{V}_4\text{O}_{11}$ -200 (f) showing the presence of O, V, and Ag; TEM images at different magnifications (g,h) and HRTEM image of $\text{Ag}_2\text{V}_4\text{O}_{11}$ -180 (i).

To test the electrochemical performance of the Ag^+ -modified vanadium-based materials, batteries were assembled using Zn foil as the anode and $\text{Ag}_2\text{V}_4\text{O}_{11}$ as the cathode material. The voltage test intervals for the Zn// $\text{Ag}_2\text{V}_4\text{O}_{11}$ batteries were 0.3–1.3 V (vs. Zn^{2+}/Zn). Figure 3a–c shows the cyclic voltammetry curves for three $\text{Ag}_2\text{V}_4\text{O}_{11}$ cathodes at the same scan rate ($0.1 \text{ mV} \cdot \text{s}^{-1}$) for four consecutive cycles. Two pairs of corresponding redox peaks can be found at 1.0/0.84 V and 0.64/0.57 V (Figure 3b) for $\text{Ag}_2\text{V}_4\text{O}_{11}$ -180 during the charge-discharge process. Similarly, $\text{Ag}_2\text{V}_4\text{O}_{11}$ -160 and $\text{Ag}_2\text{V}_4\text{O}_{11}$ -200 also have redox peaks at 1.01/0.83 V and 0.64/0.56 V (Figure 3a), and at 1.02/0.82 V and 0.68/0.54 V (Figure 3c). During charging/discharging, the two pairs of redox peaks at the cathode of $\text{Ag}_2\text{V}_4\text{O}_{11}$ correspond to $\text{V}^{5+}/\text{V}^{4+}$ and $\text{V}^{4+}/\text{V}^{3+}$, suggesting that Zn^{2+} intercalation/de-intercalation is a multi-step process. Upon comparison, it is found that the redox peaks of the $\text{Ag}_2\text{V}_4\text{O}_{11}$ cathode prepared at a hydrothermal temperature of 180 °C have the highest peak current and the smallest peak spacing (0.16 V and 0.07 V). This also indicates that the degree of electrode polarization that occurs is minimal and its electrochemical kinetics are optimal. The first and subsequent cycles of the cyclic voltammetry curve shown in Figure 3b are slightly different due to the first intercalation of Zn^{2+} resulting in a partially irreversible phase transition in the $\text{Ag}_2\text{V}_4\text{O}_{11}$ -180 cathode material. The overlap of the CV curves from the second to the fourth cycle, where the redox potentials are essentially the same, also indicates that the intercalation/de-intercalation behavior of Zn^{2+} in the $\text{Ag}_2\text{V}_4\text{O}_{11}$ -180 cathode material is highly reversible [24–28].

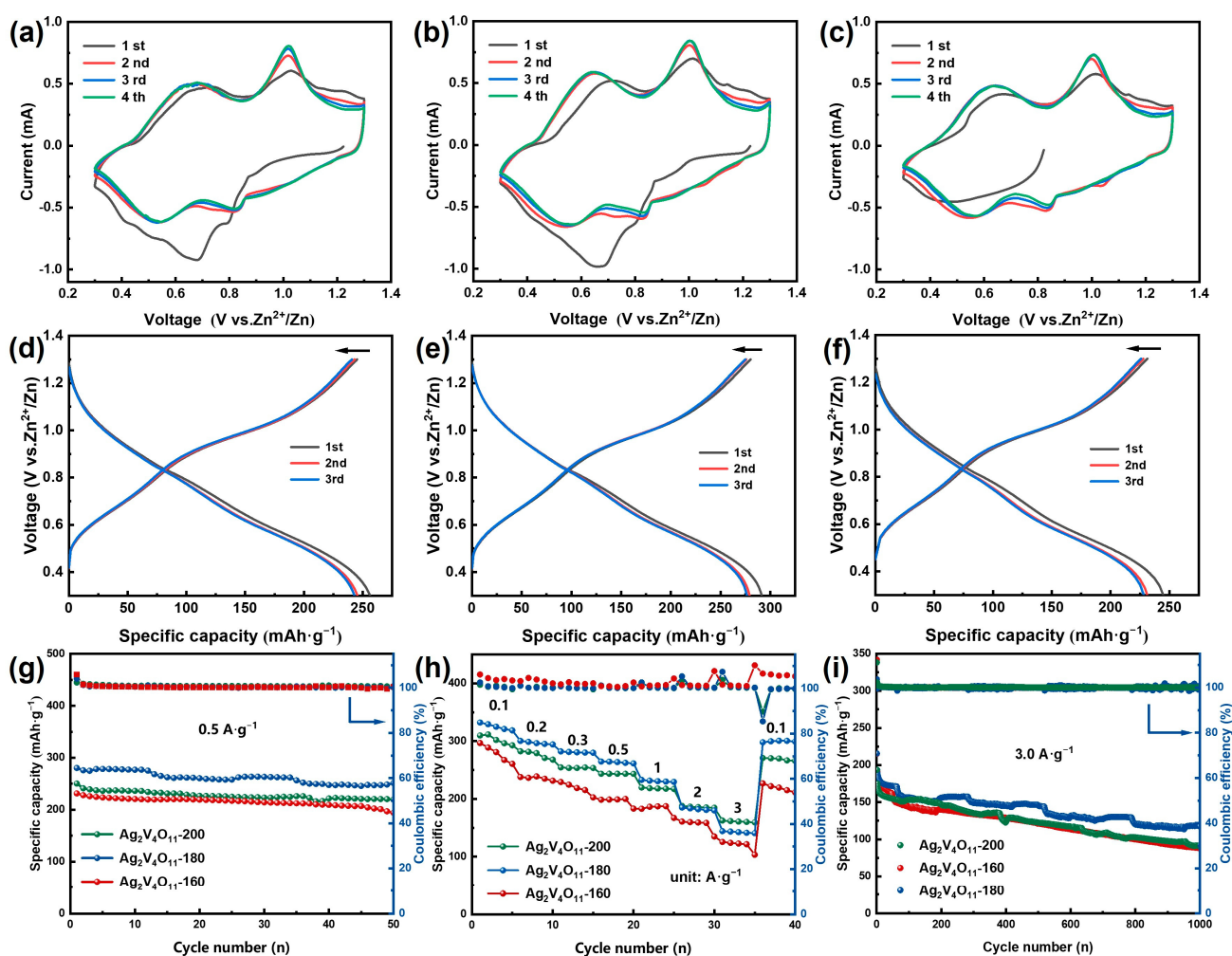


Figure 3. CV curves of (a) Ag₂V₄O₁₁-200, (b) Ag₂V₄O₁₁-180 and (c) Ag₂V₄O₁₁-160 at 0.1 mV·s⁻¹; charge-discharge profiles of (d) Ag₂V₄O₁₁-200, (e) Ag₂V₄O₁₁-180 and (f) Ag₂V₄O₁₁-160 during the first three cycles; (g) Cycle performance at 0.5 A·g⁻¹, (h) rate performance and (i) long-term cycle stability at 3 A·g⁻¹ of Ag₂V₄O₁₁-160, Ag₂V₄O₁₁-180 and Ag₂V₄O₁₁-200, respectively.

Figure 3d–f shows the charge-discharge curves for 1–3 turns of the three Ag₂V₄O₁₁ cathodes at a current density of 0.5 A·g⁻¹. It can be seen that all of these cathode materials have two charge-discharge plateaus, which are consistent with the redox peaks of the CV curves in Figure 3a–c. The discharge specific capacities of the Ag₂V₄O₁₁-200, Ag₂V₄O₁₁-180, and Ag₂V₄O₁₁-160 cathodes in first cycle are 256.3, 291.4, and 244.7 mAh·g⁻¹, respectively. During the following two cycles, the discharge specific capacities of the three samples are very close to each other, and all were lower than their initial value. After the third cycle, the discharge specific capacity of the Ag₂V₄O₁₁-180 sample decreases to 276.6 mAh·g⁻¹, but is still higher than that of Ag₂V₄O₁₁-200 and Ag₂V₄O₁₁-160 (243.0 and 231.1 mAh·g⁻¹). As shown in Table 1 the Ag₂V₄O₁₁-180 cathode performed better than most of the reported cathode materials with a similar structure, such as Cu₃V₂O₇(OH)₂·2H₂O [32] (299.8 mAh·g⁻¹ at 0.2 A·g⁻¹), CrVO₃ [33] (188.8 mAh·g⁻¹ at 0.2 A·g⁻¹), CVO [34] (312.9 mAh·g⁻¹ at 0.2 A·g⁻¹), and TiNH₄V₄O₁₀ [35] (218 mAh·g⁻¹ at 0.5 A·g⁻¹).

As shown in Figure 3g, the discharge specific capacities of the three Ag₂V₄O₁₁ cathodes are stabilized to 221.3, 251.5, and 195.8 mAh·g⁻¹ after 50 complete discharge/charge cycles, with the capacity retention rates of 86.2%, 86.3%, and 79.6%, respectively. Among them, the regular curves of the Ag₂V₄O₁₁-180 sample also indicate that it has the best reversibility and a good cycling performance during the reaction process. The capacity of the three cathode materials decays fast during the initial cycling process. This may be due to the occurrence

of an irreversible phase transition, where Zn^{2+} cannot be completely removed from the lamellar structure, resulting in a “dead zinc” site, and thus a lower ion diffusion rate. As the cycling process continues, the reversible substitution between Ag and Zn^{2+} gradually takes over. This leads to a stabilization of the charge/discharge curve of the $\text{Ag}_2\text{V}_4\text{O}_{11}$ cathode. The curves of the rate performance (Figure 3i) prove that the $\text{Ag}_2\text{V}_4\text{O}_{11}$ -180 cathode has the best tolerance at different current densities. The specific capacity of the $\text{Ag}_2\text{V}_4\text{O}_{11}$ -180 cathode is 319.2, 294.8, 280.1, 261.8, 230.0, 180.6, and 141.1 $\text{mAh}\cdot\text{g}^{-1}$ at 0.1, 0.2, 0.3, 0.5, 1.0, 2.0, and $3.0\text{ A}\cdot\text{g}^{-1}$, respectively. When the current density returns to $0.1\text{ A}\cdot\text{g}^{-1}$, the discharge capacity of this sample remains around $300.4\text{ mAh}\cdot\text{g}^{-1}$, which is close to its initial value. At the same time, its specific capacity is close to or even higher than the other previous reported cathode materials in Table 1, such as CVO [34], $\text{TiNH}_4\text{V}_4\text{O}_{10}$ [35], NVO [36], and VO_2 [37]. This confirms that the suitable reaction temperature and the introduction of Ag can cause the $\text{Ag}_2\text{V}_4\text{O}_{11}$ cathode to exhibit good structural stability and rate performance at different current densities. Figure 3j shows the long-term cycle performance of the cathode material. At a high current density of $3.0\text{ A}\cdot\text{g}^{-1}$, the initial discharge specific capacities of the $\text{Ag}_2\text{V}_4\text{O}_{11}$ -160/180/200 cathode materials are 215.2, 208.0, and $193.7\text{ mAh}\cdot\text{g}^{-1}$. After 1000 cycles, the $\text{Ag}_2\text{V}_4\text{O}_{11}$ -180 cathode material still maintains a high capacity of $117.6\text{ mAh}\cdot\text{g}^{-1}$. This value is significantly higher than the long-term cycle stability of the samples prepared at 160 and $200\text{ }^\circ\text{C}$ (87.9 and $91.3\text{ mAh}\cdot\text{g}^{-1}$). At the same time, the present sample compares favorably with CVO [34], $\text{CaV}_6\text{O}_{16}\cdot 3\text{H}_2\text{O}$ [38], and V_2O_5 [39], and is only slightly inferior to $(\text{NH}_4)_2\text{V}_6\text{O}_{16}\cdot 1.5\text{H}_2\text{O}$ [40], $\text{Ni}_{0.25}\text{V}_2\text{O}_5\cdot 0.88\text{H}_2\text{O}$ [41], and $\text{V}_2\text{O}_5\cdot 4\text{VO}_2\cdot 2.72\text{H}_2\text{O}$ [42] (Table 1).

Table 1. Summary of electrochemical performance of cathode materials in ZIBs.

Cathode Material	Potential Window (V)	Electrolyte	Specific Capacity ($\text{mAh}\cdot\text{g}^{-1}$)	Cycle Performance ($\text{mAh}\cdot\text{g}^{-1}$)	Ref.
$\text{Ag}_{1.2}\text{V}_3\text{O}_8$	0.4–1.4	2 M ZnSO_4	~ 350 ($0.05\text{ A}\cdot\text{g}^{-1}$)	/	[24]
$\text{Ag}_{0.333}\text{V}_2\text{O}_5\cdot n\text{H}_2\text{O}$	0.2–1.8	3 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$	312.1 ($0.5\text{ A}\cdot\text{g}^{-1}$)	261.7, (after 500 cycles at $0.5\text{ A}\cdot\text{g}^{-1}$)	[25]
$\text{Ag}_2\text{V}_4\text{O}_{11}\text{@rGO-90}$	0.3–1.6	1 M ZnSO_4	328 ($0.1\text{ A}\cdot\text{g}^{-1}$)	~ 150 , (after 3000 cycles at $5.0\text{ A}\cdot\text{g}^{-1}$)	[26]
$\text{Ag}_{0.333}\text{V}_2\text{O}_5$	0.2–1.6	2 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$	215 ($0.1\text{ A}\cdot\text{g}^{-1}$)	~ 80 , (after 700 cycles at $3.0\text{ A}\cdot\text{g}^{-1}$)	[28]
V_2O_5	0.3–1.5	3 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$	300 ($0.1\text{ A}\cdot\text{g}^{-1}$)	120, (after 3000 cycles at $2.0\text{ A}\cdot\text{g}^{-1}$)	[31]
$\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2\cdot 2\text{H}_2\text{O}$	0.2–1.6	2.5 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$	216 ($0.1\text{ A}\cdot\text{g}^{-1}$)	92, (after 500 cycles at $0.5\text{ A}\cdot\text{g}^{-1}$)	[32]
CrVO_3	0.4–1.6	3 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$	188 ($0.05\text{ A}\cdot\text{g}^{-1}$)	112.8, (after 1000 cycles at $5.0\text{ A}\cdot\text{g}^{-1}$)	[33]
$\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2\cdot 2\text{H}_2\text{O}$	0.4–1.6	3 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$	269.2 ($0.2\text{ A}\cdot\text{g}^{-1}$)	101.6, (after 3000 cycles at $4.0\text{ A}\cdot\text{g}^{-1}$)	[34]
VO_2	0.3–1.5	3 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$	375 ($0.1\text{ A}\cdot\text{g}^{-1}$)	220, (after 2000 cycles at $5.0\text{ A}\cdot\text{g}^{-1}$)	[37]
$\text{CaV}_6\text{O}_{16}\cdot 3\text{H}_2\text{O}$	0–1.4	3 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$	320 ($0.05\text{ A}\cdot\text{g}^{-1}$)	125, (after 70 cycles at $4.0\text{ A}\cdot\text{g}^{-1}$)	[38]
$\text{Ag}_2\text{V}_4\text{O}_{11}$	0.3–1.3	3 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$	251.5 ($0.5\text{ A}\cdot\text{g}^{-1}$)	117.6, (after 1000 cycles at $3.0\text{ A}\cdot\text{g}^{-1}$)	Our work

The presence of the pseudocapacitive effect can strongly explain the excellent rate performance and stable cycling performance at high current densities for the $\text{Ag}_2\text{V}_4\text{O}_{11}$ -180 cathode material. Therefore, the electrochemical kinetics of the $\text{Zn}/\text{Ag}_2\text{V}_4\text{O}_{11}$ batteries were further analyzed [25,31,41]. The CV curves of the $\text{Ag}_2\text{V}_4\text{O}_{11}$ cathode material at different scanning rates are shown in Figure 4a. As the scanning rate increases, the shapes of the curves remain similar, but the oxidation and reduction peaks become wider and shift towards higher (oxidation peak) or lower (reduction peak) potentials, respectively. This can be attributed to the polarization that occurs at the electrodes.

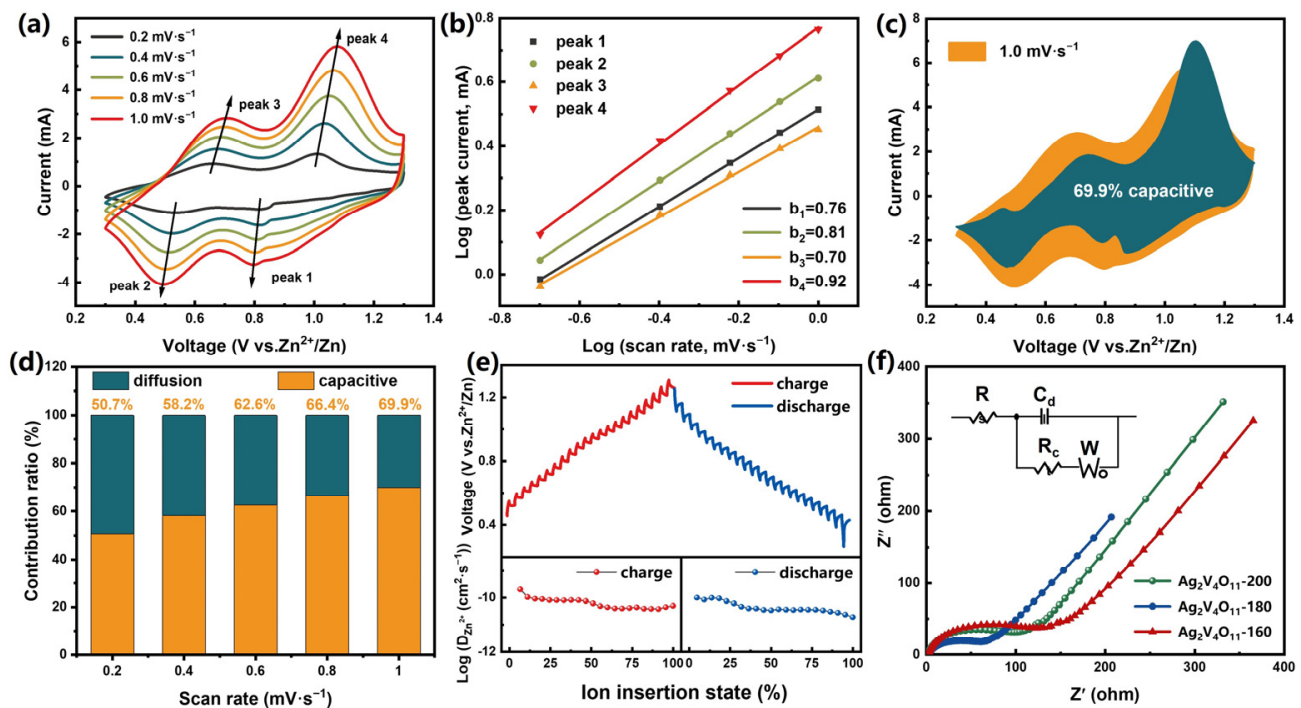


Figure 4. CV curves at various scan rate from $0.2 \text{ mV}\cdot\text{s}^{-1}$ to $1.0 \text{ mV}\cdot\text{s}^{-1}$ (a); $\log(i)$ - $\log(v)$ plots at specific peak currents (b); Capacitive contribution at $1.0 \text{ mV}\cdot\text{s}^{-1}$ (c); the pseudocapacitive contribution (orange region) at various scan rate from $0.2 \text{ mV}\cdot\text{s}^{-1}$ to $1.0 \text{ mV}\cdot\text{s}^{-1}$ (d); GITT curves and diffusion coefficient for Zn^{2+} in the second charge-discharge process (e); Nyquist plots of $\text{Zn}/\text{Ag}_2\text{V}_4\text{O}_{11}$ batteries (f).

The parameter b can be calculated from the relationship (1) between the peak current (i) and the scan rate (v), and the result is shown in Figure 4b.

$$i = av^b \quad (1)$$

It is simplified as follows:

$$\log(i) = \log(a) + b * \log(v) \quad (2)$$

where i is the peak current (mA), v is the scan rate ($\text{mV}\cdot\text{s}^{-1}$), and a and b are variables ($0.5 \leq b \leq 1.0$). Generally speaking, $b = 0.5$ indicates that the kinetic process of an electrode reaction is dominated by diffusive behavior, whereas $b = 1.0$ suggests a reaction kinetic controlled by capacitive behavior [26,28]. Combined with Figure 4b,c, the redox peaks of $\text{V}^{5+}/\text{V}^{4+}$ and $\text{V}^{4+}/\text{V}^{3+}$ correspond to b values of 0.92, 0.76, 0.70, and 0.81, respectively. This indicates that the electrochemical reactions occurring at the electrode are the result of the synergistic effect of diffusion and capacitance.

At a set scan rate, the contribution of the capacitance and ion diffusion can be calculated from the peak current (i), the scan rate (v), and the relationship between k_1 and k_2 (3).

$$i = k_1v + k_2v^{1/2} \quad (3)$$

Here, i is the peak current (mA), v is the scan rate ($\text{mV}\cdot\text{s}^{-1}$), and k_1v and $k_2v^{1/2}$ correspond to the capacitive contribution and ion diffusion contribution values, respectively. As shown in Figure 4c, the percentage of the capacitive contribution is approximately 69.9% at a scan rate of $1.0 \text{ mV}\cdot\text{s}^{-1}$. It can also be concluded that the capacitive contribution of the $\text{V}^{5+}/\text{V}^{4+}$ redox peak is more than the contribution of the $\text{V}^{4+}/\text{V}^{3+}$ redox peak. This is consistent with the b values, indicating that the $\text{V}^{5+}/\text{V}^{4+}$ redox peaks are mainly capacitively controlled in terms of kinetics. Figure 4d is a histogram of the capacitance

percentage at different scan rates. As the scan rate increases from 0.2 to 1.0 mV·s^{−1}, the corresponding capacitance contribution shows an increasing trend, which is gradually increased from 50.7% to 69.9%. This indicates that the dominance of the pseudocapacitive effect in the zinc storage process of the Ag₂V₄O₁₁-180 cathode gradually increases.

In addition, the kinetics of Zn²⁺ diffusion in the cathode electrode of Ag₂V₄O₁₁-180 were investigated by GITT. The Zn²⁺ diffusion rate (D_{GITT}) was calculated by the following formula [25,28]:

$$D_{\text{GITT}} = \frac{4}{\pi\tau} \left(\frac{m_B v_M}{M_B S} \right)^2 \left(\frac{\Delta E_s}{\Delta E_\tau} \right)^2 \quad (4)$$

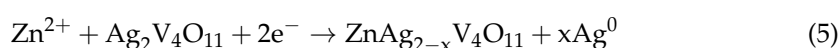
Among them, τ , m_B , v_M , and M_B are the constant pulse relaxation time, mass of active substance, molar volume, and molar mass of the electrode material, respectively. S is the interface area between the electrode and the electrolyte, while ΔE_s and ΔE_τ represent the pulse-induced change in the steady-state voltage and total cell voltage, respectively. The assembled cells were charged and discharged at a constant current (0.1 A·g^{−1}) at an interval of 20 min. The high specific capacity of the Ag₂V₄O₁₁-180 cathode is attributed to its laminar structure, which facilitates the charge transfer and shortens the ion transport path. The Zn²⁺ diffusion coefficient in the Ag₂V₄O₁₁-180 anode can be calculated to be approximately 10^{−9}–10^{−11} cm²·s^{−1}, which is comparable to that of the previously reported cathode materials [43–46]. The above electrochemical test results indicate that the fast electrochemical kinetics of the Zn//Ag₂V₄O₁₁ system can promote the efficient transfer of Zn²⁺ and show an excellent electrochemical performance. EIS tests were performed to further understand the electrochemical behavior of the Ag₂V₄O₁₁ cathode [47,48]. As shown in Figure 4f, the small semicircle observed at high frequencies represents the charge transfer resistance (R_{ct}) at the electrode/electrolyte interface, and the straight line with a slope (Z_w) corresponds to the diffusion-controlled process of the Zn²⁺ ions. It is clear that the ohmic resistance is similar before and after cycling for the three Ag₂V₄O₁₁ cathodes, while the diameter of the semicircle is smaller for the Ag₂V₄O₁₁-180 cathode material (Table 2). This indicates that the appropriate hydrothermal temperature gives this material a higher electronic conductivity than the other two materials, which is consistent with the results of the rate performance.

Table 2. Parameters of the equivalent circuit model.

Sample	R_s (Ω)	R_{ct} (Ω)	W_0 -R (Ω)
Ag ₂ V ₄ O ₁₁ -200	1.94	58	213.4
Ag ₂ V ₄ O ₁₁ -180	3.19	34.24	109.4
Ag ₂ V ₄ O ₁₁ -160	2.08	72.21	246.1

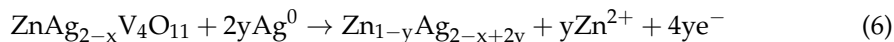
In summary, the Ag₂V₄O₁₁ cathode material exhibits excellent electrochemical properties. The reasons for this are as follows: during the discharge process, Zn²⁺ participates in a reversible substitution/intercalation reaction with part of the Ag⁺; Zn²⁺ is embedded in the main structure of the Ag₂V₄O₁₁ occupying the Ag⁺ site, forming the ZnAg_{2−x}V₄O₁₁ phase [24,26]; Ag⁺ is reduced to Ag⁰ after deintercalation from the laminate structure and deposited on the surface of the cathode material. The in-situ generated Ag⁰ particles contribute to the electrical conductivity of the material. Liang et al. report that the silver vanadium oxide electrode material may generate by-products during the first discharge, such as ZnV₂O₆ [24], Zn₄(SO₄)(OH)₆·nH₂O [26], Zn₂(V₃O₈)₂ [28,49], and Zn₃V₂O₇(OH)₂·2H₂O [50]. This may be related to the structure of the electrode materials.

The cathode electrode reaction is as follows:



During the charging process, Ag^0 is oxidized to Ag^+ and embedded again in the $\text{Ag}_2\text{V}_4\text{O}_{11}$ structure, while some of the Zn^{2+} will come out of the new phase $\text{ZnAg}_{2-x}\text{V}_4\text{O}_{11}$ into the electrolyte.

The cathode electrode reaction is as follows:



The layered structure formed by the Ag^+ intercalation layer is beneficial for enhancing the diffusion rate of Zn^{2+} and improve the kinetic behavior of the reaction. In addition, this also effectively improves the poor electrical conductivity of the cathode material and the easy collapse of the crystal structure during cycling.

4. Conclusions

In this work, layered $\text{Ag}_2\text{V}_4\text{O}_{11}$ nanoribbons were prepared by a one-step hydrothermal method and their structural properties, microscopic morphology, and elemental valence states were characterized. The $\text{Zn} // \text{Ag}_2\text{V}_4\text{O}_{11}$ cell was assembled based on this material, and its electrochemical properties and electrochemical kinetics in the $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ system were investigated.

(1) Hydrothermally synthesized $\text{Ag}_2\text{V}_4\text{O}_{11}$ is an overlapping feather-like nanoribbon material with a width of about 1–2 μm . Increasing the hydrothermal temperature promotes an increase in the spread of the “feather bone” and an increase in the number of “feather branches”.

(2) The $\text{Zn} // \text{Ag}_2\text{V}_4\text{O}_{11}$ -180 battery exhibited an excellent high specific capacity (276.6 $\text{mAh}\cdot\text{g}^{-1}$ at 0.5 $\text{A}\cdot\text{g}^{-1}$), rate performance (141.1 $\text{mAh}\cdot\text{g}^{-1}$ at 3 $\text{A}\cdot\text{g}^{-1}$), and long-term cycle stability (117.6 $\text{mAh}\cdot\text{g}^{-1}$ after 1000 cycles at 3 $\text{A}\cdot\text{g}^{-1}$). The $\text{Ag}_2\text{V}_4\text{O}_{11}$ -180 cathode material showed the best electrochemical performance compared to the samples treated at other hydrothermal temperatures.

(3) The reason for the high specific capacity and long-term cycle stability exhibited by the $\text{Ag}_2\text{V}_4\text{O}_{11}$ cathode material is the reversible conversion of Ag^+ to Ag^0 with the interlayer structure after the intercalation anchor of Ag^+ . This not only provides a fast transport channel for the intercalation and deintercalation of Zn^{2+} , but also stabilizes the charge storage and release processes during charging and discharging.

(4) The above results show that the capacity and rate performance of $\text{Ag}_2\text{V}_4\text{O}_{11}$ nanoribbons as cathode materials for zinc-ion batteries is very promising, but some improvements can still be made regarding their electron and ion conductivity. Such improvements could be achieved by compounding some special materials, such as Graphene, CNT, MXenes, Polypyrrole, Polyvinylpyrrolidone, and Polyaniline.

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