Acid-modulated Ammonium Vanadate Assist to High-Performance Zinc Ion Batteries

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Abstract. Vanadate has become one of the main cathode materials for aqueous zinc ion batteries (ZIBs) in recent years, but its low specific capacity and poor cycle life limit its further development. In this work, it is proposed to modulate vanadate morphology with acid to further improve the stability of electrode materials. The $NH_4V_4O_{10}$ nanoribbons (marked as VO) prepared by the hydrothermal method showed more active sites and reduced volume change during cycling, exhibiting improved specific capacity (631 mAh g^{-1} at 0.1 A g^{-1}) and cycle life (78% capacity retention after 3500 cycles at 5 A g^{-1}). This work provides new ideas for the development of vanadium-based ZIBs and it is important for the development of emerging energy sources.

Keywords: Zn ion battery, vanadium-based cathode, nanobelt.

1. Introduction

With the popularization and application of new energy generation, energy storage system has become one of the key technologies to solve the instability of new energy. Aqueous zinc ion batteries (ZIBs) are particularly suitable for large-scale energy storage due to their safe, environmentally friendly and low-cost characteristics [1-3]. Therefore, ZIBs have a widely used in many fields. The development of cathode materials for ZIBs has focused on improving energy density, cycle stability and reaction rate. ZIBs have attracted widespread attention in the field of scaled energy storage due to their advantages of low cost, environmental friendliness and high safety. However, existing cathode materials still have many challenges in terms of energy density, cycle stability and reaction rate.

Current cathode materials for ZIBs are mainly based on vanadium-based and manganese-based metal oxide systems, and the zinc storage mechanism of these materials is mainly based on the redox reaction of metal cations in the cathode materials [4-6]. However, this mechanism leads to a low voltage plateau, which limits the improvement of energy density. In addition, the electrostatic repulsion effect between the zinc ions and the metal cations in the cathode material affects the diffusion behavior of the zinc ions, leading to poorer kinetic conditions. Meanwhile, the valence changes of metal cations cause irreversible lattice distortions and phase transitions in the cathode material, affecting the cycling stability. The morphology of the electrode material is also critical to the performance of the ZIB. The morphology determines the specific surface area of the material, the pore size and thus further influences the electron-ion transport rate [7]. How to efficiently design the morphology of cathode materials has become one of the major challenges in research nowadays.

In this work, different concentrations of acids were designed to modulate the ammonium vanadate morphology to solve the problems of instability and poor cycling performance faced by the above cathodes. The specific surface area of the electrode material and the ion migration rate of Zn^{2+} were changed by different morphologies. Ammonium vanadate cathode materials (marked as VO) were prepared as nanoribbons with excellent specific capacity (631 mAh g^{-1} at 0.1 A g^{-1}) and cycling performance (81.9% capacity retention after 200 cycles at 1 A g^{-1} and 78% capacity retention after

3500 cycles at 5 A g^{-1}). Therefore, this study has important developmental implications for future zinc large-scale energy storage.

2. Experimental Section

2.1. Material Preparation

4 mmol of ammonium metavanadate was dissolved in 60 ml of deionized water and stirred, 2 ml of hydrochloric acid (HCl) was added drop by drop and the solution turned bright yellow, followed by the addition of 2 ml of hydrogen peroxide (H_2O_2) with a mass fraction of 30%, and the solution rapidly turned bright yellow to dark red and then to orange. Subsequently, it was put into a 100 ml reactor at 120°C for 6 h. The final sample was obtained by vacuum filtration. In order to investigate the effect of different acid concentrations on the morphology of the samples, 0.5 M, 1 M, 2 M and 3 M of HCl were configured and the samples obtained were noted as VO-0.5, VO-1, VO-2, VO-2 and VO-3.

2.2. Characterizations

The constituents of the samples were obtained by X-ray diffraction (XRD) to characterize the test. Scanning electron microscopy (SEM) was used to characterize the microscopic morphology of the samples.

2.3. Electrochemical Measurements

The prepared electrode material was configured with (polyvinylidene fluoride) PVDF and conductive carbon black in the ratio of 8:1:1, followed by the addition of a little (N-methyl-2-pyrrolidone) NMP grinding to form a slurry, which was coated on a stainless steel mesh and dried to form an cathode electrode. VO-1 was used as the positive electrode and assembled with 200 μm Zn foil and zinc trifluoromethanesulfonate (Zn $(CF_3SO_3)_2$) to form a button cell for electrochemical testing. Cyclic voltammetry (CV) is tested with an electrochemical workstation (CHI 760e), and Galvanostatic charge and discharge (GCD) curves and cycling performance are tested with a NEWARE test instrument. The operating voltage of the VO-1//Zn battery is 0.2-1.6 V.

3. Results and Discussion

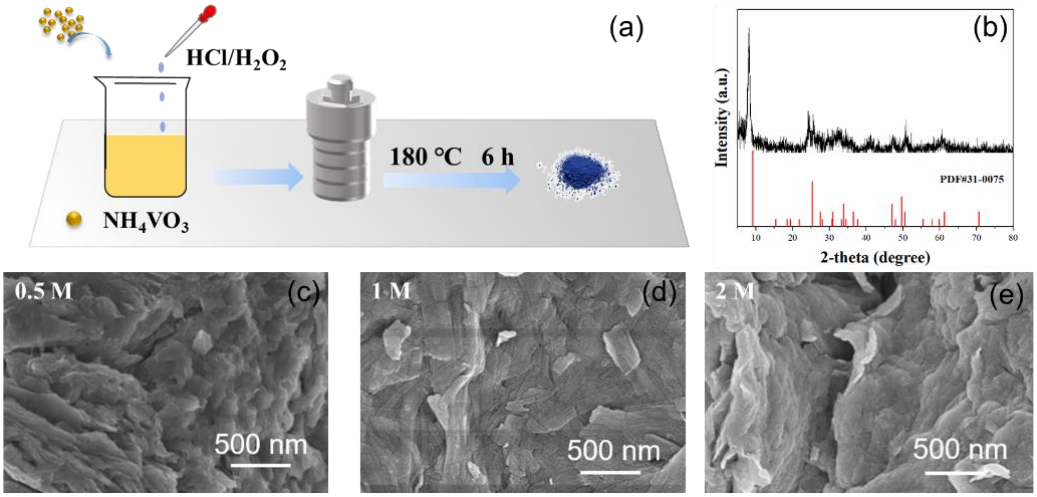

Figure 1. (a) Schematic depiction of the synthesis process for high-capacity VO cathode materials. (b) XRD of VO-1. SEM images of VO at different HCl contents (c) 0.5 M, (d) 1 M and (e) 2 M.

Fig. 1 shows a schematic diagram of the preparation of $NH_4V_4O_{10}$. Fig. 1b shows the XRD curve of the prepared sample VO-1, and the standard comparison card to compare its fully composite $NH_4V_4O_{10}$ characteristic peaks, so the sample has been successfully prepared. In order to further

investigate the effect of different concentrations of acid on the morphology of the electrode materials, SEM characterization tests were performed on the materials. From the SEM image analysis, the morphology of the samples obtained at HCl concentrations of 0.5 M and 2 M are all sheet stacked, while the electrode material when the HCl concentration is 1 M is in the form of nanoribbons, which is significantly different from the other morphologies. Nanoribbon structures can provide more active sites as well as less structural collapse due to ion shuttling during cycling compared to nanosheet stacking.

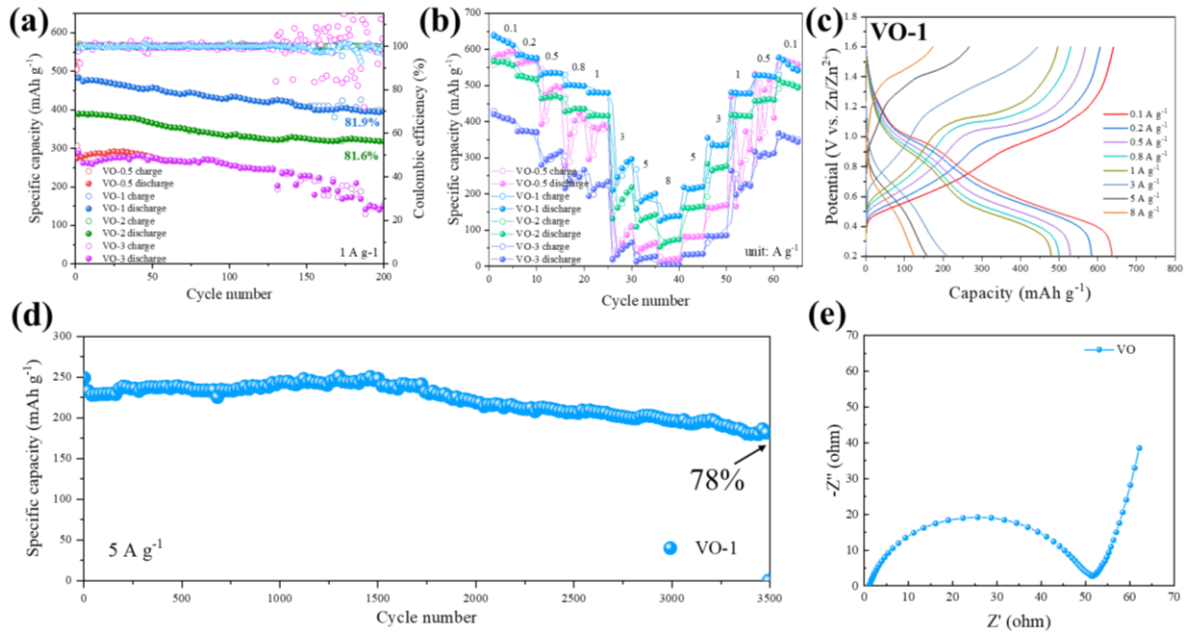

Figure 2. (a) Cycle performance at 1 A g^{-1}, (b) rate performance, (c) GCD curves at different current densities, (d) cycle performance at 5 A g^{-1} of VO-1.

In order to further verify the advantages offered by the structural morphology, electrochemical tests were performed. Fig. 1a shows the cycling profiles under different concentrations of acid modulation. It can be found that VO nanoribbons with an acid concentration of 1 M have the highest specific capacity and cycle retention. The capacity of VO-1 at 1 A g^{-1} was maintained at 81.9% under 200 cycles. Fig. 1b shows the ploidy performance under different acid modulations. The specific capacities of VO at current densities of 0.1, 0.2, 0.5, 0.8, 1, 3, 5, and 8 A g^{-1} are 631, 579, 535, 500, 480, 288, 200 and 137 mAh g^{-1}, respectively. Fig. 2c shows the GCD graph of VO-1 with a clear charge/discharge curve. As shown in Fig. 2d, the VO-1 was further tested at a high current of 5 A g^{-1} and could be cycled for 3500 cycles with capacity maintained at 78%. Fig. 2e shows the EIS curve of the VO-1, which consists of a semicircle and a one sloping straight line, typical of battery characteristics.

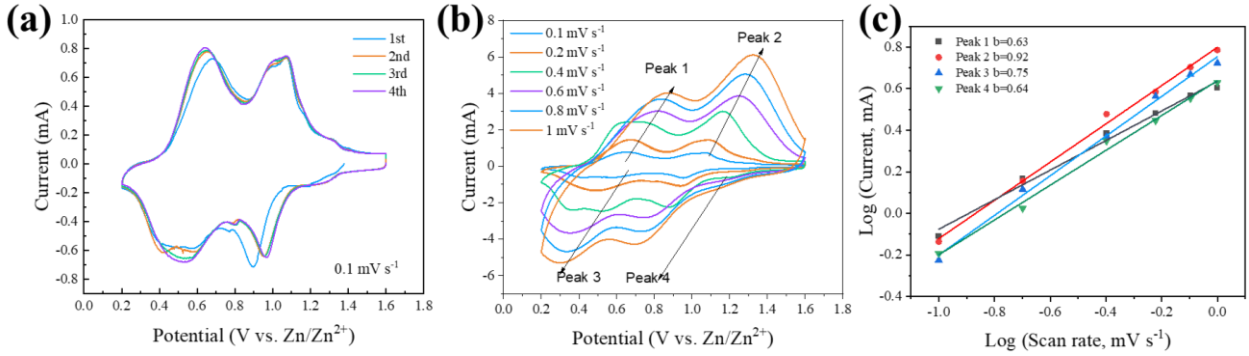

Figure 3. (a) CV curves for the first four laps of VO-1. (b) CV curves at different scan rates of VO-1. (c) b value of VO-1 based the CV curves.

In order to further investigate the electrochemical reaction kinetics of the cathode materials, CV curves were performed. Fig. 3a shows the CV curves for the first four turns of the VO-1 at a scan rate of 0.1 mV s^{-1}, and it can be seen that all but the first turn has a high degree of repeatability, indicating good reversibility. Fig. 3b shows the CV curves at different scan rates, and two pairs of redox peaks can be clearly observed. As shown in Fig. 3c, the b-values of the four peaks can be calculated according to the formula $i=av^b$ [8, 9], which are 0.63, 0.92, 0.75, and 0.64. The above results indicate that the reaction mechanism of the cell is dominated by pseudocapacitance and supplemented by diffusion control.

4. Summary

In summary, we propose an acid modulation strategy to address the current bottleneck faced by cathode materials. Acid modulation of ammonium vanadate morphology and structure facilitates the preparation of high specific capacity, long cycle cathode materials. The VO-1 prepared in this work can reach a maximum specific capacity of 631 mAh g^{-1} at 0.1 A g^{-1} and can be cycled 200 times at 1A g^{-1} with 81.9% capacity retention. In addition, it can be recycled for 3500 cycles at 5 A g^{-1}, showing outstanding cycling stability. This work can contribute to the future development of cathodes for zinc-ion energy storage batteries.

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