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Preparation of V$_2$O$_5$ Porous Hollow Spheres and Study on Excellent Cycling Stability of Lithium Battery

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ABSTRACT

Through one-step simple polyol-assisted (ethylene glycol) process, V$_2$O$_5$ hollow micro-spheres about 3 micrometres in size were successfully synthesized. The structure is neat, the outer wall were porous. Testing its electrochemical properties with V$_2$O$_5$ hollow materials as cathode materia of lithium ion battery, the results showed that under the ratio of 1 C, the initial charge and discharge specific capacity were 236.8 mAh g$^{-1}$, 213 mAh g$^{-1}$, even if after 100 cycles, the charge and discharge specific capacity were still 220 mAh g$^{-1}$ and 219.7 mAh g$^{-1}$ respectively. Relative to the charge and discharge capacity of the second cycle, the keep rate were 93.2%, 92.9% respectively, has good cycle stability.

1. Introduction

E
nery crisis and environmental pollution restricted the development of the society and people's lives to a great extent. In recent decade years, scientific research workers have been trying to the new energy research and the traditional energy friendly transformation and storage, which have become a problem of priority. Energy device development research of lithium ion battery which has identified its advantage of energy storage and environmental friendly change can be traced back to the 1930s and has been industrialized widely until recent years. Lithium-ion batteries (LIB) using LiCoO$_2$ as cathode material and carbon as the anode materials, with theoretical capacity of 274 mAh g$^{-1}$, has the good cycle stability. Therefore, to a great extent, LIB can satisfy the people's basic needs such as travel, communication. But the cobalt is limited and expensive, forcing people to choose other more appropriate anode materials, such as LiNiO$_2$, LiMn$_2$O$_4$, LiMnO$_3$, LiFePO$_4$ and transition metal oxides (V$_2$O$_5$, MnO$_2$, Fe$_2$O$_3$, etc.) materials.$^{[1-7]}$ Vanadate Series oxide materials, such as V$_2$O$_5$, VO$_x$, V$_2$O$_3$, VO, etc, as lithium cathode materials, have great potential industrial value. Zhang huamin's research team of dalian institute of chemical technology and rongke energy storage cooperated to successfully industrialize the all-vanadium liquid-flow battery in 2013.Vanadium series materials in addition to the charge and discharge process, through its redox reactions can also be done by the embedded process of Li$^+$, such as micro V$_2$O$_5$ nano-materials, as a liti-
um-ion battery cathode material research already has more than 30 years, from the simple one dimensional structure to three-dimensional structure has carried on the thorough discussion, especially the internal hollow structure, laminated, shell, mesoporous structure. Porous hollow inside the outer wall of V₂O₅ materials research is not too much, this subject adopts simple step solvent thermal process and then high temperature sintering process; by adjusting the concentration of the raw material successfully achieve the purpose of regulating the phase structure.

2. Experiment

Respectively take 0.5 g, 0.7 g and 0.9 g ammonium vanadate (NH₄VO₃) and 40 ml glycol into 50 ml stainless steel autoclave with a teflon lining, magnetic stirring 2 h. With the increase of NH₄VO₃, the solution color from pale yellow to deep yellow. Then, putting the autoclave into vacuum drying oven at 200°C for 12 h. The resulting green products were collected by centrifugation at 10000 rpm for 3 min and washed with absolute ethanol three times. The well-collected solid were dried at 60°C for 12 hours to produce the precursor and it was then calcined at 500°C for 2 hours. They were marked as 0.5 g-1, 0.7 g-2, 0.9 g-3 respectively.

3. Electrochemical Characterization

Electrochemical analyses were performed using coin-type cells(CR2032). The diameter of the electrode is 12 mm, the thickness of the coating is 200 μm and the density of the active material is about 1 mg cm⁻². Working electrodes were prepared by active materials, carbon black and polyvinylidene fluoride(PVDF) at a weight ratio of 70:20:10 onto Al foil. Finally the well-coated foil were dried at 80°C for 12 h in air. The electrolyte was used 1 M LiPF6 mixed with while carbon dioxide (EC), dimethylcarbonate (DMC ) and diethyl carbonate (DEC) in a ratio of 1:1:1 (v:v:v). The cells were assembled in an argon-filled M Braun glovebox model Unilab using airtight glass containers. The galvanostatic charge-discharge cycling measurements were performed using CT2001A LAND Cell test system. The cyclic voltammetry (CV) was tested in the voltage range of 2-4 V by an electrochemical workstation (LK2005A).

4. Results and Discussions

Through solvent thermal at 200°C for 12 h and high temperature calcining in the air, raw material NH₄VO₃ at different levels (0.5 g, 0.7 g and 0.9 g) and ethylene glycol (HOCH₂CH₂OH) reacted to produce a different structure of the microspheres as shown in Figure 1. When the content of ammonium vanadate (NH₄VO₃) was 0.5 g, as shown in Figure a1 and a2, the core-shell microspheres with a particle size of about 3 μm were obtained. The inner and outer walls of the microspheres were very loose and there were many holes between the particles. When raw material (NH₄VO₃) content increased to 0.7 g, hollow microspheres about 2 μm were produced (Figure b1, b2). Broken spheres can help us to see clearly the interior of the hollow structure and the gaps between the outer walls of the particles. Continue to increase the amount of raw materials to 0.9 g, we still obtained hollow spheres while the size of hollow structure has been reduced about 1 μm in diameter (Figure c1, c2), but the hollow sphere structure trending to collapse and adhesion.

Figure 1. FESEM Images of V₂O₅ Microspheres with Different Content of NH₄VO₃
(a1, a2) 0.5 g-1; (b1, b2) 0.7 g-2; (c1, c2) 0.9 g-3

Figure 2 (a, b, c) showed the XRD patterns of the three samples which were assigned to the orthorhombic V2O5 phase (JCPDS card no. 41-1426, space group: Pnma (56), a =11.516 Å, b = 3.566 Å, c = 3.777 Å), without obvious hybrid peaks. Compared with the standard card, the diffraction peak intensity of each crystal surface was enhanced.

Figure 2. XRD Pattern of V₂O₅ Microspheres with Different Content of NH₄VO₃
(a) 0.5 g-1; (b) 0.7 g-2; (c) 0.9 g-3

Figure 3 showed discharge-charge cycling performance of V₂O₅ hollow spheres obtained with the raw material content of 0.7 g, as cathode material of lithium ion battery in 2-4 V(vs. Li/Li⁺) voltage range. As shown in figure 3, the initial charge and discharge capacity of the hollow
spheres were 236.8 mAh g⁻¹, 213 mAh g⁻¹ at 1 C (300 mAh g⁻¹), corresponding to efficiency is 111.2% (figure 4). Discharge capacity is lower than the charging capacity, which is due to formation of solid electrolyte interface (SEI) happened on the electrode surface via deposition reaction for the first charge-discharge process resulting in the loss of irreversible capacity. In the second cycle, the charge and discharge capacity of the hollow spheres was 235.9 mAh g⁻¹, 236.3 mAh g⁻¹ respectively with the efficiency 99.8%, closing to 100% (figure 4), within the error range, it was considered to be completely reversible. After 50 cycles, the discharge specific capacity were 217.7 mAh g⁻¹, 216.8 mAh g⁻¹, which charge and discharge efficiency was close to 100% (figure 4), even if the cycle reached to 100 cycles, charge and discharge capacity is still 220 mAh g⁻¹, 219.7 mAh g⁻¹, relative to the first charge and discharge specific capacity, the retention rate were 92.9%, 100% (Figure 4), the cycle stability is superior to other materials of the same structure. The excellent electrochemical performance is attributed to its 3 D micro spherical structure, the outer wall porous and hollow inner. The 3D micro structure provides stable structural support, outer wall of the sphere provides Li⁺ adsorption and separation, and helps the electrolyte pass through the porous outer wall channel smoothly. The strong surface area of the inner wall multiplied the adsorption site of Li⁺, and the diffusion distance of lithium ions in the hollow structure was minimized.

5. Conclusion

The hollow V₂O₅ microspheres were successfully prepared by controlling the content of the material (NH₄VO₃) through a simple one-step solvent heat and subsequent high-temperature calcination process. When the amount of NH₄VO₃ increased from 0.5g to 0.9g, the hollow microstructure changed from double shell structure to hollow structure, and the size of the microspheres also decreased from 4 to 2 μm. High electrochemical performance was achieved by synthesizing hollow microspheres, resulting in a specific discharge capacity of 219.7 mAh g⁻¹ at 1C after 100 cycles, exceeding the same structure of other materials.

References


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