The Preparation of VO_2(B) Cathode Material for Lithium-ion Battery with High Capacity and Good Cycling Performance

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Abstract. Fiber-like VO_2(B) was successfully synthesized by using V_2O_5 and ethanol as reactants via a magnetic stirring solvothermal process. The stirring rates significantly affected the phase, morphology and the cycling performance of as-synthesized products. When the stirring rate was 867 rpm, the fiber-like particles were 3-5 μm long and 50-100 nm wide, and showed better dispersion than the sample of VO-0, the electrochemical performance test demonstrated that the initial discharge capacity of VO-867 was 223 mAh/g, and maintained 186 mAh/g after cycling for 50 times, the retention rate of the capacity was 83.4%, which showed best cycling property of all samples.

1 Introduction

Nowadays, the deteriorating of the ecological environment and the depleting of the traditional energy made the development of human society face enormous challenges, searching for an alternative and efficient green energy, has become an imperative things for the sustainable development of human society[1-3]. The advantage of high energy density, long life, no memory effect, safety and environmental made the Lithium-ion batteries be the best energy storage equipment[4-7].

As we know that the successful application of lithium-ion battery technology was highly depended on the used of the electrode material, so how to choose the electrode material would in turn limits the safety, energy density and the power density of the lithium-ion battery system. Compared with the conventional lithium-ion battery cathode material ($LiCoO_2$[4], $LiFePO_4$[8]), vanadium oxides (V_2O_5, V_6O_{13}, VO_2, etc.) with the advantage of low cost, high specific capacity, high security and easy of preparation have been widely researched in recent years [9,10]. Among which, VO_2(B) has been one of the most promising cathode materials due to its open framework structure which permitted the lithium ions rapidly intercalation/deintercalation between the layers, the special structure gave it a maxium reversible capacity of 320 mAh/g in the 4-1 V voltage range[11-14]. However, the defect of low electronic conductivity and poor stable circulation severely affected its practical application. In recent years, researchers have taken a series of effective measures to overcome its shortcomings, all kinds of morphologies of VO_2(B) have been prepared, such as nanorods[15,16], nanoribbons[17,18], nanotubes[19,20], and nanowires[21], however, these nanostructure materials displayed low discharge capacity and poor cycling properties[22], The fading of the capacity was probably owing to the high surface energies and large specific surface areas, which leading to the easier aggregation of the sample during process of charging and discharging, thus resulting in the increases of the charge transfer

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resistance[23]. Therefore, how to improve the cycling properties of VO_2(B) was still a great challenge for researchers and material scientists.

Yuxin Tang and co-workers[24] proposed a stirring hydrothermal method and successfully synthesized the elongated titanate nanotubes with length up to tens of micrometers, meanwhile, this method effectively prevented agglomeration of the sample, and provided a pathway for electron transport, thus improved the electrochemical performance greatly. In this work, Fiber-like VO_2(B) was successfully synthesized by using V_2O_5 and ethanol as reactants via a magnetic stirring solvothermal process. Afterwards, we discussed the influence of the mangnetic stirring rate on the phase, morphologies and electrochemical properties of the samples.

2 Experimental

2.1 synthesis

All the reagents were analytical grade and used without any further purification. In a typical synthesis, 0.4 g V_2O_5 was dispersed into the solution of 20 mL deionized water and 30 mL anhydrous ethanol, after stirring for several minutes, the uniformly yellow suspension was obtained and transferred into a 100 mL teflon lined autoclave. The autoclave was placed into the oil bath and heated to 190 ^oC for 24 h with magnetic stirring, and then cooled to room temperature naturally, the products were washed with deionized water for 3 times and then dried in a vacuum freeze-dryer for 24 h. In order to investigate the relation between stirring rate and morphology, the stirring rate was regulated for 0 rpm, 867 rpm and 1730 rpm, and the products were marked as VO-0, VO-867 and VO-1730, respectively.

2.2 Characterization

The X-ray powder diffractometer (XRD) with a Cu Kα radiation source (λ = 0.154 nm, the scanning rate of 6 °/min) was used to analyze the phase of the products. The Hitachi S-4800 field emission scanning electron microscopy (FESEM) was carried out to observe the morphology of the products.

2.3 Electrochemical performance measurements

The positive electrode was prepared by mixing active material, acetylene black carbon power and polyvinylidene fluoride (PVDF) binder in a weight ratio of 7/2/1, grinding the mixture with some N-methy1-2pyrrolidone (NMP), then the slurry was coated equably on Al foil. The Al foil was dried in vacuum at 90 ^oC for 12 h.The 1mol/L LiPF6 mix with ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) in a volume ratio of 2/2/1, then assembled the cells in the glove box. Charge-discharge tests were performed by a BTS Cycler (Shenzhen, China), the Cyclic voltammetry (CV) measurement and electrochemical impedance spectroscopy(EIS) measurement were characterized by a Zahner (Germany) IM6ex electrochemical workstation.

3 Results and discussion

3.1 XRD analysis

Figure 1 showed the XRD patterns of the samples with different stirring rates, as shown in figure 1, the peaks of the samples were basically agreement with standard diffraction peaks of VO_2(B) (JCPDS no. 81-2392). However, the characteristic diffraction peaks of V_3O_7 and V_2O_5 have been found near 14° and 26° respectively, which may be attributed to the reaction was not completely.

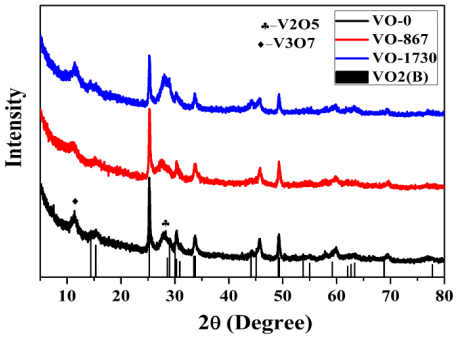
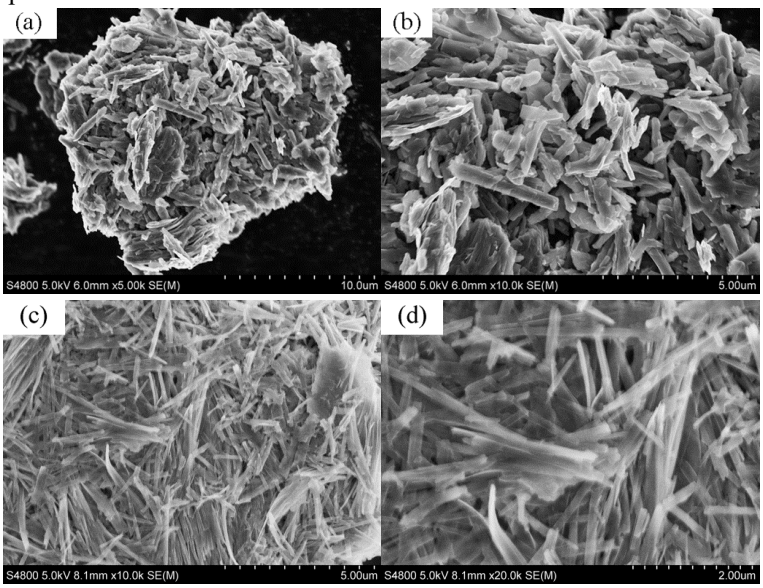


Figure 1. XRD patterns of the samples with different stirring rates.

3.2 SEM analysis

Figure 2 showed the SEM images of the samples with different stirring rates of VO-0(a,b), VO-867(c,d) and VO-1730(e,f), respectively. It can be seen from figure 2(a,b) that the sample with no stirring speed was composed of fiber-like particles, the fibrous were 1-2μ m long and 100-300nm wide, what is more, they were easy to aggregation. With the stirring rate increasing, the length of the fibrous increased greatly, meanwhile, the width of them decreased significantly, when the stirring speed increased to 867 rpm, the fiber-like particles can approach to 3-5μ m long and 50-100 nm wide (figure c and figure d), however, when the stirring speed increased to 1730 rpm (figure e and figure f), the length of the fibrous were shorter than that of the sample of VO-867, indicating that too high of the speed would destroy the structure of the sample, which would further influence the electrochemical performance.



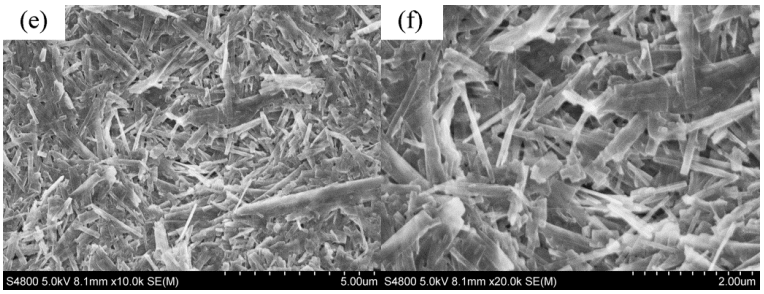


Figure 2. SEM images of the samples with different stirring rates of VO-0(a,b), VO-867(c,d) and VO-1730(e,f).

3.3 Electrochemical properties

Figure 3 showed the Nyquist plots of the samples, the Nyquist plots were measured by EIS (electrochemical impedance spectra) after cycling for 3 times, It can be seen from figure 3 that the charge transfer impedance (Rct) value of VO-0, VO-867 and VO-1730 in the high frequency region's semicircles were corresponding to 908 Ω, 551.5 Ω and 762.4 Ω, obviously the Rct value of the samples with stirring speed were smaller than that of the sample with no stirring rate, among which, the Rct value of VO-867 was found to be the smallest, indicating that the sample of fiber-like can be better contact with the conductive material in battery, which makes uniform voltage distribution and smaller resistance during the process of lithium ion intercalating to the surface of the electrode.

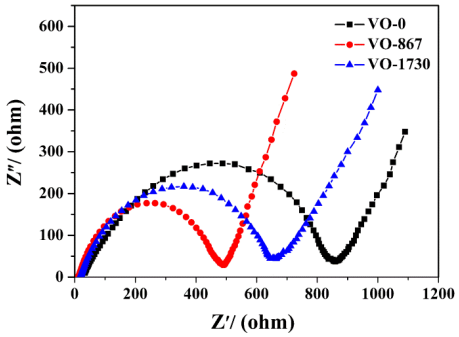


Figure 3. the Nyquist plots of the samples with different stirring rates.

Figure 4 displayed the cycling performance of the samples with different stirring rates of VO-0, VO-867 and VO-1730 at the current density of 32.4 mA/g (0.1 C), it can be seen from figure 6 that the discharge specific capacities were 308 mAh/g, 223 mAh/g and 291 mAh/g after the first cycle, corresponding to the samples of VO-0, VO-867 and VO-1730, respectively, and maintained 177 mAh/g, 186 mAh/g and 144 mAh/g after 50 cycles, the retention rates of the capacities were 57.4%, 83.4% and 49.5%, respectively. Obviously, the sample of VO-867 had the best cycling performance, which was attributed to its special fibrous structure that composed of nanobelts, these nanobelts were more longer and thinner than the other two samples of VO-0 and VO-1730, meanwhile, they were stacking and intertwined together, which permitted the faster transmission of lithium-ion and reduce the damage to the structure, thus greatly improved the cycling performance of the sample.

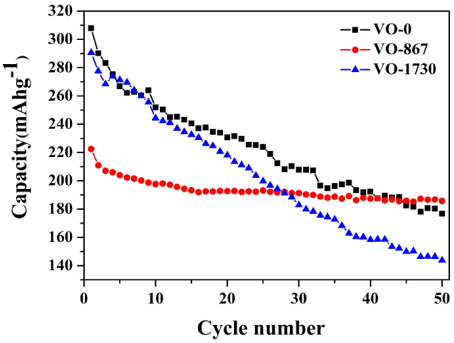


Figure 4. the cycling performance of the samples.

Figure 5 showed the cyclic voltammetry curves of VO-0, VO-867 and VO-1730 with the voltage range of 1.5-3.5 V at the scanning speed of 0.2 mV/s after cycling for 3 times. A pair of oxidation and reduction peaks could be observed in the figure, which represented the extraction and insertion of Li^+ during the electrochemical processes. With the stirring rate increasing, the reduction peaks shift to higher voltage and the oxidation peaks shift to lower voltage, of all the samples, the area of the curve in the sample of VO-0 was the biggest, which represented the sample of VO-0 had the biggest capacity, In addition, the peaks of VO-867 were highest symmetric, indicating that its cycling properties was the best. Which was consistent with the result of the cycling performance.

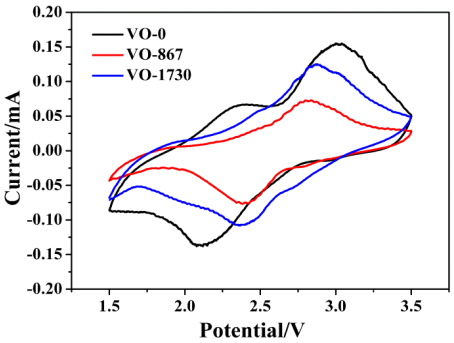


Figure 5. The cyclic voltammetry(CV) curve of the samples.

4 Conclusion

VO_2(B) with fibrous structure has been successfully synthesized via a solvothermal method with magnetic stirring in a oil bath. The morphology of the sample was controlled by the stirring rate. With stirring rate increasing, the length of the fibrous increased and the width of them decreased significantly, meanwhile, they were better dispersion, when the stirring rate increased to 867 rpm, the fibrous can approach to 3-5μ m long and 50-100 nm wide, electrochemical performance test demonstrated that the initial discharge capacity of VO-867 was 223 mAh/g, and maintained 186 mAh/g after cycling for 50 times, the retention rate of the capacity was 83.4%, which showed best cycling property of all samples.

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