Synthesis and Electrochemical Properties of Fibrous V$_6$O$_{13}$ for Li-ion Batteries

Wan Zhendong, Zou Zhengguang*, Chen Hongxu, Hou Zhongliang

Key Laboratory of Non-Ferrous Materials and New-Processing Technology of Ministry of Education, College of Material Science and Engineering, Guilin University of Technology, Guilin, Guangxi 541004, China

Email: zouzgglut@163.com

Abstract. In this paper, fibrous-shaped of V$_6$O$_{13}$ were successfully synthesized via V$_2$O$_5$ and ethanol as reactants through the method of magnetic stirring in the oil bath. Compared to the prepared sample without mechanical force-driven, the sample prepared by this method has a fibrous morphology with good dispersion. It can be seen that as the speed increases, the width of the fibers decreases, the fiber length increases after SEM tests. After the electrochemical tests, it can be seen that the attrition rate of capacity will be successfully inhibited in the process of charging and discharging when the fibrous-shaped V$_6$O$_{13}$ as a lithium ion battery cathode material. When the stirring rate was 0 rpm and possessed a reversible capacity of 72 mAh/g after 50 deep cycles. By contrast, the stirring rate was 1200 rpm and possessed a reversible capacity of 102 mAh/g after 50 deep cycles. It increased 41.6%.

1. Introduction

In recent years, owing to the crisis of energy and environment, searching for a kind of batteries materials with low-cost and environment friendly has been one of the focuses of energy materials[1-2]. The features such as stable in the air, have layer structure and low preparation cost made the vanadium oxide a promising material in the field of Li-ion batteries[3-5].

Very recently, many vanadium oxides have been synthesized such as V$_2$O$_5$, V$_6$O$_{13}$, V$_3$O$_7$ and VO$_2$(B) [6-9]. Among which V$_6$O$_{13}$ has been one of the most potential materials in Li-ion batteries. Owing to the advantage of layer structure, such as a higher theoretical reversible capacity of 420mAh/g and the higher working voltage that is much than 1.5V[10]. Pure V$_6$O$_{13}$ has been gained by many methods, such as thermal decomposition, sol-gel and hydrothermal method[11-14]. However, the instability structure made it a poor cycling property during the process of charging and discharging. In a word, it still a great challenge to improve the cycle performance of the materials[15-17].

In conventional hydrothermal technique, the structure of prepared V$_6$O$_{13}$ is easy to reunite because of its slow dissolution-recrystallization process and low growth kinetic of raw material at static condition. It increases the resistance of the electrode and collector and impedes insertion of lithium. Ultimately, the particles lose electrochemical conductivity and the circulation performance decreases.

It has been known for the stirring process can provide a uniform mixing of the reactants in the solution, increasing the reaction rate and maintaining the same reaction conditions as the same temperature and concentration. Therefore, it is possible to produce similar product form on a large scale. Inspired by this, we develop a new method which named the stirring hydrothermal method. On the basis of conventional hydrothermal technique, mechanical stress is introduced to change the material structure. Thus, the problem of particles agglomeration in conventional hydrothermal process...
was solved.
In this work, fibrous-shaped of $V_6O_{13}$ were successfully synthesized via $V_2O_5$ and ethanol as reactants through the method of magnetic stirring in the oil bath. Afterwards, the influence of the fiber length, the speed of magnetic stirring on the electrochemical properties of the fibrous $V_6O_{13}$[18-19] were discussed.

2. Experimental

2.1. Synthesis Route

All the reagents are analytical grade and with no need for any further refine. In a typical procedure, 0.4g $V_2O_5$ powder and 25mL anhydrous ethanol were dispersed in 20mL deionized water. After stirring for several minutes the uniformly yellow suspension was obtained, then transferred it into a 100mL teflon-lined autoclave. The autoclave was sealed at last and placed into the oil bath pot heated to 190℃ for 6h with magnetic stirring. The stirring rate was regulated for 0 RPM, 400 RPM and 1200 RPM respectively. Our detailed study confirms that the sample's morphology was controlled by a stirring hydrothermal method with different revolutions. After reaction, taking out the autoclave from the oil bath and then cooled it to the room temperature, the product was centrifuged with deionized water for 3 times, collecting the precipitation and put it into the freezing dryer to -50℃ for 24h. Finally, the precursors were calcined at 350℃ for 1h under the conditions of $N_2$. Samples were marked as VO-0, VO-400 and VO-1200, respectively.

2.2 Characterization

The phase of the products was performed by X-ray powder diffraction(XRD), using Japan JSM-5610LV X-ray diffraction with Cu Kα radiation ($\lambda=1.5406\AA$). The morphology of the products was characterized by Hitachi S-4800 field emission scanning electron microscopy(FESEM).

2.3 Electrochemical Performance Measurements

The positive electrode was prepared by active material, acetylene black carbon power and polyvinylidene fluoride (PVDF) binder in a weight ratio of 70:20:10. grinding the mixture with the N-methyl-1-pyrrolidone(NMP) as solvent, then coated the slurry equably on Al foil. The coated electrode was dried in vacuum at 90℃ for 12h. The electrode was 1mol/L LiPF6 mixed with ethylene carbonate(EC), dimethyl carbonate(DMC) and diethyl carbonate (DEC) in a volume ratio of 2:2:1. The cells were assembled in a glove box. Charge-discharge tests were performed by a BTS Cycler (Shenzhen, China) at a voltage range of 3.5-1.5V. Cyclic voltammetry (CV) tests measured between 1.5 and 3.5 V at a scan rate of 0.2 mVs$^{-1}$ and electrochemical impedance spectroscopy(EIS) measurement (cell voltage of 5.0mV, frequency range from $1x10^2$ to $10^5$ Hz) were characterized by Zahner(Germany) IM6ex electrochemical workstation.

3. Results and Discussion

3.1. XRD Analysis
**3.2 SEM Analysis**

Fig. 1 XRD patterns of the VO-0, VO-400, VO-1200 before sintering (a) and after sintering (b)

The two figures above show the XRD patterns of different samples before sintering (Fig. 1a) and after sintering (Fig. 1b). It can be seen that from Fig. 1a that all peaks of the precursors were basically coincided with the standard diffraction peaks of the V$_6$O$_{13}$ (JCPDS 71-2235). As shown in Fig. 1a, the diffraction peaks were so wake. Meanwhile, the characteristic diffraction peaks of V$_2$O$_5$ have been found near 26° which was owing to the incomplete reaction. Fig. 1b shows the XRD patterns of the samples after sintering in nitrogen atmosphere. The diffraction peaks of the sintered samples were strongly consistent with the standard card than precursors. The reason are as follows, the precursors had further reaction when sintering at high temperature. It also can be seen the characteristic diffraction peaks of V$_3$O$_7$ near 26° from Fig. 1b, which attributed to incomplete reduction of V$_2$O$_5$. 
Fig. 2 shows the SEM images of the precursors prepared by magnetic stirring in different stirring speeds. It can be seen from the Fig. 2 that the width of the fibrous decreased with the speed increased. The average fibrous widths of samples are 260nm, 200nm and 130nm which corresponding to VO-0, VO-400 and VO-1200. Meanwhile, the length of fibrous increased as the width decreased. However, the distributions of the VO-400 and VO-1200 fibers are more scattered and less prone to aggregation than VO-0.

Fig. 3 shows the SEM images of the VO-400 react for 2h(a, b) and 4h(c, d)

In order to further study the growth mechanism of fibrous V$_6$O$_{13}$, the reaction time of VO-400 was decreased to 2h and 4h. Fig. 3 shows the SEM of the reaction product in 2h or 4h. It can be seen from the Fig.3.ab when the reaction time of VO-400 was 2h, many flaky vanadium oxides in the sample was existed. However, the number of the flake-like vanadium oxides was significantly reduced and the size of them decreased as well when the reaction time was up to 4h as shown in Fig.3cd. Compared to Fig3ab and Fig3cd, we infer that the magnetic stirring mainly plays two roles in the synthesis of V$_6$O$_{13}$,
one is to accelerate the reaction rate, and the other is to provide power for the fiber-like V₆O₁₃ during the synthesis. In order to keep the whole reaction system stable, the vanadium oxide existed with sheet-like structure on the initial stage of reaction, which could reduce the surface free energy of the vanadium oxide. Mainly function of the magnetic stirring was to accelerate the reaction rate during this period. With the reaction time going on, the system got to a relative stable state slowly and the role of the magnetic stirring was mainly to provide power for the system to form the fiber-like V₆O₁₃.

The whirlpool formed in the system because of Magnetic stirring, and the light weight of the fibrous V₆O₁₃ would be precipitated along sides of the vortex. While the flake-like V₆O₁₃ stay in the bottom of the whirlpool because its heavier mass, and its mass would be reduced by colliding with other flake-like vanadium oxides at the bottom during the process of stirring. Eventually, the fiber-like V₆O₁₃ were formed.

![Fig.4 XRD patterns of the final product with different reaction times](image)

To validate those inferences, the sample of VO-400 reacted for 2h, 4h and 6h were measured by XRD after calcination. It can be seen from Fig.4 that the XRD patterns of VO-400 reacted for 2h is similar to the diffraction peak of V₃O₇ (JCPDS 71-0454). However, with the reaction time increasing, the characteristic peaks of V₃O₇ gradually weakened. When the reaction time reached for 6h, the diffraction peaks of V₃O₇ around 24° had completely disappeared. Meanwhile, the characteristic peaks of V₆O₁₃ near 45° have been found. As Fig.4 shown that the XRD pattern of VO-400 reacted for 6h is basically consistent with the standard pattern of the V₆O₁₃. Which is attributed to the alcohol that has not been fully reacted in the system of 2h, so that residual ethanol continues to restore V₃O₇. The magnetic stirring accelerate the reaction rate at the moment. When the reaction time increased to 4h, the alcohol has reacted totally, and the magnetic stirring provide power to form the fibrous V₆O₁₃. Those are consistent with the result of the SEM analysis about Fig.3.

3.3 Electrochemical Properties
In order to study the electrochemical properties of fibrous $\text{V}_6\text{O}_{13}$, EIS was tested before and after cycling for 3 times as shown in Fig.5. It can be seen in Fig.5a that the samples of VO-0, VO-400 and VO-1200 in the high frequency region's semicircles correspond to the 1285Ω, 897Ω and 899Ω. That indicates sample of fiber-like can be better contact with the conductive materials in batteries. It is in favor of the voltage distribution of batteries thus diminish resistance during the process of lithium ion intercalating to the surface of the electrode. However, after cycling for 3 times as shown in Fig.5b that the charge transfer resistances in the high frequency region's semicircle are 576Ω, 241Ω and 544Ω. Those data corresponding to the samples of VO-0, VO-400 and VO-1200. However, the VO-1200 has better cycling performance than that of VO-400 as shown in Fig.6. It could be caused by the electrolyte was not completely saturated with sample VO-1200 during the first three cycles. Therefore, with the less active materials of VO-1200, the movement of electric charge is more difficult that means the moving resistance of the electric charge fluctuates greatly. But with the further progress of the cycle, the electrolyte fully saturated with sample VO-1200, the attenuation of capacity can be slowed down. Which indicated that the change of the fiber width of the sample has a close influence on the performance of the sample. It turned out that after cycling for 3 times the AC impedance is significantly less than those date without any circle. This is caused by the electrochemical drive improved the electrochemical activity in the process of charging and discharging thus opened the $\text{Li}^+$ path between anode and cathode materials in the process of extraction and insertion.

Fig.5 Electrochemical impedance spectra of the different samples before(a) and after 3 cycle(b)

Fig.6 The cycling performances of VO-0, VO-400 and VO-1200 at the current density of 0.5C

Fig.6 shows the charge-discharge curves of V-0, V-400 and VO-1200 at the current density of 210 mA/g (0.5C), the discharge specific capacities were 283mAh/g, 255 mAh/g and 245mAh/g after the first cycle. Those date corresponding to the samples of V-0, V-400 and VO-1200, respectively. The discharge specific capacities maintained 101mAh/g, 130 mAh/g and 144 mAh/g after 20 cycles, the capacity attrition rates were 64%, 49% and 41%, respectively. However, the discharge capacities were 72, 82 and 102mAh/g after cycling 50 times, and the attrition rates of the capacity were 76%, 67% and 58% compared with the first cycle. It indicated that the capacity attrition rate decreased greatly with
the stirring speed increasing in the process of synthesis $\text{V}_6\text{O}_{13}$. On the one hand, the fiber-like particles in the samples of VO-400 and VO-1200 had intertwined together to form the structure of three-dimensional network. On the other hand, which effectively reduced the destruction when lithium ion intercalation and extraction from the cathode material during the process of charging and discharging.

![Image](image_url)

**Fig.7** The cyclic voltammetry (CV) curve of the different samples after 3 cycles

Fig.7 displays the cyclic voltammetry curves of V-0, V-400 and VO-1200 with the voltage range of 1.5-3.5V at the scanning speed of 0.2mV/s after cycling for 3 times. Three oxidation peaks and three reduction peaks can be observed in the Fig.7, which represents the extraction and insertion of Li$^+$ during the electrochemical processes. The peaks of each sample are highly symmetric, indicating that the electrochemical properties of them are relatively stable. What's more, the sample of VO-400 have the highest peak among all the three samples, which indicates that more active materials can be recycled exist in the sample of VO-400. VO-400 has the highest capacity during the process of charging and discharging, which is consistent with the result of the cycling performance. In addition, a weak peak at 3.35V appears in the samples of VO-400 and VO-1200, which can be attributed to the stronger adsorption capacity of the fibrous $\text{V}_6\text{O}_{13}$.

**4 Conclusions**

In summary, fibrous $\text{V}_6\text{O}_{13}$ was synthesized by using $\text{V}_2\text{O}_5$ as raw material and the morphology was controlled by magnetic stirring in the oil bath. The samples were characterized by XRD, SEM and others. The result showed that the fibrous $\text{V}_6\text{O}_{13}$ had better dispersion, the electrochemical performance test demonstrated that the fibrous $\text{V}_6\text{O}_{13}$ showed low loss rate of the discharge capacity.

**Acknowledgements**

Supported by the National Natural Science Foundation of China (51562006).

**References**

[1] Doughty D, Roth E P. A general discussion of Li ion battery safety[J]. Electrochemical Society Interface, 2012, 21 (2): 37~44.

[2] Xu K. Nonaqueous liquid electrolytes for lithium-based rechargeable batteries[J]. Chemical Reviews. 2004, 104(10): 4303~4418.

[3] Song J Y, Wang Y Y, Wan C C. Review of gel-type polymer electrolytes for lithium-ion batteries[J]. Journal of Power Sources, 1999, 77 (2): 183~197.

[4] Etacheri V, Marom R, Elazari R, et al. Challenges in the development of advanced Li-ion batteries: a review[J]. Energy & Environmental Science, 2011, 4(9): 3243~3262.

[5] Tarascon J M, Armand M. Issues and challenges facing rechargeable lithium batteries[J]. Nature, 2001, 414 (6861): 359~367.
[6] Li X L, Chen X J, Chen X Y, et al. Hydrothermal synthesis and characterization of VO2 (B) nanorods array[J]. Journal of Crystal Growth, 2007, 309(1): 43–47.

[7] Dellinas C, Cognacclradou H, Cocciantelli J M, et al. The LixV2O5 system: an overview of the structure modifications induced by lithium intercalation[J]. Solid State Ionics, 1994, 69(3-4): 257–264.

[8] Wadsley A D. Crystal chemistry of non-stoichiometric pentavalent vanadium oxide: crystal structure of Li1+xV3O8[J]. Acta Crystallographica, 1957, 10(1): 261–267.

[9] BJÖRK H, Sven L, Gustafsson T, et al. Superlattice formation in the lithiated vanadium oxide phases Li0.67V6O13 and LiV6O13[J]. Acta Crystallographica Section B, 2001, B57(6): 759–765.

[10] Murphy D, Christian P, DiSalvo F, et al. Vanadium Oxide Cathode Materials for Secondary Lithium Cells[J]. Journal of The Electrochemical Society, 1979, 126:497-499.

[11] Howing J, Gustafsson T, Thomas J O. Low-temperature structure of V6O13[J]. Acta Crystallographica Section-Structural Science, 2003, 59(1): 747–752.

[12] Barker J, Koksbang R. The interfacial impedance variation of V6O13 composite electrodes during lithium insertion and extraction[J]. Electrochimica Acta, 1995, 40(6): 673–679.

[13] Murphy D W, Christian P A, DiSalvo F J, et al. Vanadium oxide cathode materials for secondary lithium cells[J]. Journal of The Electrochemical Society. 1979, 126(3): 497–499.

[14] Hua S N, Phang S. Optimization of the vanadium oxide (V6O13) electrode in nonaqueous secondary lithium cell[J]. Journal of Power Sources, 1983, 10(3):279–290.

[15] Soudan P, Pereira-Ramos J P, Farcy J, et al. Sol-gel chromium-vanadium mixed oxides as lithium insertion compounds[J]. Solid State Ionics, 2000, 135(1-4): 291–295.

[16] Leger C, Bach S, Pereira-Ramos J P. The sol-gel chromium-modified V6O13 as a cathodic material for lithium batteries[J]. Journal of Solid State Electrochemistry, 2006, 11(1): 71

[17] He J Y, Long F, Zou Z G. Hydrothermal synthesis and electrochemical performance of Mn-doped V6O13 as cathode material for lithium-ion battery[J]. Ionics, 2015, 21 (4): 995–1001.

[18] Broussely M, Jumel Y, Gabano J P. Lithium Batteries with Voltage Compatibility with Conventional Systems[J]. Journal of Power Sources, 1980, 5(1): 83–87.

[19] Zhan S Y, Wang C Z, Nikolowskik, et al. Electrochemical properties of Cr doped V2O5 between 3.8 V and 2.0 V[J]. Solid State Ionics, 2009, 180(20-22): 1198–1203.