

Soft Solution Processing of Lithium Vanadium Oxide Nanorods as Cathode Materials for Rechargeable Lithium Ion Batteries

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Lithium vanadium oxides including γ - LiV_2O_5 and LiV_3O_8 have been prepared by soft solution methods. γ - LiV_2O_5 nanorods with diameters of 30-40 nm have been prepared by a simple solvothermal method using ethanol as a solvent, which also serves as a reducing agent. The γ - $\text{LiV}_2\text{O}_5/\text{Li}$ cell demonstrated an initial specific capacity of 259 mAh/g and 199 mAh/g at the 20th cycle. Meanwhile, LiV_3O_8 nanorods with diameters of about 40 nm have been obtained by a novel hydrothermal-based two-step method. A specific capacity of 302 mAh/g was obtained in the range of 1.8 - 4.0 V in the second cycle and 282 mAh/g at the 20th cycle. It indicates that the lithium vanadium oxide nanorods prepared by the above methods have potentiality to be used as cathode material in rechargeable lithium ion batteries.

Key words: lithium vanadium oxides, nanorods, soft solution processing, rechargeable lithium ion batteries

1. INTRODUCTION

Worldwide research and development is in progress for rechargeable lithium ion batteries because of its wide application in portable electronic goods, electric vehicle systems and dispersed-type energy storage system. Much of this effort is focused on developing the cathode material for lithium ion batteries because the performance and cost of the batteries are often decided by the properties of the cathode material. In the last 20 years, vanadium oxides have been widely investigated as cathode materials in lithium ion batteries due to their low cost, low toxicity, high specific energy, and long cycle life. Lithium ion can react with V_2O_5 to form various compounds such as LiV_3O_8 [1-5], LiV_2O_5 (LiV_2O_5 has many modifications including α -, β -, ω -, γ - LiV_2O_5) [6-10], LiV_2O_4 [11], $\text{Li}_{0.6}\text{V}_{2.6}\text{O}_{4.8}$ [12] etc. Among them, γ - LiV_2O_5 and LiV_3O_8 were most intensively studied [1-10].

The preparation method has significant influences on the electrochemical behavior of γ - LiV_2O_5 and LiV_3O_8 ,

therefore a great deal of work has been done on their preparation to improve their electrochemical performance. In the case of γ - LiV_2O_5 , it is difficult to synthesize γ - LiV_2O_5 because there are two valence states (V^{5+} and V^{4+}) of vanadium co-existing in this compound. By conventional solid-state reaction or wet-chemistry method, the mixture of LiVO_3 , V_2O_5 , and VO_2 or V_2O_3 was heated at 350-600 °C under vacuum or N_2 protected atmosphere in order to control the valence balance of V^{4+} and V^{5+} [8-10]. Another synthetic method is a procedure described by Murphy et al. [7], in which V_2O_5 was reduced with appropriate amount of lithium iodide in acetonitrile under argon. The above methods are complicated and cost a deal. For the preparation of LiV_3O_8 , the conventional preparation method was high temperature melting in which LiV_3O_8 was produced by reaction between Li_2CO_3 and V_2O_5 at 680 °C [2, 4]. The product LiV_3O_8 prepared by this method had a low capacity of 180 mA h/g in the range of 1.8-4.0 V. Meanwhile, it is difficult to control the

composition, homogeneity and particle size of the final products. Many improved solution methods have also been proposed [2-5]. The solution method does not need a high reaction temperature, and the products could reach a high homogeneity and high capacity.

It is known that the electrochemical behavior of cathode materials strongly depends on the particle size: the smaller the particle size, the lower the cell polarization and the higher the cell capacity [8]. In this paper, soft solution methods including a solvothermal route and a modified hydrothermal-based method have been performed to prepare γ -LiV₂O₅ and LiV₃O₈ nanorods, respectively.

2. EXPERIMENTAL

For the preparation of γ -LiV₂O₅, LiOH and V₂O₅ were put into a 50 ml Teflon-lined autoclave. The autoclave was filled with ethanol (CH₃CH₂OH) up to 80% of the total volume. After the autoclave was kept at 160 °C under autogeneous pressure for 24 h, it was allowed to cool to room temperature naturally. The as-formed solid precipitate was filtered, washed with ethanol, and dried at 100 °C for 2 h.

For the preparation of LiV₃O₈, LiOH, V₂O₅ (Li : V = 1 : 3, molar ratio), and NH₄OH were dissolved in the deionized water. The pH of the resultant dark green solution was 9. The solution was then transferred to a 50 ml Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 160 °C under auto-generated pressure for 12 h. After hydrothermal treatment, a colorless clear solution whose pH changed to 7 was obtained. This solution was dried in air at 100 °C to evaporate the water till an orange gel was prepared. The gel was then heat-treated at 300 °C for 12 h to give the final product.

The structure of the products was examined by X-ray diffractometry (XRD, Japan Rigaku D/Max-3C) using CuK α radiation ($\lambda = 1.5405 \text{ \AA}$). The morphology was investigated by transmission electron microscopy (TEM, Model Hitachi H-700H, 200 KV).

Electrochemical characterization of the products was performed in cells with metallic lithium as the negative electrode and a liquid organic electrolyte [LiPF₆ in a volume ratio of 50:50 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC), absorbed in porous polypropylene separators, Celgard 2400]. The cathode was a mixture of the active material, acetylene black and polytetrafluoroethylene (PTFE) in a weight ratio of 80:10:10. The cells were assembled in an argon-filled

dry box. Charge-discharge tests were carried out at a constant current density of 0.3 mA / cm² in a range of 1.8-4.0 V. All the tests were performed at room temperature.

3. RESULTS

Figure 1 shows the XRD pattern of the solvothermally prepared γ -LiV₂O₅. All the diffraction peaks are identical to those of orthorhombic γ -LiV₂O₅ according to JCPDS card 18-756. No impurity phases such as V₂O₅, Li₃VO₄ and LiVO₂ are detected in the product from its XRD pattern. In our experiment, the synthesis of γ -LiV₂O₅ is carried out using a great excess of ethanol as a solvent through a solvothermal process. A portion of the is oxidized by V₂O₅ to form aldehyde, which is experimentally confirmed through chemical analysis of the final solution mixture. From the above results, it can be seen that the ethanol acts not only as a solvent but also as a reducing agent in the synthesis of γ -LiV₂O₅ powders. Thus, the formation mechanism of γ -LiV₂O₅ through the reaction of LiOH, V₂O₅ and excess ethanol under the solvothermal condition can be expressed as the following:

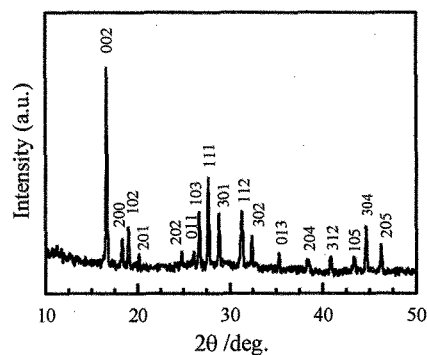
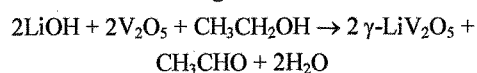


Fig.1 XRD pattern of γ -LiV₂O₅

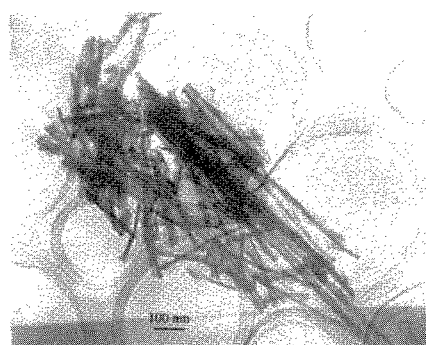


Fig.2 TEM image of γ -LiV₂O₅

A typical TEM image of the γ -LiV₂O₅ is shown in Figure 2. It clearly shows that γ -LiV₂O₅ particles have a rod-like morphology with diameters of 30-40 nm and lengths of 0.4-2 μ m.

Figure 3 shows the XPS spectra of the starting material V₂O₅ and the as-synthesized γ -LiV₂O₅. It is obvious that the binding energy of V 2p for the as-synthesized γ -LiV₂O₅ is lower than that for the starting material V₂O₅. The binding energy of V 2p_{3/2} for the starting material V₂O₅ is 517.5 eV, which agrees with the literature value of V₂O₅ [13]. The binding energy of V 2p_{3/2} for the as-synthesized γ -LiV₂O₅ is 516.7 eV, which is between those of V 2p_{3/2} for V₂O₅ and VO₂ (516.3 eV [13]). The average valence of vanadium in V₂O₅, γ -LiV₂O₅ and VO₂ is +5, +4.5 and +4, respectively.

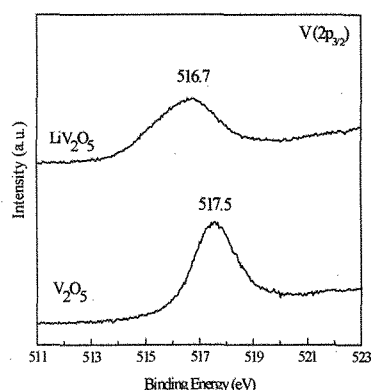


Fig.3 XPS spectra image of V₂O₅ and γ -LiV₂O₅

The charge-discharge curves of the cell with γ -LiV₂O₅ during the first cycle are illustrated in Figure 4. It can be seen that the specific discharge capacity of the cell attains 259 mAh/g in the range of 1.5-4.2 V. The capacity at the end of 2.4-2.3 V voltage plateau is 157 mAh/g.

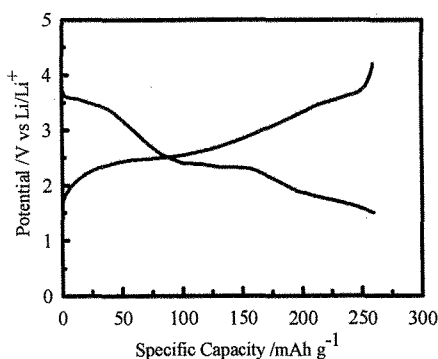


Fig.4 Charge/discharge curves of γ -LiV₂O₅.

Figure 5 shows the cycle performance of the cell. In the first 5 cycles, the specific capacity reduces quickly and then maintains stable in the subsequent cycles. The specific capacity is 199 mAh/g after 20 cycles. It indicates that the γ -LiV₂O₅ nanorods prepared by this solvothermal method have potentiality to be used as a cathode material in rechargeable lithium batteries.

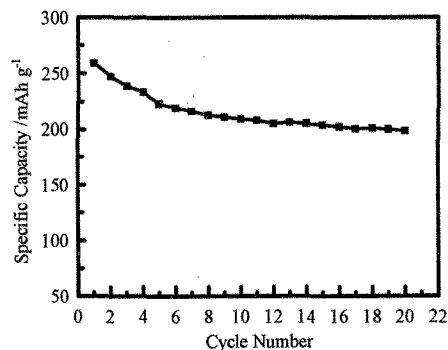


Fig.5 Cycle performance of γ -LiV₂O₅.

Figure 6 shows the XRD pattern of the LiV₃O₈ product heated at 300 °C. In the XRD pattern of all the reflections, to within experimental error, can be indexed to the monoclinic LiV₃O₈ with lattice constants a=6.68 Å, b=3.60 Å, and c=12.03 Å (JCPDS card 18-754).

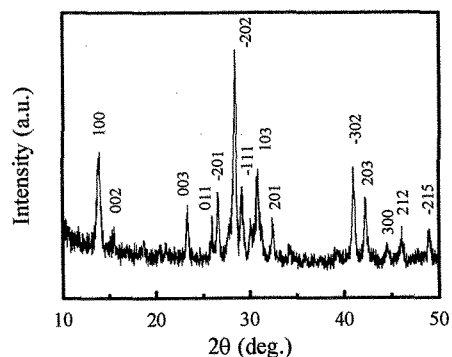


Fig.6 XRD pattern of LiV₃O₈

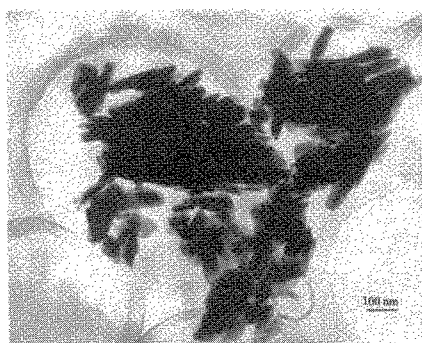


Fig.7 TEM image of LiV₃O₈

Figure 7 shows the TEM image of the as-prepared LiV_3O_8 . It can be seen that the LiV_3O_8 crystallites appear to display rod-like morphology with diameters of 30-40 nm and lengths of 300-500 nm.

The charge-discharge curves at the second cycle of cell from LiV_3O_8 are illustrated in Figure 8. It is found that the specific capacities of the sample is 302 mAh/g in the range of 1.8 - 4.0 V, which is considerably higher than the capacities of 220 ~ 274 mAh/g of LiV_3O_8 synthesized by other solution methods [3-7].

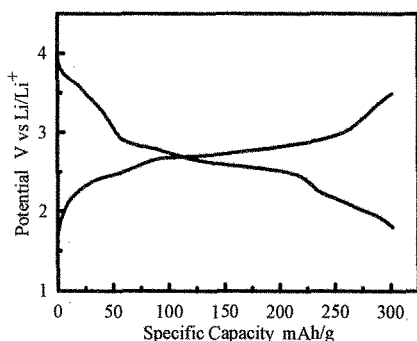


Fig.8 Charge/discharge curves of LiV_3O_8

In Figure 9, the discharge capacities are shown as a function of cycle number. It can be seen that the samples synthesized via this hydrothermal-based method show better capacity retention. The capacity is 282 mA h/g after 20 cycles.

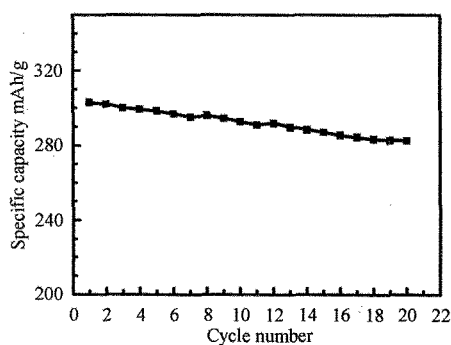


Fig.9 Cycle performance of LiV_3O_8

4. CONCLUSION

In this paper, a simple and low-cost solvothermal method has been developed to synthesize $\gamma\text{-LiV}_2\text{O}_5$ nanorods by using ethanol as a solvent as well as a reducing agent. Preliminary electrochemical tests indicated that the $\gamma\text{-LiV}_2\text{O}_5/\text{Li}$ cell has an initial specific capacity of 259 mAh/g in the range of 1.5-4.2 V. Meanwhile, LiV_3O_8 nanorods with diameters of about 40 nm have been obtained by a novel two-step method which was based on the hydrothermal reaction. The

as-prepared LiV_3O_8 nanorods showed a good charge-discharge and cycle performance. A specific capacity of 302 mAh/g was obtained in the range of 1.8 - 4.0 V in the second cycle and 282 mAh/g in the 20th cycle. It indicates that the lithium vanadium oxide nanorods prepared by the above methods have potentiality to be used as cathode material in rechargeable lithium batteries.

References

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