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Novel chemical method for synthesis of LiV_3O_8 nanorods as cathode materials for lithium ion batteries

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Abstract

A novel method which is based on the hydrothermal reaction was employed to synthesize LiV_3O_8 . First, the mixture solution of LiOH , V_2O_5 , and NH_4OH was subjected to the hydrothermal reaction. The hydrothermal treatment yielded a clear, homogeneous solution. The evaporation of this solution led to the formation of a precursor gel. The gel was then heated at different temperatures in the range of 300–600 °C. The characterization by X-ray diffraction (XRD), transmission electron microscopy (TEM), and Fourier transform infrared (FTIR) indicated that LiV_3O_8 nanorods have been obtained by this novel synthesis method. The electrochemical performance of the LiV_3O_8 nanorods have been investigated, which indicates that the highest discharge specific capacity of 302 mAh/g in the range of 1.8–4.0 V was obtained for the sample heated at 300 °C, and its capacity remained 278 mAh/g after 30 cycles.

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1. Introduction

Lithium vanadium oxides have been extensively studied because of their possible application as a cathode material for rechargeable lithium batteries. Due to their low cost, they are one of the promising substitutes for the expensive LiCoO_2 cathode presently commercially used. LiV_3O_8 , as a species of the lithiated vanadate family, has very attractive characteristics such as high specific energy, good rate capacity, and long cycle life. It is well known that the preparation methods and post-treatments have significant influences on the electrochemical properties of LiV_3O_8 . The conventional 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 [1,2]. This method has met difficulty to control the composition and homogeneity of the final products. Meanwhile,

the product LiV_3O_8 had a low capacity of 180 mAh/g in the range of 1.8–4.0 V. Afterwards, many improved solution methods were proposed [3–7]. The solution method does not need a high reaction temperature, and the products could reach a high homogeneity and high capacity.

As one of the solution methods, hydrothermal method has been extensively used for the synthesis of inorganic compounds. Chirayil et al. had obtained a new layered lithium vanadium oxide $\text{Li}_x\text{V}_{2-\delta}\text{O}_{4-\delta}\cdot\text{H}_2\text{O}$ via hydrothermal method using tetra-methyl ammonium as template [8]. Oka et al. had prepared AV_3O_8 ($A = \text{K}, \text{Rb}, \text{and Cs}$) by the hydrothermal method from V_2O_5 powders dispersed in $\text{A}(\text{NO}_3)_3$ solutions at 250 °C. The results showed that the structure of RbV_3O_8 was found to be isostructural with KV_3O_8 and CsV_3O_8 [9,10]. However, attempts to make LiV_3O_8 and NaV_3O_8 hydrothermally were unsuccessful.

Some reports have also noticed the importance of crystallinity on the electrochemical properties of LiV_3O_8 . It was shown that the poorly crystallized LiV_3O_8 or LiV_3O_8 modified by ultrasonic treatment or hydrothermal introduction

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of small amounts of inorganic compounds such as H_2O , CO_2 and NH_3 achieved an improved electrochemical performance [11,12]. However, to our best knowledge, there is no report on the synthesis of nano scale LiV_3O_8 so far. It is known that the electrochemical behavior of cathode materials strongly depends on the particle size: the bigger the particle size, the higher the cell polarization and the lower the cell capacity [13]. In the present paper, LiV_3O_8 nanorods have been prepared by a novel method which is based on the hydrothermal reaction, the experimental procedure and results are described further.

2. Experimental

2.1. Synthesis and characterization of LiV_3O_8

The starting materials were analytically pure LiOH , V_2O_5 and $\text{NH}_3\cdot\text{H}_2\text{O}$ (1 mol/l). First, stoichiometric LiOH and V_2O_5 ($\text{Li}:\text{V} = 1:3$, molar ratio) were blended in the deionized water. LiOH was dissolved completely and part of V_2O_5 was dissolved. When $\text{NH}_3\cdot\text{H}_2\text{O}$ was added to the above mixture, V_2O_5 was dissolved completely into solution. The pH of the solution was 9. The resultant dark green solution was then transferred to a 50 ml Teflon lined 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 seven 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 different temperatures in the range of $300\text{--}600^\circ\text{C}$ for 12 h.

The gel was characterized by thermo-gravimetric analysis (TGA) using a Model STA 449C (Germany, NETZSCH-Gerätebau GmbH Thermal Analysis). The structure of the heat-treated products was examined by X-ray diffractometry (XRD, Japan Rigaku D/Max-3C) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$). The morphology was investigated by transmission electron microscopy (TEM, Model Hitachi H-700H, 200 kV). Fourier transform infrared (FTIR) absorption spectra were obtained by using a Nicolet Magna-IR 560 spectroscopy.

2.2. Electrochemical measurements

Electrochemical characterization of the products was performed in cells with metallic lithium as the negative electrode and a liquid organic electrolyte [LiPF_6 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 poly (tetrafluoroethylene) (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/cm^2 in a range of 1.8–4.0 V. All the tests were performed at room temperature.

3. Results and discussion

3.1. TGA results

The TGA result of the precursor gel which was derived by hydrothermal reaction and subsequent evaporation of water is illustrated in Fig. 1. It can be seen that in the range of $140\text{--}320^\circ\text{C}$, the weight loss is about 15%. Above 320°C , the weight remains stable up to 600°C . The weight loss process can be divided into two stages. The first weight loss begins at 140°C and ends at 230°C with a weight loss of 13%, which mainly resulted from the evaporation of NH_3 and water. The second weight loss occurred in the range of $250\text{--}320^\circ\text{C}$ with a weight loss of 2%, which was caused by the de-intercalation of some strongly-bound water.

3.2. The XRD and the structure of LiV_3O_8

Fig. 2 shows the XRD patterns of the products heated at 300 , 350 , 400 and 600°C . These XRD patterns reflect the structural variation during the treatment process. With an increase in heat temperature the intensity of peaks becomes stronger and the full width of half maximum intensity (FWHM) decreases, which indicates that the crystallinity becomes higher. In addition, it is noted that there is an obvious difference among the four XRD patterns. The relative intensity of (1 0 0) peaks at around 13.86° becomes stronger with increasing heat temperature. In the 600°C diffraction pattern, the intensity of (1 0 0) peak is stronger than any other peaks. While in the 300°C diffraction pattern, the relative intensity of (1 0 0) peak has much decreased. It suggests that the particle shape of LiV_3O_8 depends on the heat temperature, and higher heat temperature favors the preferential ordering of crystallites. It is known that the intercalation process of Li^+ ion between the layers of the cathode is a diffusion process. Therefore the preferential ordering which

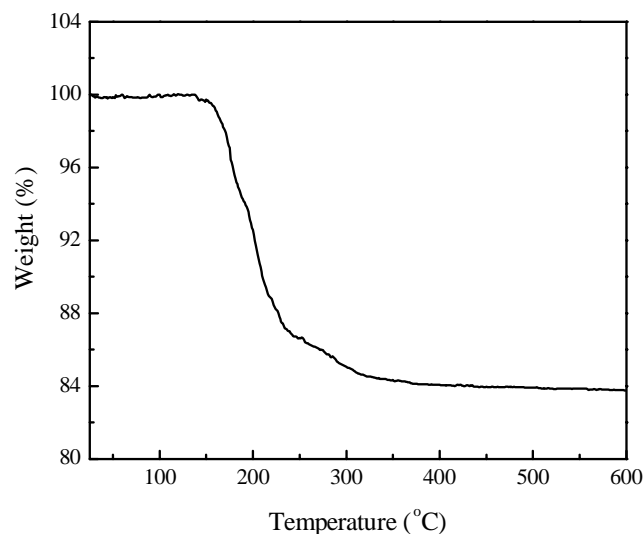


Fig. 1. TGA curve of the precursor gel.

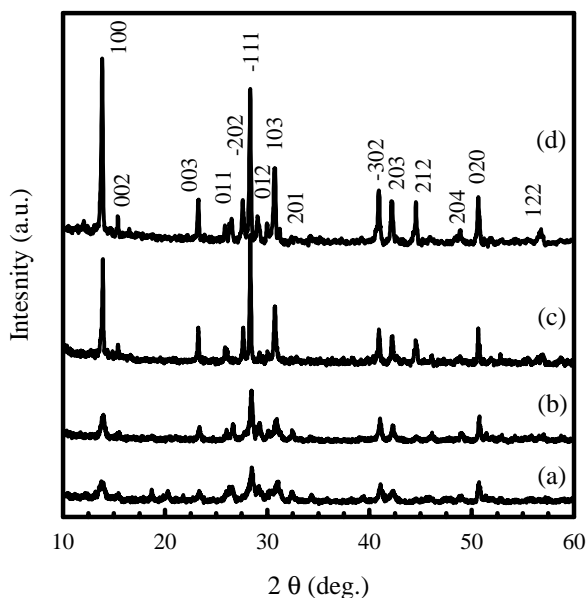


Fig. 2. The XRD patterns of the samples heat-treated at: (a) 300; (b) 350; (c) 400; (d) 600 °C.

would lead to a long path for Li^+ ion is not advantageous to intercalation [7].

3.3. The morphology of the synthesized LiV_3O_8

The TEM micrographs of the synthesized LiV_3O_8 , at different heat temperatures, are demonstrated in Fig. 3. It can be seen that the heat treatment has caused a change in the LiV_3O_8 crystallinity and morphology. The sample treated at 300 °C (Fig. 3a) consists of an agglomeration of small rods. The shapes of the rods are not well recognized, indicating they are relatively poorly crystallized. The diameters of the rods are about 40 nm and the lengths are mostly less than 600 nm. Fig. 3b is the micrograph of the sample treated at 350 °C. Comparing to the 300 °C sample, the 350 °C sample is well rod-shaped. The diameters of the rods are about 70 nm while the lengths are diverse in the 0.5–2 μm range. The 400 °C sample which is shown in Fig. 3c consists of wider (>150 nm) and longer rods. The sizes of the particles treated at 600 °C are much larger than that of the 400 °C sample, the micrograph of which is not shown here. These

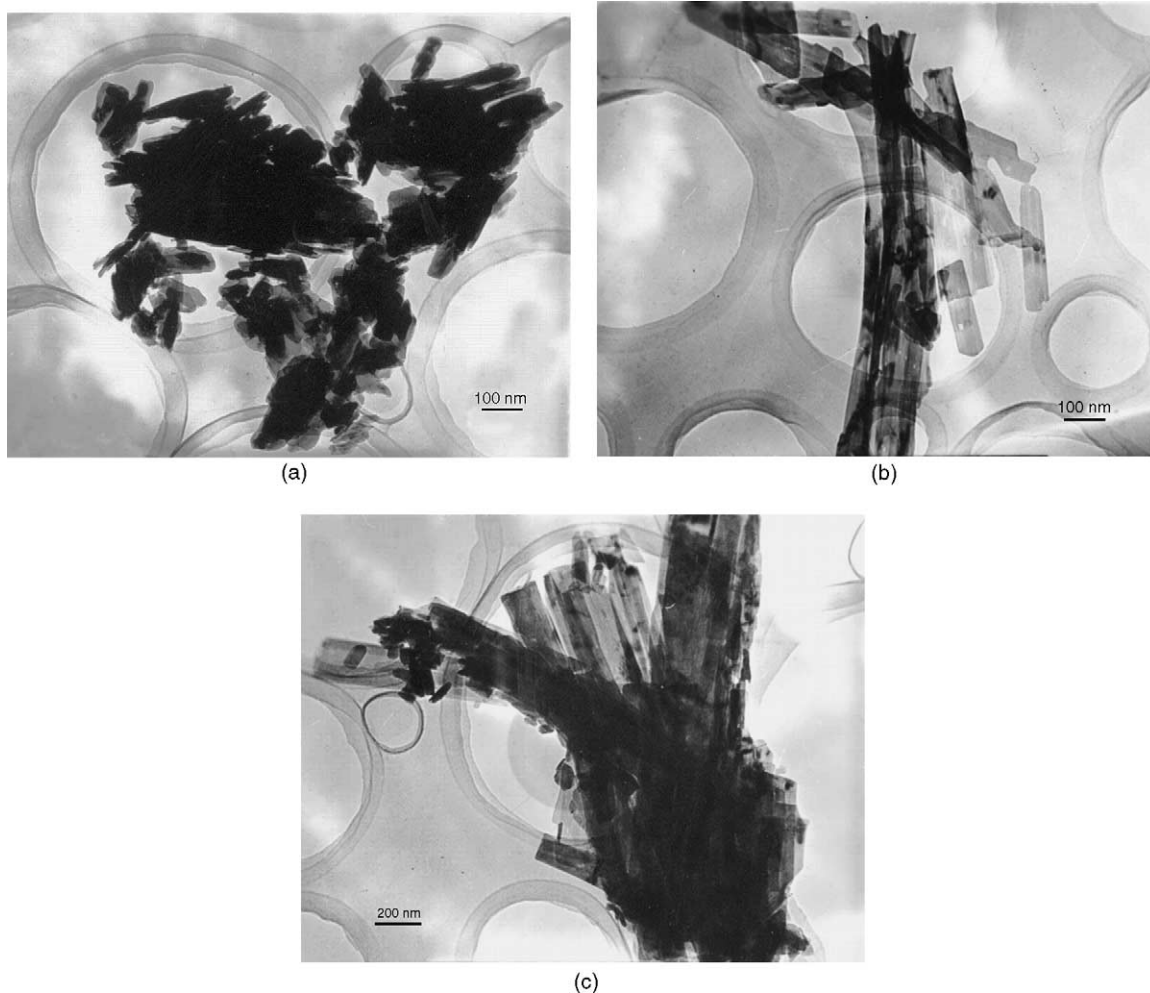


Fig. 3. TEM micrographs of the samples heat-treated at: (a) 300; (b) 350; (c) 400 °C.

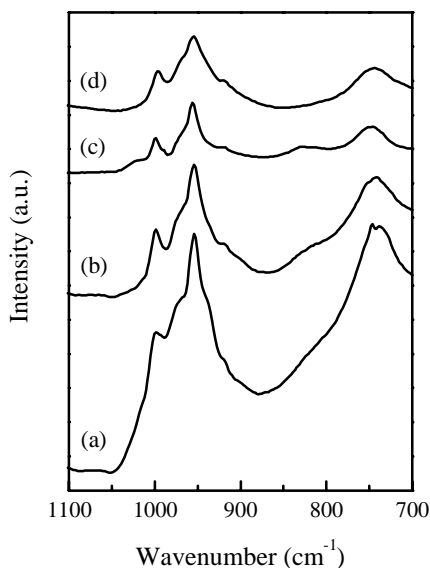


Fig. 4. The FTIR spectra of the samples heat-treated at: (a) 300; (b) 350; (c) 400; (d) 600 °C.

results are in agreement with the XRD data. With the increase in temperature, the particles of the products become larger and more crystallized.

3.4. FTIR of the synthesized LiV_3O_8

FTIR spectra of LiV_3O_8 obtained at different heat temperatures are shown in Fig. 4. For the four curves, it can be seen that the FTIR absorption in the spectral region of $700\text{--}1100\text{ cm}^{-1}$ is dominated by bands at 995, 954 and 744 cm^{-1} , respectively. This data is compared with LiV_3O_8 synthesized from solid state reactions, where major FTIR bands corresponding to $\text{V}=\text{O}$ and $\text{V}-\text{O}-\text{V}$ vibrations are located at 996, 954 and 746 cm^{-1} , respectively [14]. The sample treated at 300 °C gives the same FTIR responses as that of crystalline LiV_3O_8 , suggesting that it is almost iso-structural with the latter.

3.5. Electrochemical properties of the synthesized LiV_3O_8

The charge–discharge curves at the second cycle of cells from products heat-treated at 300, 350, 400, 600 °C, respectively, are illustrated in Fig. 5. It is found that the specific capacities of the samples decrease with increasing the heat temperature. The discharge capacity for the 300 °C sample is 302 mAh/g in the range of 1.8–4.0 V, which is much higher than that of 600 °C sample (190 mAh/g). Notably, the value of 302 mAh/g is considerably higher than the capacities of 220–274 mAh/g of LiV_3O_8 synthesized by other solution methods [3–7], and exceeds the capacity of about 280 mAh/g of hydrothermally and ultrasonically treated LiV_3O_8 [11,12]. From the XRD data we have known that the sample treated at higher temperature has higher crys-

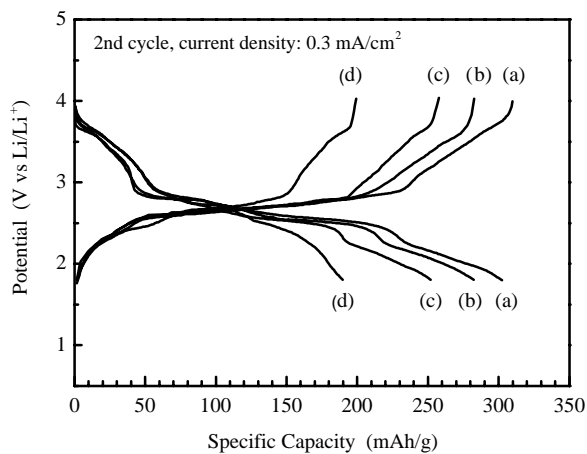


Fig. 5. Charge–discharge curves of the samples heat-treated at: (a) 300; (b) 350; (c) 400; (d) 600 °C. Current density: 0.3 mA/cm^2 .

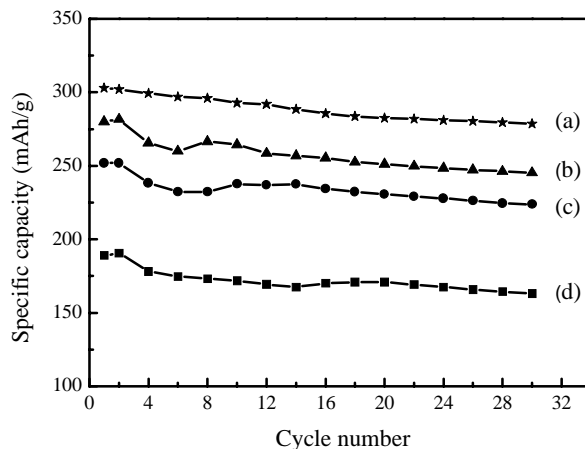


Fig. 6. The cycle performance of the cells with LiV_3O_8 heat-treated at: (a) 300; (b) 350; (c) 400; (d) 600 °C as cathode active material. Current density: 0.3 mA/cm^2 . Voltage window: 1.8–4.0 V.

tallinity. The above results also suggest that the well crystallized sample does have poor specific capacity, which is in agreement with the previous studies [3–7,11,12].

In Fig. 6, the discharge capacities are shown as a function of cycle number. It can be seen that the samples synthesized via this novel method show better capacity retention. The capacity of the 300 °C samples is 278 mAh/g after 30 cycles. Meanwhile, the 300 °C sample shows better cycling behavior compared with the samples treated at higher temperature.

4. Conclusion

In this study, a novel method which is based on the hydrothermal reaction has been performed to synthesize LiV_3O_8 nanorods. This hydrothermal reaction did not directly yield a solid product. A gel which was used as the precursor for the post heat treatment was obtained after evaporation of the hydrothermal treated solution. The gel was homogeneous and ultrafine, which should be the rea-

son why the LiV_3O_8 nanorods could be obtained in this study. Heat treatment at different temperatures influenced the particle size and crystallinity of the products, which consequently affected their electrochemical performance. The sample treated at 600°C shows a good crystallinity and a low discharge capacity. In contrast, the sample treated at 300°C shows a poorer crystallinity while a better capacity of 302 mAh/g in the range of $1.8\text{--}4.0\text{ V}$, and its capacity remained 278 mAh/g after 30 cycles.

Acknowledgements

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