

Citric acid complex method of preparing inverse spinel LiNiVO_4 cathode material for lithium batteries

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Abstract

A new kind of citric acid complex method has been developed in this study for synthesizing inverse spinel LiNiVO_4 powder which can be used as the cathode active materials for lithium ion batteries with a very high voltage (4.8 V versus Li). Li_2CO_3 , NiCO_3 and NH_4VO_3 were used as raw materials, and citric acid was used as a complex agent. Fine LiNiVO_4 powders with particle size 0.5 μm or less were successfully prepared at 500 °C in 1 h. Compared to the conventional solid state reaction methods, the citric acid complex method greatly reduced the temperature and the time for preparing pure LiNiVO_4 . The resulting LiNiVO_4 powders were also characterized by TGA, XRD, SEM, IR and ICP techniques. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cathode material; Citric acid complex method; Inverse spinel LiNiVO_4

1. Introduction

Recent rapid advance in lithium ion secondary batteries has triggered intensive research on lithium-incorporated cathode materials for improving the energy, life cycle, and safety of the batteries. Among the cathode active materials, lithium–nickel orthovanadate, LiNiVO_4 , is an interesting intercalation compound, because it displays a high voltage of 4.8 V and is the first cathode material with an inverse structure that has been proposed for Li and Li-ion battery applications [1]. In the structure of inverse spinel LiNiVO_4 , the Li and Ni atoms are thought to occupy the octahedrally coordinated interstices equally and randomly and the V atoms are thought to occupy the tetrahedrally coordinated interstices [2]. Thus, compared to normal spinel LiMn_2O_4 , the Li and Ni atoms in LiNiVO_4 take the place of the two Mn atoms and the V atoms take the place of the Li atoms. The mixed degree of the cations in the inverse spinel LiNiVO_4 is up to 100% so that it exhibits a very high voltage (versus Li) [2]. The use of high voltage cathode materials is one way to achieve high energy. Therefore, this material offers a great promise for increasing the energy density of the batteries.

LiNiVO_4 is a potential cathode material for lithium ion secondary batteries, but it is difficult to synthesize by conventional solid-state reactions. Bernier et al. [3] prepared

LiNiVO_4 using LiVO_3 and NiCO_3 as raw materials with a reaction temperature of 500 °C for 7 days. Instead of NiCO_3 , Ito [4] used NiO as one raw material and prepared LiNiVO_4 at 1000 °C for 4 days. Fey and Perng [5] prepared LiNiVO_4 by reacting LiNiO_2 with V_2O_5 or V_2O_3 at 400 °C for 4 h and then at 800 °C for 8 h. Lu et al. [6] developed a new method for preparing LiNiVO_4 using LiOH , V_2O_5 and $\text{Ni}(\text{CH}_3\text{COO})_2$ as precursors at 700 °C for 2 h. The above processes, despite being successful in preparing LiNiVO_4 , are not economical because of the large amount of energy consumed and the long reaction time required.

In order to reduce the reaction temperature and the time for preparing pure LiNiVO_4 powder, the citric acid complex method for synthesizing inverse spinel LiNiVO_4 powder was adopted in this study. The synthesized conditions for LiNiVO_4 were investigated and the resulting LiNiVO_4 powders were further characterized by TGA, XRD, FT-IR and SEM. The effects of the temperature and the time during the processes on the purity and the grain size of LiNiVO_4 are also discussed in this paper.

2. Experimental

Li_2CO_3 (AR, 99%), NiCO_3 (AR, 99%) and NH_4VO_3 (AR, 99%) were added in molar ratio 0.5:1:1 (the molar ratio of Li:Ni:V = 1:1:1) to an appropriate amount of distilled water sequentially under magnetic stirring at temperature 80 °C. A citric acid solution was slowly added to the mixed dispersive

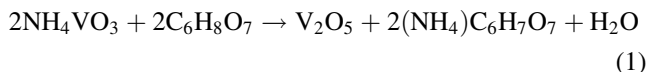
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solution. Gas evolution occurred in this process. A blue-green clear solution formed when gas evolution stopped. A loose powder of dry gel precursor was obtained by concentrating the solution at 80 °C and then complete dehydration in vacuum at 120 °C. The final product LiNiVO_4 powder was obtained by sintering the precursor at 500 °C for 1 h in the air.

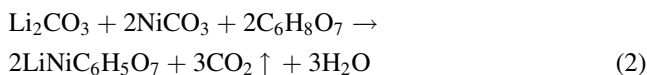
Thermal analyses of the product were performed using a Perkin-Elmer TGA-7 analyzer on sample weights of about 5 mg and with a heating rate of 10.0 °C/min in an oxygen atmosphere. Powder XRD measurements were made with a D/max-3C diffractometer using a diffracted beam monochromator and Cu $K\alpha$ radiation. SEM characterization of the sample was carried out on a scanning electron microscope Hitachi, S-570. IR absorption spectra of the samples were obtained using an EQUINOX-55 Fourier transform infrared spectrometer (KBr pellet). The chemical compositions of products were analyzed by a Jarrel-Ash ICPA-9000 inductively coupled plasma atomic emission spectrophotometry.

3. Results and discussion

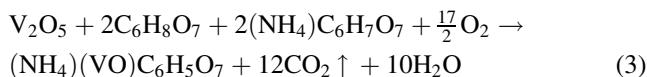
When $\text{C}_6\text{H}_8\text{O}_7$ was added to the mixture solution, V_2O_5 first formed when NH_4VO_3 reacted with $\text{C}_6\text{H}_8\text{O}_7$:



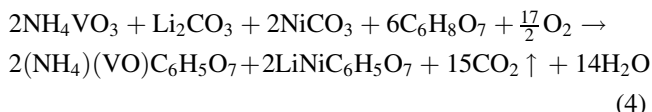
The vigorous gas evolution in the process was resulted from the reaction of Li_2CO_3 and NiCO_3 with $\text{C}_6\text{H}_8\text{O}_7$, in which CO_2 gas and $\text{LiNiC}_6\text{H}_5\text{O}_7$ were produced:



In acidic solution, V_2O_5 is an oxidant, which could partially oxidize $\text{C}_6\text{H}_8\text{O}_7$. V(V) in V_2O_5 was, thus, reduced to V(IV) forming $(\text{VO})^{2+}$ ions with gas evolution. Then $(\text{VO})^{2+}$ ion reacted with $(\text{NH}_4)\text{C}_6\text{H}_7\text{O}_7$ producing $(\text{VO})(\text{NH}_4)\text{C}_6\text{H}_5\text{O}_7$:



It can be seen from the Eqs. (1)–(3) that the total reaction equation is as follows:



The total reaction in Eq. (4) indicated that the dried gel precursor might be composed of $\text{LiNiVO}_4 \cdot (\text{VO})(\text{NH}_4)\text{C}_6\text{H}_5\text{O}_7$, which can be explained by the analysis of thermal decomposition process of the precursor.

Fig. 1 shows the TG and DTG curves of the dried gel precursor. It revealed that before 250 °C, there was a weight loss 3.6%, apparently due to the evaporation of the residual

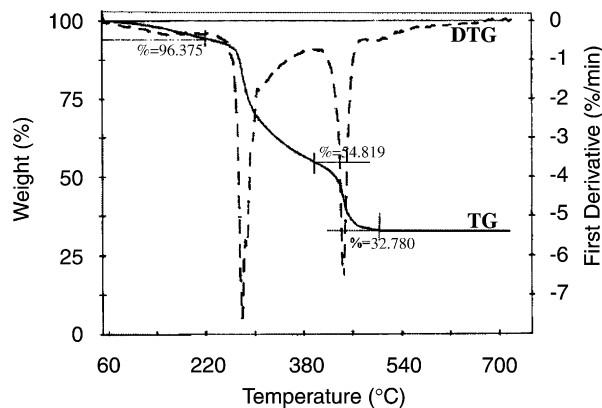
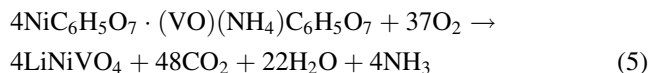


Fig. 1. TG and DTG curves of the precursor.

water. The decomposition process mainly occurred at the temperature range from 250 to 500 °C. This reaction was associated with a weight loss 63.6%, which was attributed to the complex decomposition process of lithium, vanadium and nickel citrates. The weight loss of the specimens stopped at temperatures above 500 °C. The total weight loss of the decomposition process, 63.6%, was comparable to the calculated value of 65.9% based on the proposed total decomposition equation in air atmosphere:



To realize the formation of LiNiVO_4 , the precursor was heated at different temperatures for different times, then cooled in the furnace to room temperature. The products were analyzed by XRD. The XRD patterns of the samples obtained at different temperatures for 1 h are presented in Fig. 2. It can be seen from Fig. 2 that the sample obtained at 450 °C is a mixture phase of LiNiVO_4 (main phase) and NiO (miscellaneous phase) (Fig. 2a). When the heating temperature was 500 °C, the diffraction peaks of NiO completely disappeared (Fig. 2b). The XRD patterns of the samples obtained at above 500 °C exhibit the characteristic diffraction lines of LiNiVO_4 without any miscellaneous phase,

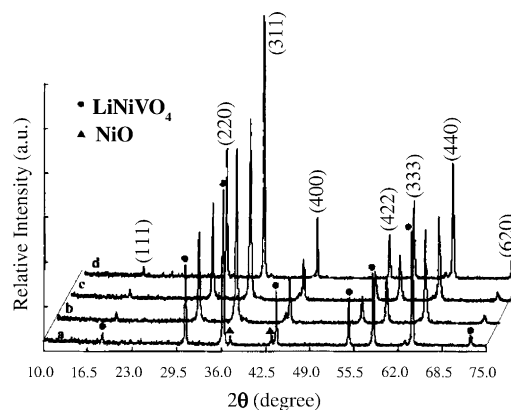


Fig. 2. XRD patterns of the products obtained at different temperatures (°C): (a) 450; (b) 500; (c) 600; (d) 720 for 1 h, respectively.

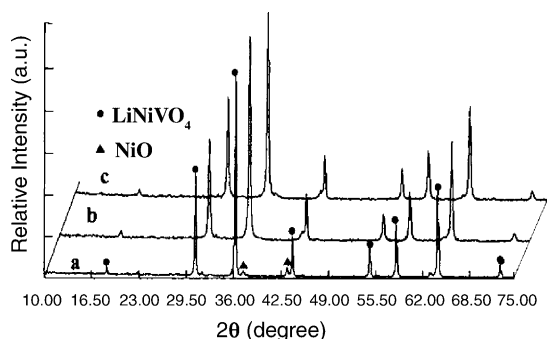


Fig. 3. XRD patterns of the products obtained at 500 °C for different time (h): (a) 0.5; (b) 1; (c) 2, respectively.

which completely match that of the inverse spinel structure listed in JCPDS file no. 38-1395 [7], confirming that a pure compound of LiNiVO₄ formed. In order to investigate the influence of the decomposition time on the purity of LiNiVO₄, the precursor was heated at 500 °C for 0.5, 1 and 2 h, cooled to room temperature, and then analyzed by XRD, respectively. The XRD patterns are given in Fig. 3. The analysis results indicated that the diffraction peaks of NiO appeared for the sample obtained at 500 °C for 0.5 h. The pure compound of LiNiVO₄ can be obtained only at 500 °C or above and for 1 h or more. The results demonstrated that LiNiVO₄ was successfully prepared at a temperature as low as 500 °C for only 1 h by thermal decomposition of the precursor. In contrast, a temperature above 700 °C and a treatment time longer than 2 h were usually necessary to obtain desired crystalline LiNiVO₄ powder by conventional solid-state reaction processes.

In addition, from the XRD patterns of Figs. 2 and 3, it also can be seen that the relative intensities of the diffraction lines increased and the width of the diffraction lines decreased with the temperature being raised and the time being prolonged, which indicated that the crystallines tended to improve and the grain sizes increased for the particles.

The IR spectra of the samples prepared at 500 °C for 0.5, 1 and 2 h are shown in Fig. 4. In the absorption spectra of the sample obtained at 500 °C for 0.5 h (Fig. 4a), the band at

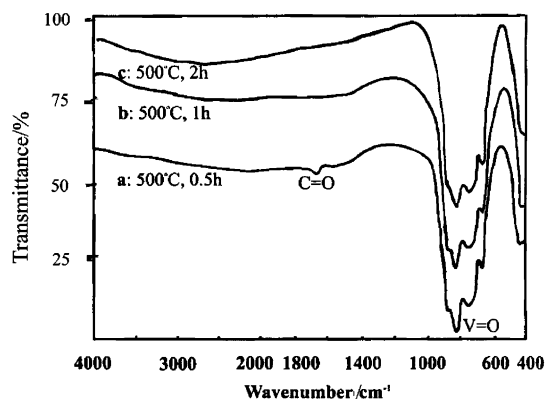


Fig. 4. IR spectra of the products prepared at 500 °C for different time.

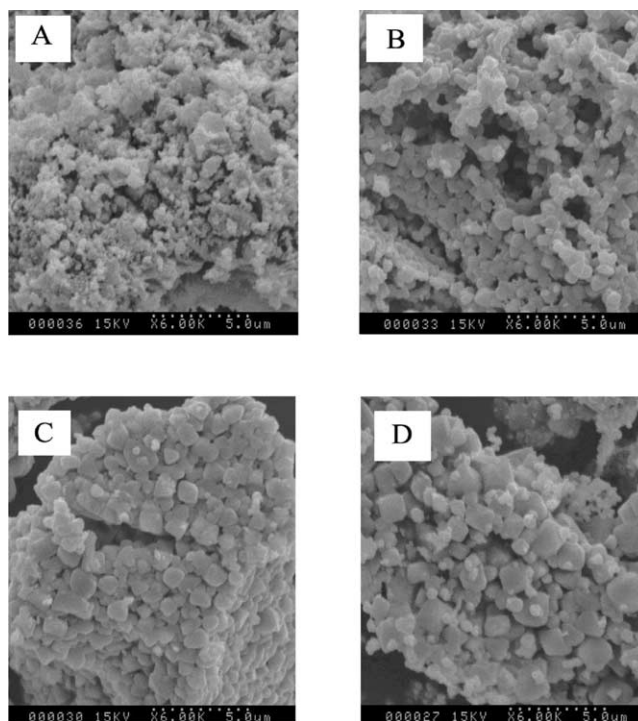


Fig. 5. SEM micrographs of LiNiVO₄ powder prepared at different temperatures and time: (a) 500 °C for 1 h; (b) 600 °C for 1 h; (c) 720 °C for 1 h; (d) 500 °C for 2 h.

around 1600 cm⁻¹ suggests the presence of a carbonyl group [8]. The bands at 900–600 cm⁻¹ are associated with the stretching vibrations of V–O bonds of VO₄ tetrahedra in LiNiVO₄ [9]. It suggested that there were a little residual citrates in the product. As the calcination time increases, the absorption of the carbonyl group disappears, and only the V–O bonds exist in the sample (Fig. 4b and c). This indicates that the citrates were completely decomposition and the pure LiNiVO₄ was formed at 500 °C for 1 h or more. The element analysis of the product obtained at 500 °C for 1 h was Li_{0.985}Ni_{0.987}VO₄ (the molar ratio of Li:Ni:V is 0.985:0.987:1) by ICP, which indicated that the proportion of the cations in the product was very close to that expected compound LiNiVO₄. This revealed that the amount of cations did not change during the processes of reaction and calcinations. These results are consistent with the XRD results. Fig. 5 displays a series of typical SEM micrographs of LiNiVO₄ samples prepared at various temperatures and times. It can be seen from Fig. 5 that the particles of LiNiVO₄ powder obtained at 500 °C for 1 h showed a fluffy morphology, mainly resulting from the incoherent aggregation of smaller particles having diameters of 0.5 μm or less (Fig. 5a). With the increasing of the temperature or the expanding of the time, the outlines of particles became clearly discernible, the clusters of particles separated each other, and its crystalline grains grew up. The grain-size of partial particles was larger than 1 μm when heated at 500 °C for 2 h (Fig. 5c) or at 720 °C for 1 h (Fig. 5d). The product with smaller particles has relatively larger specific surface,

which is more favorable for Li-ion diffusion as the cathode materials.

4. Conclusions

The inverse spinel LiNiVO_4 powders which can be used as the cathode materials with a very high voltage for lithium ion battery was successfully prepared by the citric acid complex method. The results of experimental indicated that the fine LiNiVO_4 powders with submicrometre-sized particles and perfect inverse spinel crystal structure can be obtained by thermal decomposition of the precursor at 500°C for 1 h in the air. Comparing with the traditional solid-state reaction methods for preparing LiNiVO_4 , the temperature was reduced from above 700 to 500°C and time was shortened from days or 10 to 1 h. The expected LiNiVO_4 with fine particles and perfect inverse spinel structure could be easily prepared using this method.

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