

# Hydrothermal synthesis of $\text{LiNiVO}_4$ cathode material for lithium ion batteries

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## Abstract

A newly-developed hydrothermal process has been used to prepare  $\text{LiNiVO}_4$  by reacting nickel acetate,  $\text{LiOH} \cdot \text{H}_2\text{O}$ , and  $\text{NH}_4\text{VO}_3$  in isopropanol.  $\text{LiNiVO}_4$  powders with particle size ranging from 0.2 to 0.3  $\mu\text{m}$  were successfully prepared at as low as 200°C in 2 h. Compared to the solid state reaction processes, the hydrothermal process greatly reduced the temperature for preparing  $\text{LiNiVO}_4$ . The subsequent calcination at above 500°C significantly enhanced the crystallinity of  $\text{LiNiVO}_4$  powder. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Lithium ion batteries; Hydrothermal synthesis; Crystallinity

## 1. Introduction

In recent years, the demand for portable power sources with high energy density has greatly increased due to the development and popularity of portable electronic devices such as camcorders, cellular phones, and notebook computers. The use of high voltage cathode materials is one way to achieve high energy density. Currently, three major structural systems of high voltage cathode materials are available for lithium-ion batteries: (1) layered  $\text{LiCoO}_2$ ,  $\text{LiCo}_y\text{Ni}_{1-y}\text{O}_2$ , or  $\text{LiNiO}_2$ ; (2) spinel  $\text{LiMn}_2\text{O}_4$ ; and (3) inverse spinel  $\text{LiNiVO}_4$ .

Interest in newly developed  $\text{LiNiVO}_4$  has arisen due to its high cell voltage of 4.8 V [1–6].  $\text{LiNiVO}_4$  was first synthesized by Bernier et al. [7] in 1961.  $\text{LiVO}_3$  and  $\text{NiCO}_3$  were used as starting materials with a reaction temperature of 500°C for 7 days. This method took so much time and energy so that it was not economic. Ito [8] prepared  $\text{LiNiVO}_4$  by reacting  $\text{LiVO}_3$  and  $\text{NiO}$  at 1000°C for 4 days. This process was also disadvantageous due to the high reaction temperature and long reaction time. Fey et al. [1,3] developed a new preparation method for  $\text{LiNiVO}_4$  by reacting  $\text{LiNiO}_2$  and  $\text{V}_2\text{O}_3$  or  $\text{V}_2\text{O}_5$  at 700°C for 2 h in air. Prabaharan et al. [9] synthesized  $\text{LiNiVO}_4$  at

temperatures as low as 320°C using the aqueous glycine–nitrate combustion process.

In order to reduce the reaction temperature and time for preparing  $\text{LiNiVO}_4$  powder, the hydrothermal process was adopted in this study. In the basic hydrothermal process, starting chemicals are dissolved in water or other solvents with a proper mineralizer added. Then, the solution is placed in a high pressure reactor and heated at an elevated temperature to induce chemical reactions. Since high pressure is applied in the hydrothermal process, the solubility of reactants is thereby increased and the desired compounds can be synthesized at lower temperatures. The low reaction temperature is advantageous for suppressing particle grain growth and reducing energy consumption.

This work investigated the formation and microstructure of  $\text{LiNiVO}_4$  powder prepared by the hydrothermal process in isopropanol. The effects of calcination on the crystallinity and grain size of the hydrothermally derived  $\text{LiNiVO}_4$  powder were also studied.

## 2. Experimental

Appropriate amounts of  $\text{LiOH} \cdot \text{H}_2\text{O}$ ,  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{NH}_4\text{VO}_3$  were dissolved in isopropanol. The precursor solution was poured into a high pressure stainless steel reactor. The temperature was elevated at a rate of

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4°C/min with an agitation rate of 200 rpm. The precursor solution was then heated isothermally at 200°C for 2 h. The powder was obtained by a membrane separation process and subsequent drying. The dried powder was characterized by a Mac Science, MXP3, X-ray diffractometer. A Hitachi, S-800 scanning electron microscope was used to observe the microstructure. The powder obtained from the precursor solution was further calcined in an electrical furnace to increase crystallinity. Infrared spectra of these samples were recorded on a Hitachi, 270-30, infrared spectrophotometer for detecting the presence of any organic remnants.

### 3. Results and discussion

The XRD pattern of the  $\text{LiNiVO}_4$  powder prepared by the hydrothermal processing of 0.3 M precursor solution at 200°C is shown in Fig. 1(A), which exhibits the characteristic diffraction lines of  $\text{LiNiVO}_4$  without any miscellaneous phases. The XRD pattern of the obtained  $\text{LiNiVO}_4$  powder completely matched that of an inverse spinel structure listed in a JCPDS file [10]. The results demonstrate that  $\text{LiNiVO}_4$  was successfully prepared at as low as 200°C by a hydrothermal process. However, the intensity of the XRD pattern in Fig. 1(A) is fairly weak. In order to increase the crystallinity of the powder, the concentration of the precursor solution was then increased to 0.6 M and the experiment was re-performed. The XRD pattern of the resultant powder is presented in Fig. 1(B). As deduced from Fig. 1(A) and (B), it seems that crystallinity cannot

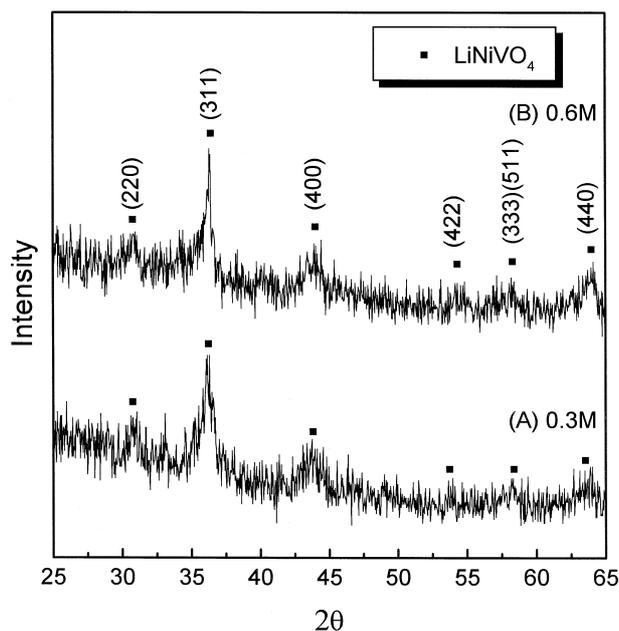
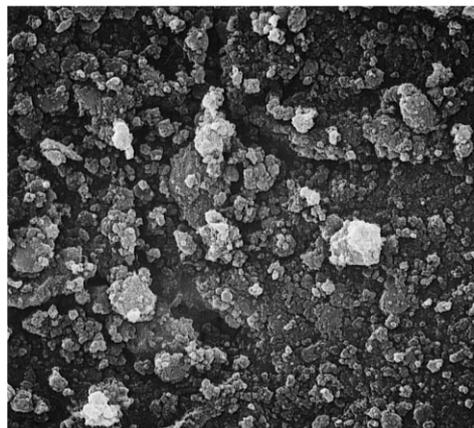
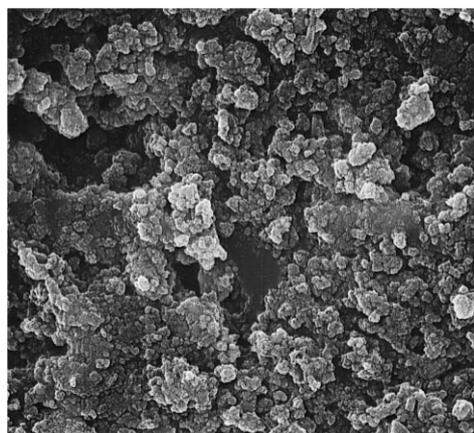


Fig. 1. X-ray diffraction patterns of  $\text{LiNiVO}_4$  powders prepared by the hydrothermal processing at 200°C. The concentrations of the precursor solution for (A) and (B) are 0.3 M and 0.6 M, respectively.



(a)



(b)

Fig. 2. Scanning electron micrographs of  $\text{LiNiVO}_4$  powder prepared by the hydrothermal processing at 200°C. The concentrations of the precursor solution for (A) and (B) are 0.3 M and 0.6 M, respectively.

be increased by increasing the concentration of the precursor solution from 0.3 M to 0.6 M. The scanning electron micrographs of these  $\text{LiNiVO}_4$  products are shown in Fig. 2. The particles had submicron dimensions, ranging from 0.2 to 0.3  $\mu\text{m}$ . The sticky-looking substance adsorbed onto the surface of these particles was most likely organic remnants.

The powders prepared from the hydrothermal process were further calcined at 300, 400, 500, 600, 700, 800, and 900°C isothermally for 2 h. The XRD patterns of the hydrothermally derived  $\text{LiNiVO}_4$  powders calcined at various temperatures are shown in Fig. 3. The intensity of XRD peaks increased with increasing calcining temperature. At 500°C or above, the crystallinity of  $\text{LiNiVO}_4$  became satisfactory and their XRD patterns manifested an inverse spinel structure. In contrast, a temperature above 700°C was necessary to obtain satisfactory crystalline  $\text{LiNi}$ -

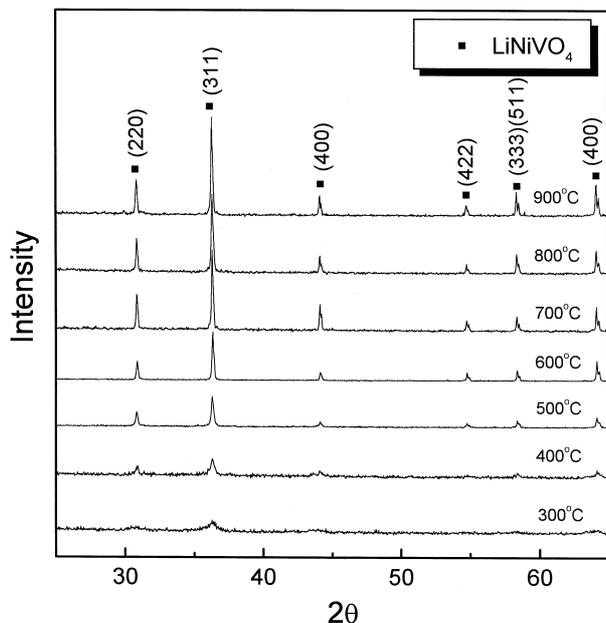


Fig. 3. X-ray diffraction patterns of the hydrothermally derived  $\text{LiNiVO}_4$  powders calcined at various temperatures for 2 h.

$\text{VO}_4$  powder by a conventional solid-state reaction process.

Fig. 4 shows the infrared spectra of hydrothermally derived  $\text{LiNiVO}_4$  powder calcined at various temperatures for 2 h. The band at  $3500\text{ cm}^{-1}$  is characteristic of the O–H group, and the bands at  $1600$  and  $1450\text{ cm}^{-1}$  result from the absorption of the C=O group [11]. The band at  $1000\text{--}600\text{ cm}^{-1}$  is caused by the V–O bonds of  $\text{VO}_4$

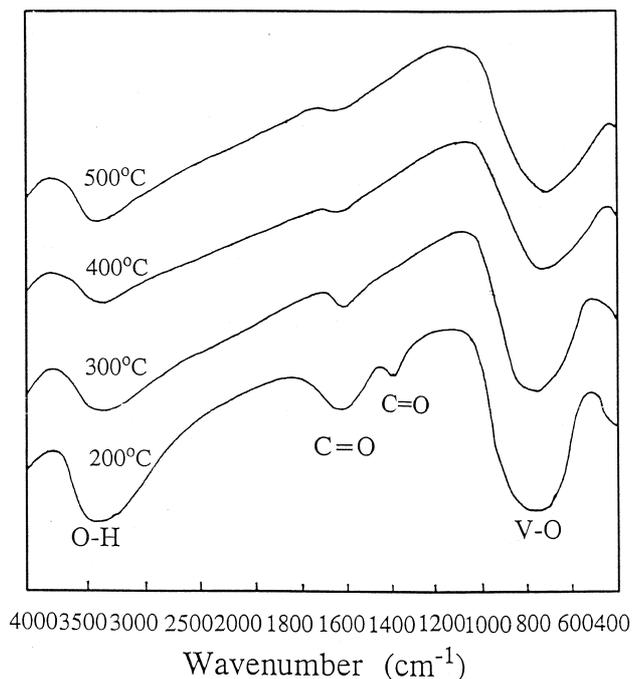


Fig. 4. Infrared spectra of the hydrothermally derived  $\text{LiNiVO}_4$  powders calcined at various temperatures for 2 h.

tetrahedron [12,13]. As seen from Fig. 4, the absorption intensity of the CO group and O–H group decreased with an increase in calcining temperature, indicating a reduction in the amount of organic remnants. After heating to  $700^\circ\text{C}$ ,



(a)



(b)



(c)

Fig. 5. Scanning electron micrographs of the hydrothermally derived  $\text{LiNiVO}_4$  powders calcined at (A)  $300^\circ\text{C}$ , (B)  $400^\circ\text{C}$ , and (C)  $500^\circ\text{C}$  for 2 h.

the OH group completely disappeared. These organic remnants might originate from nickel acetate, the starting reagent.

The microstructures of the  $\text{LiNiVO}_4$  products calcined at 300°C, 400°C, and 500°C are shown in Fig. 5(A), (B), and (C), respectively. These micrographs reveal that the amount of sticky-looking organic remnants decreased with an increase in calcining temperature. After calcination at 500°C, the powder showed a particulate appearance and no significant grain growth was observed.

#### 4. Conclusions

- (i) Monophasic  $\text{LiNiVO}_4$  powder was successfully prepared by the developed hydrothermal method at as low as 200°C.
- (ii) To increase the crystallinity of  $\text{LiNiVO}_4$  prepared by the hydrothermal process, subsequent calcination is necessary. After calcination at 500°C or above, crystallinity of  $\text{LiNiVO}_4$  increased significantly.
- (iii) The hydrothermal process can greatly lower the temperature required to synthesize highly crystalline  $\text{LiNiVO}_4$  compared to traditional solid state reaction processes.

#### Acknowledgements

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