

# The effects of the stoichiometry and synthesis temperature on the preparation of the inverse spinel $\text{LiNiVO}_4$ and its performance as a new high voltage cathode material

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Accepted 17 October 1996

## Abstract

The high temperature solid-state reaction between  $\text{LiNiO}_2$  and  $\text{V}_2\text{O}_3$  (or  $\text{V}_2\text{O}_5$ ) in air used to prepare  $\text{LiNiVO}_4$  has been further studied. This quaternary Li–Ni–V–O reaction is strongly dependent on reaction temperature and lithium stoichiometry in  $\text{Li}_x\text{Ni}_{2-x}\text{O}_2$  and has produced a highly crystalline  $\text{LiNiVO}_4$  material whose structure has been confirmed to be an inverse spinel by Rietveld analysis with a Bragg  $R$ -factor of 1.18 in the absence of crystal orientation preference. The cell performance of  $\text{LiNiVO}_4$  prepared at various temperatures or by varying  $x$ -values in  $\text{Li}_x\text{Ni}_{2-x}\text{O}_2$  has been examined in lithium coin cells and indicated that preparation at low temperatures or when  $x = 0.89$  provided an electrode material with higher cell capacity. © 1997 Elsevier Science S.A.

**Keywords:** Cathodes; Spinel compounds; Lithium; Vanadium; Nickel

## 1. Introduction

In 1993, we discovered that  $\text{LiNiVO}_4$ , at 4.8 V, exhibits the highest observed cell voltage for any intercalation or insertion reaction and has an inverse spinel structure contrary to common belief that it is spinel [1]. Both  $\text{LiNiVO}_4$  and its isostructural compound  $\text{LiCoVO}_4$  can be high voltage cathode materials for lithium secondary cells.

The striking difference in cell voltage between  $\text{LiNiVO}_4$  (4.8 V) and its analogue  $\text{LiCoVO}_4$  (4.2 V) implies that nickel atoms in the inverse spinel structure may play a critical role. A new preparation method for  $\text{LiNiVO}_4$  was developed by reacting an  $\text{LiNiO}_2$  precursor and  $\text{V}_2\text{O}_3$  or  $\text{V}_2\text{O}_5$  in air at 700 °C for 2 h [2]. Since lithium–nickel oxides are usually prepared as nonstoichiometric  $\text{Li}_x\text{Ni}_{2-x}\text{O}_2$  ( $0.6 < x < 1$ ) [3], hypothetically they could be the starting materials for the synthesis of nonstoichiometric  $\text{Li}_x\text{Ni}_{2-x}\text{VO}_4$  compounds. If they can be synthesized, these compounds may reveal the role that nickel atoms play in cell voltage behavior.

It has been shown that both  $\text{LiMgVO}_4$  and  $\text{LiZnVO}_4$  can be converted from olivine or phenacite to spinel by high-pressure modification [4,5]. In addition, spinel compounds can be disordered through cation mixing and converted to

inverse spinel [6]. Therefore, our preparation method may have had a similar effect by producing an  $\text{LiNiVO}_4$  compound with an inverse spinel structure instead of the commonly accepted spinel structure.

Our goals were to determine if various nonstoichiometric  $\text{LiNiVO}_4$  compounds could be prepared by reacting  $\text{Li}_x\text{Ni}_{2-x}\text{O}_2$  with  $\text{V}_2\text{O}_3$  and to study how  $\text{LiNiVO}_4$  preparation is affected by synthesis conditions and lithium stoichiometry in  $\text{Li}_x\text{Ni}_{2-x}\text{O}_2$ . The electrochemical behavior of the inverse spinel  $\text{LiNiVO}_4$  produced with  $\text{Li}_x\text{Ni}_{2-x}\text{O}_2$  was examined in coin-type test cells.

## 2. Experimental

$\text{Li}_x\text{Ni}_{2-x}\text{O}_2$  ( $0.60 < x < 1.05$ ) materials were prepared by reacting stoichiometric ratios of  $\text{LiOH} \cdot \text{H}_2\text{O}$  and  $\text{Ni}(\text{OH})_2$  at 700 °C for 2 h in air [7].  $\text{LiNiVO}_4$  samples were obtained by reacting stoichiometric mixtures of  $\text{Li}_x\text{Ni}_{2-x}\text{O}_2$  and  $\text{V}_2\text{O}_3$  in air, first at 500 °C for 4 h and then at 800 °C for 6 h. Powder X-ray diffraction (XRD) measurements were made with a Siemens D5000 diffractometer equipped with a diffracted beam monochromator and  $\text{Cu K}\alpha$  radiation.

Coin-type test cells were constructed as described previously [1]. The electrolyte used was 1 M  $\text{LiBF}_4$  dissolved in

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a mixture of 66% dimethyl carbonate (DMC), 17% ethylene carbonate (EC) and 17% propylene carbonate (PC) by volume.

### 3. Results and discussion

A close similarity was observed between the XRD patterns for the products formed from the reactions of  $\text{Li}_x\text{Ni}_{2-x}\text{O}_2$  ( $x=0.25-1.03$ ) with  $\text{V}_2\text{O}_5$ . Because parts of these patterns are very similar to that of  $\text{LiNiVO}_4$  there is no evidence that nonstoichiometric  $\text{Li}_x\text{Ni}_{2-x}\text{VO}_4$  was ever formed. When lithium or nickel was stoichiometrically deficient, a complicated mixture of  $\text{Li}_3\text{VO}_4$ ,  $\text{NiV}_2\text{O}_7$ , and  $\text{Ni}_3(\text{VO}_4)_2$  was formed in addition to the main product (cf. Fig. 1(a)). When lithium or nickel was stoichiometrically excessive, impurities such as  $\text{Li}_3\text{VO}_4$  and  $\text{NiO}$  were formed (cf. Fig. 1(c)). Typical examples of the above XRD patterns of  $\text{LiNiVO}_4$  prepared under different stoichiometrical conditions are illustrated in Fig. 1.

After studying synthesis temperatures from 600 to 975 °C using the solid-state method, we determined that 800 °C was the optimal preparation temperature for pure  $\text{LiNiVO}_4$  because  $\text{LiVO}_3$  impurities were formed between 600 to 700 °C and  $\text{NiO}$  impurities were formed at >900 °C. The effect of synthesis temperature on the purity of  $\text{LiNiVO}_4$  is clearly exhibited in Fig. 2. The presence of impurities such as  $\text{NiO}$  or  $\text{LiVO}_3$  in the different temperature ranges seems related to the electrical conductivity behavior of  $\text{LiNiVO}_4$ . Ito et al. [8] measured the electrical conductivity of  $\text{LiNiVO}_4$  from 450 to 1000 °C in air. Above 800 °C, the activation energy

was about 2.8 eV while below 800 °C, the activation energy was about 0.99 eV. At 800 °C,  $\text{LiNiVO}_4$  existed in a single phase which may explain why that was also the optimal preparation temperature for pure  $\text{LiNiVO}_4$ .

Several XRD data of pure  $\text{LiNiVO}_4$  were selected for Rietveld profile refinement analysis. The data and calculations were a reasonable but not a perfect fit to an inverse spinel structure because the Bragg  $R$ -factor (see Refs. [9–11]) could not be reduced below the 9% range, similar to what was found in our previous work [1].

In order to improve the Rietveld analysis results, we looked into the effect of crystal orientations on XRD profiles since  $\text{LiNiVO}_4$  is a highly crystalline material. Fig. 3 displays the effect of grinding on the region of diffraction angles ( $2\theta$ ) from 10 to 70° in the XRD patterns of  $\text{LiNiVO}_4$ . Fig. 3(a) shows the XRD patterns for the same sample of pure  $\text{LiNiVO}_4$  which was reloaded three consecutive times. The Bragg peaks near 55°, 58°, and 64° diffraction angles appeared as doublets which were very sensitive to the changes in crystal orientations each time. The  $\text{LiNiVO}_4$  sample was mechanically ground thoroughly for 1 h. Fig. 3(b) shows the XRD patterns for the ground sample which was reloaded three consecutive times. Surprisingly, the Bragg peaks near 55°, 58° and 64° appeared as singlets and remained constant in intensity. The XRD data in Fig. 3(b) was used to rerun a Rietveld profile refinement analysis and achieved better results as shown in Fig. 4. The dotted line denotes  $\text{LiNiVO}_4$  data points while the solid line represents a calculated pattern assuming an inverse spinel structure. The lower panel in Fig. 4 shows the

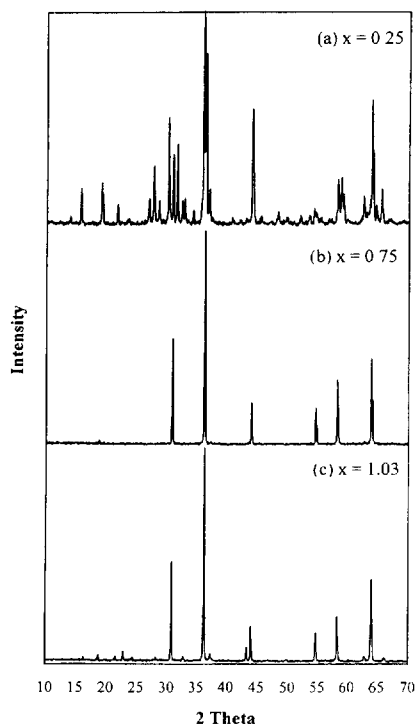


Fig. 1. XRD patterns of  $\text{LiNiVO}_4$  prepared with different  $x$  values in  $\text{Li}_x\text{Ni}_{2-x}\text{O}_2$ : (a)  $x=0.25$ , (b)  $x=0.75$ , and (c)  $x=1.03$ .

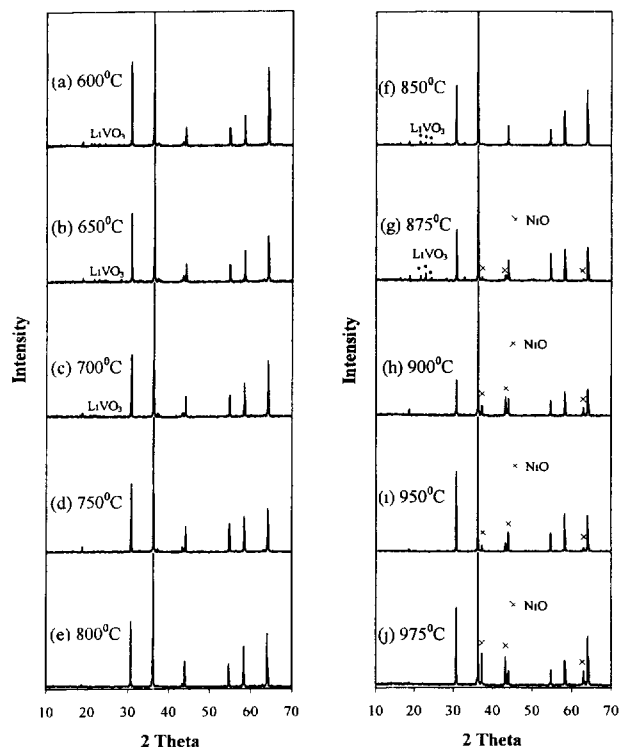


Fig. 2. XRD patterns of  $\text{LiNiVO}_4$  prepared at different temperatures: (a) 600 °C; (b) 650 °C; (c) 700 °C; (d) 750 °C; (e) 800 °C; (f) 850 °C; (g) 875 °C; (h) 900 °C; (i) 950 °C; and (j) 975 °C.

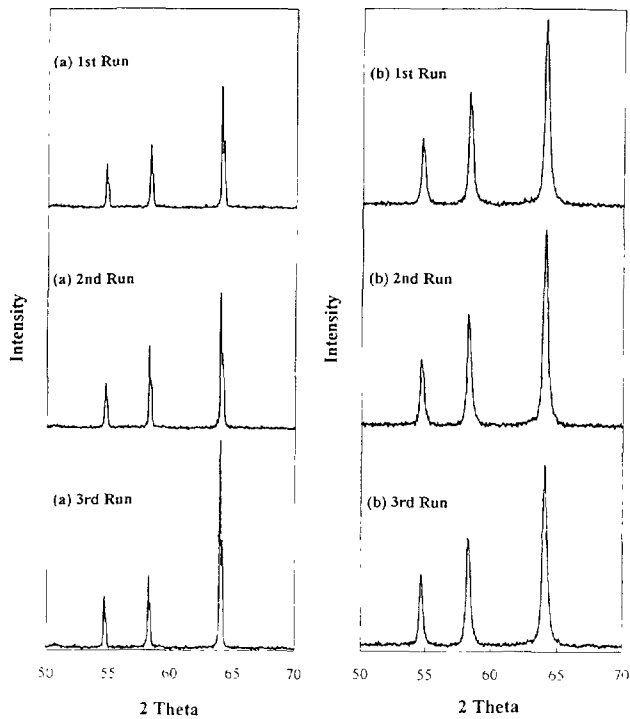


Fig. 3. The effect of grinding on the XRD patterns of  $\text{LiNiVO}_4$  (a) before grinding, and (b) after grinding

difference between the measured and calculated pattern where the largest difference is less than 2%. The Bragg  $R$ -factor was 1.18 and confirmed that the structure of  $\text{LiNiVO}_4$  was indeed inverse spinel.

Selected cell performance data of  $\text{Li}/\text{LiNiVO}_4$  cells are listed in Table 1. Cell capacity was the highest when  $x = 0.89$  and 0.96 in the  $\text{Li}_x\text{Ni}_{2-x}\text{O}_2$  cathode starting material. The reason for the decrease in first charge capacity with an increase in  $x$  value is not fully understood. In the first cycle, the irreversible capacity loss in these cells was large and their remaining capacity was small. The highest capacity during charge and discharge was 50.4 and 16.3 mAh/g, respectively, so their preliminary cell performance did not measure up to that of the  $\text{Li}/\text{LiNiVO}_4$  cell we tested in a previous study which had a capacity during charge and discharge of 80 and 45 mAh/g [1]. The method used for preparing the  $\text{LiNiVO}_4$  precursor was the primary difference between these two studies. In this work, we used a high-temperature solid-state method without a precursor versus a low-temperature copre-

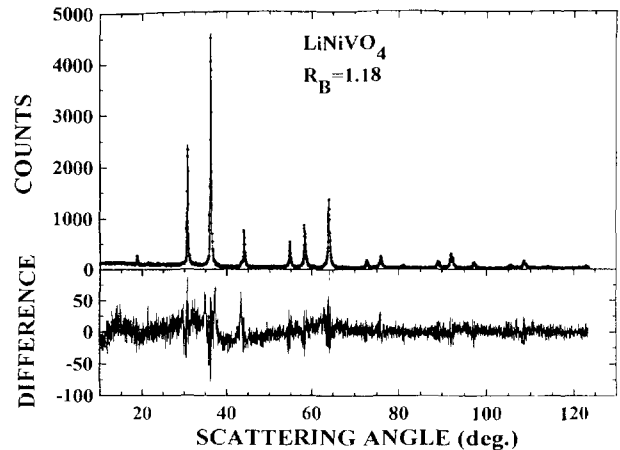


Fig. 4. Rietveld profile refinement analysis for the powder XRD pattern of  $\text{LiNiVO}_4$

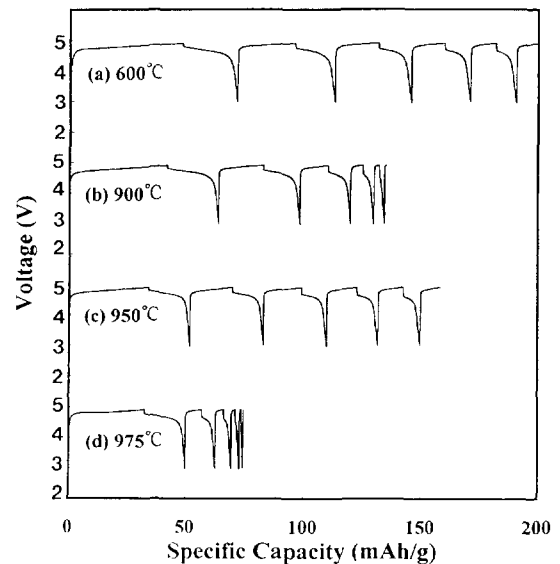


Fig. 5. Effect of the synthesis temperature on cell capacity and cycle behavior.

cipitation method with a precursor used in our previous work [1].

Cells with cathode materials prepared at 600 °C had a charge capacity of 48.1 mAh/g while those with cathode materials prepared at 975 °C only had a charge capacity of 32.0 mAh/g (Fig. 5). Higher preparation temperatures resulted in diminished cell capacity, probably because lithium

Table 1  
Selected capacity data of  $\text{Li}/\text{LiNiVO}_4$  cells

LiNiVO <sub>4</sub> prepared from reacting Li <sub>x</sub> Ni <sub>2-x</sub> O <sub>2</sub> and V <sub>2</sub> O <sub>5</sub>	Capacity (mAh/g)					
	$x = 0.89$		$x = 0.96$		$x = 1.03$	
	Charge	Discharge	Charge	Discharge	Charge	Discharge
1st cycle	50.4	16.3	46.0	18.7	32.0	14.8
2nd cycle	24.6	8.0	18.1	12.4	14.8	10.1

reacted with the preparation vessel substrate resulting in lithium mass loss, and mobile lithium atoms could not move freely through partially fused tunnels.

### Acknowledgements

The authors are grateful for the supports of this research by Moli Energy (1990) Ltd., Canada and the National Science Council, Republic of China under Grant No. NSC85-2214-E-008-008.

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