

Short communication

# Structural and electrochemical properties of $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$ prepared by a wet process

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Received 21 February 2003; accepted 20 March 2003

## Abstract

$\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  ( $0.7 \leq y \leq 0.95$ ) solid solution has been prepared by a wet process. According to X-ray diffraction analysis, these materials are found to have a rhombohedral layered structure ( $R\bar{3}m$ ) and are an isostructure  $\text{LiNiO}_2$ . The  $I(104)/I(003)$  intensity ratio is increased with Ti concentration, which indicates the cation mixing between transition metal layer and lithium layer is occurred. The  $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  compounds have well-developed layered structures and a particle size of  $\sim 1 \mu\text{m}$ . The titanium and nickel in the lattice is found to be trivalent and bivalent, respectively. The first discharge capacity of  $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  is 10–25  $\text{mAh g}^{-1}$ . These values are inferior to those of  $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  prepared by a solid-state reaction (30  $\text{mAh g}^{-1}$ ). The low discharge capacities are due to local structural change during the first charge, where transition metal ions in the lithium layer block the diffusion of Li ions.

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**Keywords:** Lithium secondary battery; Cathode material;  $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$

## 1. Introduction

$\text{LiNiO}_2$  has been proposed as a cathode material for lithium secondary batteries [1].  $\text{LiNiO}_2$  is a non-stoichiometric compound with the formula of  $[\text{Li}_{1-z}\text{Ni}_z]^{2+}[\text{Ni}^{3+}\text{Ni}_z^{2+}]\text{O}_2$  ( $0 \leq z \leq 0.2$ ) as determined by the preparation on conditions [2,3]. A small amount of structural disorder due to the displacement of nickel and lithium ions in  $\text{LiNiO}_2$  strongly affects the electrochemical properties such as the working voltage and the rechargeable capacity. As the de-intercalation reaction proceeds below  $x = 0.5$  in  $\text{Li}_x\text{NiO}_2$ , some irreversible structural rearrangements occur, which lead to irreversible electrochemical reactions [4]. The solid solution of  $\text{LiNi}_y\text{M}_{1-y}\text{O}_2$  ( $\text{M} = \text{Cr}, \text{Mn}, \text{Co}, \text{etc.}$ ) has been studied in order to improve the efficiency of batteries containing  $\text{LiNiO}_2$  [5–8]. Most of the compounds, except those containing cobalt, show cation mixing between the layers.

In the previous study [9], Ti ions were used substitute the Ni ions in  $\text{LiNiO}_2$  prepared by a solid-state reaction, since these are advantages in terms of lower atomic weight and clear reduced (III)–oxidized (IV) states in the Li-intercalation reaction. An attempt has been made to determine the partially-disordered layer structure induced by the

substitution of Ti ions in  $\text{LiNiO}_2$ , in which  $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  should be a solid solution between  $\text{LiNiO}_2$  and  $\text{LiTiO}_2$ . In addition  $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  should have the partially-disordered structure  $\text{LiTiO}_2$  [10,11].

In this study, the structural and electrochemical properties of  $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  prepared by a wet process are studied and the results compared with those for  $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  synthesized by a solid state reaction.

## 2. Experimental

The  $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  compounds were prepared by a wet process using citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ) as follows.  $\text{Li}_2\text{CO}_3$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{C}_6\text{H}_8\text{O}_7$  were dissolved with a mole ratio of 1:1:3 in distilled water. In order to make the  $\text{TiO}(\text{H}_2\text{O}_2)^{2+}$  complex,  $\text{TiCl}_3$  was added to 0.1 M  $\text{H}_2\text{O}_2$  solution. The  $\text{TiO}(\text{H}_2\text{O}_2)^{2+}$  complex solution was slowly added to the lithium nickel citrate solution. The solution was adjusted to a pH of 6–7 with aqueous  $\text{NH}_4\text{OH}$ . Finally, the citrate sol was formed. The solution was evaporated at  $80^\circ\text{C}$  and the subsequent organometallic complexes were decomposed into organic compounds and the metal oxide precursor at  $300^\circ\text{C}$ . The metal oxide precursor was pre-heated at  $600^\circ\text{C}$  for 10 h and annealed at  $700$  or  $800^\circ\text{C}$  for 20 h in air to obtain  $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$ .

The X-ray diffraction patterns were recorded using a MAC Science MXP 18 XRF diffractometer with Ni-filtered

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Cu K $\alpha$  radiation by step scanning ( $0.02^\circ$ ) in the  $2\theta$  range  $10^\circ$ – $80^\circ$ . Scanning electron microscopy (SEM) was performed with a Hitachi S800 microscope in order to examine the morphology of the samples. The valence state of transition metal ions was investigated by X-ray photoelectron spectroscopy (XPS). The XPS spectra were obtained by means of a ESCA-LAB 200R, VG Scientific spectrometer. A Mg K $\alpha$  X-ray source (1253.6 eV) was used. The base pressure of the sample chamber in the spectrometer was lower than  $10^{-9}$  Torr. All binding energies were corrected with the C 1s line at 284.5 eV.

To examine the electrochemical properties of  $\text{Li}_x\text{Ni}_y\text{Ti}_{1-y}\text{O}_2$ , an electrochemical cell was fabricated as follows. A cathode was prepared with 89 wt.%  $\text{Li}_x\text{Ni}_y\text{Ti}_{1-y}\text{O}_2$ , 10 wt.% acetylene black, and 1 wt.% PTFE binder. The electrolyte was a 1 M  $\text{LiPF}_6$ -ethylene carbonate (EC): diethyl carbonate (DEC) (1:1) solution. A lithium metal anode was used. Test cells were assembled in a glove-box filled with argon gas. The cells were cycled in the voltage range 3.0–4.2 V at a constant current density ( $50 \mu\text{A cm}^{-2}$ ) using a galvanostatic charge–discharge cycle tester.

### 3. Results and discussion

According to XRD analysis, the  $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  ( $0.7 \leq y \leq 0.95$ ) compounds are found to be isostructural with  $\text{LiNiO}_2$ , which has the rhombohedral layered structure ( $R\bar{3}m$ ). The XRD patterns of  $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  ( $0.7 \leq y \leq 0.95$ ) synthesized at  $800^\circ\text{C}$  are shown in Fig. 1. The  $I(104)/I(003)$  intensity ratio is increased with Ti concentration in  $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$ . It is understood that a small amount of the transition metal ion (Ni, Ti) is positioned in the lithium site due to the partial disordering, which leads to quasi two-dimensional structural character. Considering that the ionic radii of Ni(II) ( $0.83 \text{ \AA}$ ) and Ti(III) ( $0.81 \text{ \AA}$ ) are similar to that of Li ion ( $0.90 \text{ \AA}$ ) rather than that of Ni(III) ( $0.74 \text{ \AA HS}$ ,  $0.70 \text{ \AA LS}$ ), the Ni(II) and Ti(III) ions can be

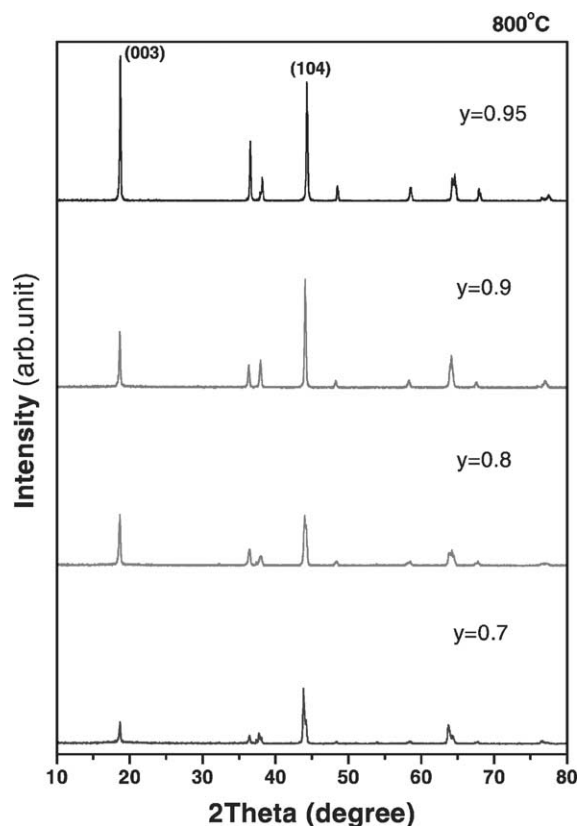


Fig. 1. X-ray diffraction patterns for  $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  ( $0.7 \leq y \leq 0.95$ ) synthesized at  $800^\circ\text{C}$ .

partially positioned in the lithium site. The cell parameter is gradually increased with the rate of Ti substitution due to the presence of larger Ti ions and the formation of a lower oxidation state of nickel. The structural properties of  $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  ( $0.7 \leq y \leq 0.95$ ) synthesized at  $700^\circ\text{C}$  are similar to those of  $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  heat-treated at  $800^\circ\text{C}$ .

Electron micrographs show the  $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  compounds to have a well-developed layered structure and the particle size of the samples is 2–3  $\mu\text{m}$ , which is smaller than that of

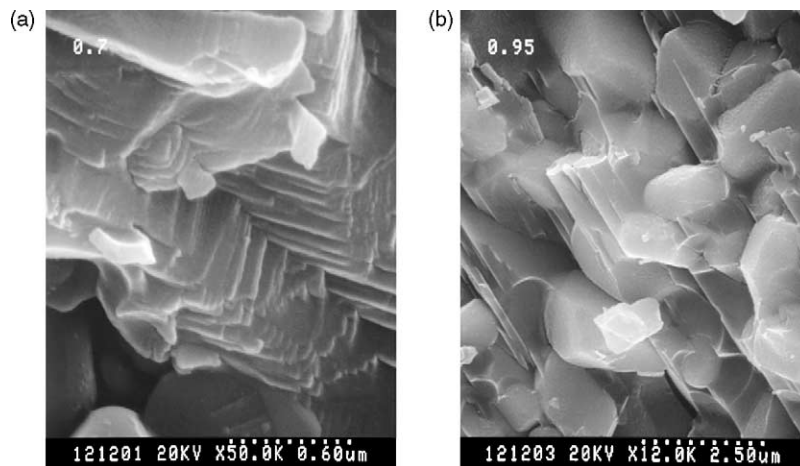


Fig. 2. Scanning electron micrograph of  $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  synthesized at  $800^\circ\text{C}$ : (a)  $y = 0.7$ ; (b)  $y = 0.95$ .

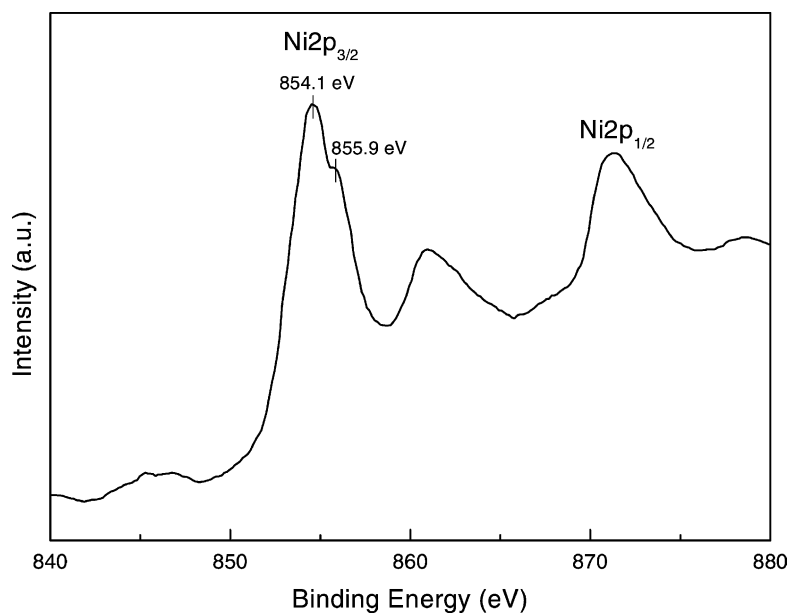


Fig. 3. X-ray photoelectron spectra for Ni  $2p_{3/2}$  of  $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  synthesized at  $800^\circ\text{C}$ .

$\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  prepared by a solid-state reaction ( $\leq 10\ \mu\text{m}$  Fig. 2).

From XPS analysis, the valence states of Ti and Ni ions are found to be  $\text{Ti}^{3+}$  and  $\text{Ni}^{3+/2+}$ , respectively. Ti  $2p_{3/2}$  lines with binding energy (BE) of 456.8 eV correspond to Ti(III). The major Ni  $2p_{3/2}$  line with a binding energy of 854.1 eV and a shoulder with a binding energy of 855.9 eV correspond to  $\text{Ni}^{2+}$  and  $\text{Ni}^{3+}$ , respectively (Fig. 3). This implies that Jahn–Teller distortion in  $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  is reduced with decreasing  $\text{Ni}^{3+}$  ions due to the substitution of  $\text{Ti}^{3+}$  ions.

The electrochemical behavior of a Li// $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  cell was examined at a constant current density ( $50\ \mu\text{A cm}^{-2}$ ). The first charge–discharge curve of  $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  ( $y = 0.95$ ) synthesized at  $800^\circ\text{C}$  is shown in Fig. 4. The compound shows a large irreversible capacity loss and polarization. This behavior is shown by all the compounds. The first discharge capacities of  $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  are 15–25  $\text{mAh g}^{-1}$ . These values are lower than those of  $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  prepared by a solid-state reaction ( $30\ \text{mAh g}^{-1}$ ). The discharge capacities of the  $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  compounds are drastically decreased during prolonged cycles. The low discharge

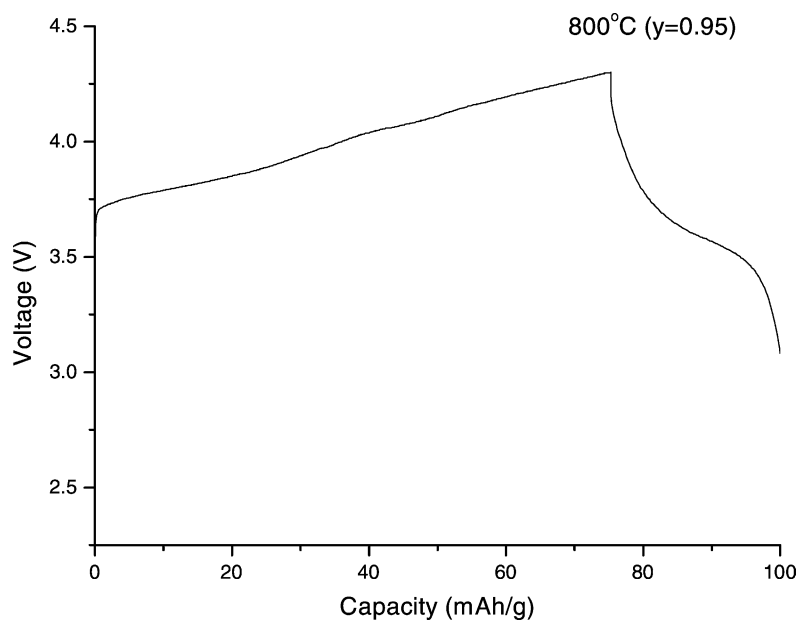


Fig. 4. Charge–discharge curves of Li// $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  ( $y = 0.95$ ) synthesized at  $800^\circ\text{C}$ .

capacities and poor cycle behavior are due to local structural changes during the first charge, where transition metal ions in the lithium layer block the diffusion of Li ions.

#### 4. Conclusions

$\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  ( $0.7 \leq y \leq 0.95$ ) compounds are found to have a rhombohedral layered structure ( $R\bar{3}m$ ) and are an isostructure of  $\text{LiNiO}_2$ . The first discharge capacities of  $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  are inferior to those of  $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$  prepared by a solid-state reaction. The low discharge rates are due to local structural change during the first charge, where transition metal ions in the lithium layer block the diffusion of Li ions.

#### Acknowledgements

This work was supported by Grant No. R-05-2001-000-00195-0 from the Basic Research Program of the Korea Science & Engineering Foundation.

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