

# Synthesis and electrochemical characteristics of $\text{Li}(\text{Ni} \cdot \text{M})\text{O}_2$ ( $\text{M} = \text{Co}, \text{Mn}$ ) cathode for rechargeable lithium batteries

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## Abstract

The synthesis and electrochemical characteristics of  $\text{LiNiO}_2$  and  $\text{Li}(\text{Ni} \cdot \text{M})\text{O}_2$  ( $\text{M} = \text{Co}$  or  $\text{Mn}$ ) as the cathode materials for rechargeable lithium batteries were investigated. It was clarified from these investigations that  $\text{LiNiO}_2$  has been produced from crystalline  $\text{NiO}$ , which was derived from  $\text{Ni}(\text{OH})_2$  and  $\text{LiOH}$ , and that the property of  $\text{NiO}$  had some influence on the  $\text{LiNiO}_2$  preparation. It was assumed that the formation of the layered structure has been inhibited by the existence of the  $\text{Ni}$  vacancy and  $\text{Ni}^{3+}$  ion in  $\text{NiO}$ . The synthesis of a solid solution of  $\text{Li}(\text{Ni} \cdot \text{Co})\text{O}_2$  suggested that a part of the  $\text{Ni}$  replacement by  $\text{Co}$  might inhibit the formation of the  $\text{Ni}$  vacancy of  $\text{NiO}$  and promote the formation of the layered structure. The capacity fading with increase in cycle number was suppressed by the replacement of a part of  $\text{Ni}$  with  $\text{Co}$ . We considered that the capacity fading was suppressed by the development of the layered structure wherein formation of  $\text{Ni}$  vacancy was suppressed by replacement with  $\text{Co}$ .  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  prepared under the stream of oxygen gas showed a small irreversible capacity at first cycle and higher cycling capacity of  $\sim 180 \text{ mA h g}^{-1}$ . © 1997 Elsevier Science S.A.

**Keywords:** Rechargeable lithium batteries; Cathodes, Nickel; Cobalt, Manganese

## 1. Introduction

Lithium nickel oxide ( $\text{LiNiO}_2$ ) is an attractive materials in rechargeable lithium secondary batteries because of its low cost and its possibility of a high charge/discharge capacity. However, higher lithium de-intercalation brings it to a structural rearrangement leading to a decrease in discharge capacity [1]. Therefore, the solid solution of  $\text{Li}(\text{Ni} \cdot \text{Co})\text{O}_2$  and  $\text{Li}(\text{Ni} \cdot \text{Mn})\text{O}_2$  were proposed as a novel cathode for lithium batteries instead of  $\text{LiNiO}_2$  [2,3]. The purpose of this paper is to investigate the influence on the replacement of  $\text{Ni}$  atom by another atom. We studied the synthesizing process and the electrochemical properties of  $\text{LiNiO}_2$  and  $\text{Li}(\text{Ni} \cdot \text{M})\text{O}_2$  ( $\text{M} = \text{Co}, \text{Mn}$ ) from the point of view of crystal structure, stoichiometry ( $\text{Li}/(\text{Ni} \cdot \text{M})$  ratio) and charge/discharge properties as a cathode for lithium batteries.

## 2. Experimental

$\text{LiNiO}_2$ ,  $\text{Li}(\text{Ni} \cdot \text{M})\text{O}_2$  ( $\text{M} = \text{Co}, \text{Mn}$ ) and  $\text{LiCoO}_2$  were prepared by mixing  $\text{Ni}(\text{OH})_2$ ,  $\text{Co}(\text{OH})_2$ ,  $\gamma\text{-MnOOH}$  and  $\text{LiOH} \cdot \text{H}_2\text{O}$  under a stream of oxygen gas or in air at 150–

1000 °C. The reaction products were characterized by X-ray diffraction (XRD) and inductively coupled plasma (ICP) emission spectroscopy. Cathodes used for electrochemical tests were prepared by pressing a mixture of cathode materials ( $\text{LiNiO}_2$ ,  $\text{Li}(\text{Ni} \cdot \text{M})\text{O}_2$  ( $\text{M} = \text{Co}, \text{Mn}$ ) or  $\text{LiCoO}_2$ ) and Teflonized acetylene black (cathode material and Teflonized acetylene black = 2/1 in weight ratio) at a pressure of 1 ton  $\text{cm}^{-2}$  on a stainless-steel mesh. The cathodes were dried under vacuum at 200 °C for 2 h. Charge/discharge tests were carried out in experimental test cells using lithium metal as an anode. The charge/discharge test mode was constant current cycling (1 mA  $\text{cm}^{-2}$ ) between 3.0 and 4.3 V. The electrolyte solution was a mixture of propylene carbonate (PC) and diethyl carbonate (DEC) (20/80 in volume ratio) in which 1 M  $\text{LiPF}_6$  was dissolved as the electrolyte.

## 3. Results and discussion

### 3.1. Synthesis of materials and their characterization

#### 3.1.1. $\text{LiNiO}_2$

Figs. 1 and 2 show the XRD patterns of the reaction products prepared by mixing  $\text{Ni}(\text{OH})_2$  and  $\text{LiOH} \cdot \text{H}_2\text{O}$  at 150–800 °C. It was clarified that the formation of  $\text{LiNiO}_2$  has been

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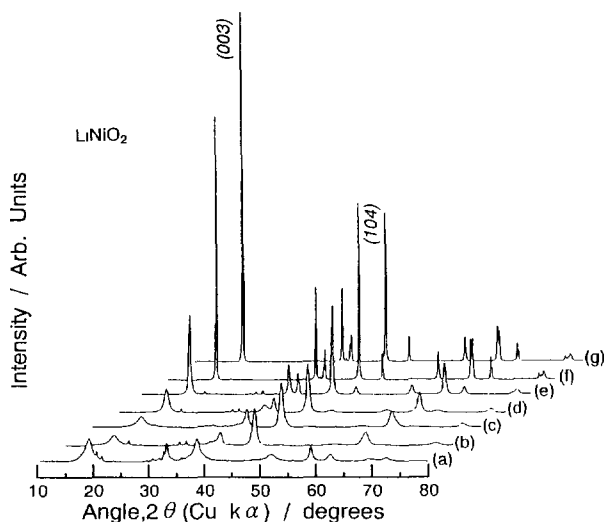


Fig. 1. X-ray diffraction patterns of reaction products prepared by mixing Ni(OH)<sub>2</sub> and LiOH·H<sub>2</sub>O at (a) 150 °C, (b) 300 °C, (c) 450 °C, (d) 500 °C, (e) 600 °C, (f) 750 °C and (g) 800 °C under oxygen atmosphere.

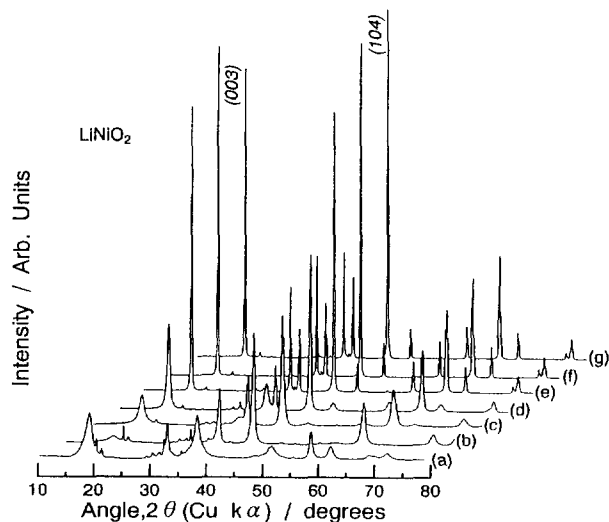


Fig. 2. X-ray diffraction patterns of reaction products prepared by mixing Ni(OH)<sub>2</sub> and LiOH·H<sub>2</sub>O at (a) 150 °C, (b) 300 °C, (c) 450 °C, (d) 500 °C, (e) 600 °C, (f) 750 °C, and (g) 800 °C in air.

initiated at 300 and 450 °C under a stream of oxygen gas and in air, respectively. These temperatures agreed with the synthesis temperature of crystalline NiO, which was derived from Ni(OH)<sub>2</sub>. Consequently, it was confirmed that LiNiO<sub>2</sub> was produced from NiO and LiOH. Ueda et al. [4] reported that NiO was a parent structure to form LiNiO<sub>2</sub>. In particular, we considered that LiNiO<sub>2</sub> has been produced from crystalline NiO. The intensity ratio of  $I(003)/I(104)$  of LiNiO<sub>2</sub> increased with increase in temperature under a stream of oxygen gas but did not increase in air. We considered that the property of NiO had some influence on LiNiO<sub>2</sub> preparation.

Fig. 3 shows the schematic diagrams of variation of NiO with oxidation. NiO is oxidizing easily in air and the thus-obtained NiO<sub>1+δ</sub> exhibited the nature of a p-type semiconductor (Fig. 3(a)). It assumed that the existence of the Ni

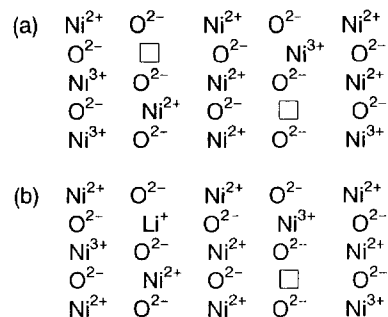


Fig. 3. Schematic diagrams of (a) NiO<sub>1+δ</sub> and (b) Li-NiO<sub>1+δ</sub>.

vacancy and Ni<sup>3+</sup> ion in NiO matrix had an influence on the formation of LiNiO<sub>2</sub>. If Ni vacancy reacts with Li<sup>+</sup> ion, Ni<sup>2+</sup> ion will be formed in the LiNiO<sub>2</sub> matrix (Fig. 3(b)). If the Ni vacancy does not react with the Li<sup>+</sup> ion, the Ni vacancy will remain. We considered that the Ni<sup>2+</sup> ion and the Ni vacancy would inhibit the formation of the layered structure of LiNiO<sub>2</sub>.

We reported that NiO<sub>1+δ</sub> was derived from crystalline NiO [5]. Crystalline NiO was produced at higher temperatures in air. Therefore, it was considered that the formation of NiO<sub>1+δ</sub> and LiNiO<sub>2</sub> would take place at the same time in air, and that the intensity ratio of  $I(003)/I(104)$  of LiNiO<sub>2</sub> did not increase.

From above that, it was considered that suppression of the Ni vacancy was very important factor for the preparation of LiNiO<sub>2</sub>.

### 3.1.2. Li(Ni·M)O<sub>2</sub> (M = Co, Mn)

Fig. 4 shows the XRD patterns of the reaction products prepared by mixing Ni(OH)<sub>2</sub>, Co(OH)<sub>2</sub> and LiOH·H<sub>2</sub>O at 150–800 °C in air. The atomic ratio of Li:Ni:Co was 1.0:0.8:0.2. The intensity ratio of  $I(003)/I(104)$  of LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> increased, despite the reaction took place in

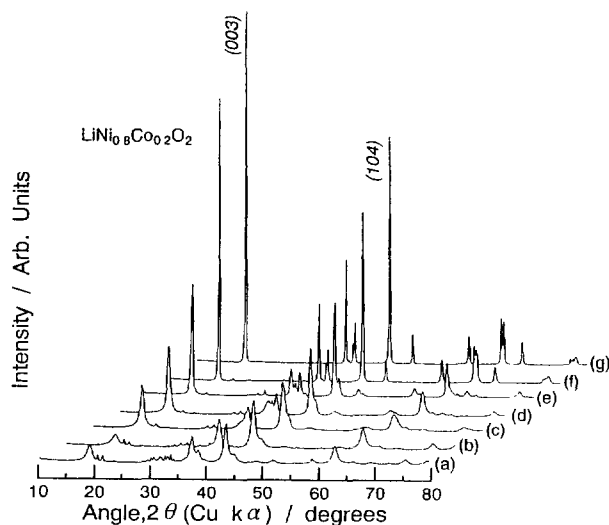


Fig. 4. X-ray diffraction patterns of reaction products prepared by mixing Ni(OH)<sub>2</sub>, Co(OH)<sub>2</sub> and LiOH·H<sub>2</sub>O at (a) 150 °C, (b) 300 °C, (c) 450 °C, (d) 500 °C, (e) 600 °C, (f) 750 °C and (g) 800 °C in air. The atomic ratio of Li:Ni:Co was 1.0:0.8:0.2.

air. It was assumed that a part of the Ni replacement by Co was influenced by the development of the layered structure.

Fig. 5 shows variations of the upper limit temperature for maintaining stoichiometry ( $\text{Li}/(\text{Ni} \cdot \text{Co}) = 1.0$ ) with Co content of  $\text{Li}(\text{Ni} \cdot \text{Co})\text{O}_2$ . As shown in this figure, the upper limit temperature elevated with increase in Co content. We considered that the reduction of Li was caused by vaporizing of the remaining LiOH and decomposition of products, and the reduction of Li increased with increase in Ni vacancy. That suggested that addition of Co has a suppressive effect on the Ni vacancy formation in the NiO matrix. However, the upper limit temperature under a stream of oxygen gas is higher. Therefore, it was considered that the oxygen atmosphere is also preferable for the synthesis of  $\text{Li}(\text{Ni} \cdot \text{Co})\text{O}_2$ .

Fig. 6 shows the XRD patterns of reaction products prepared by mixing  $\text{Ni}(\text{OH})_2$ ,  $\gamma\text{-MnOOH}$  and  $\text{LiOH} \cdot \text{H}_2\text{O}$  at 150–800 °C in air.

The atomic ratio of  $\text{Li}:\text{Ni}:\text{Mn}$  was 1.0:0.9:0.1. The intensity ratio of  $I(003)/I(104)$  of  $\text{LiNi}_{0.9}\text{Mn}_{0.1}\text{O}_2$  did not increase.

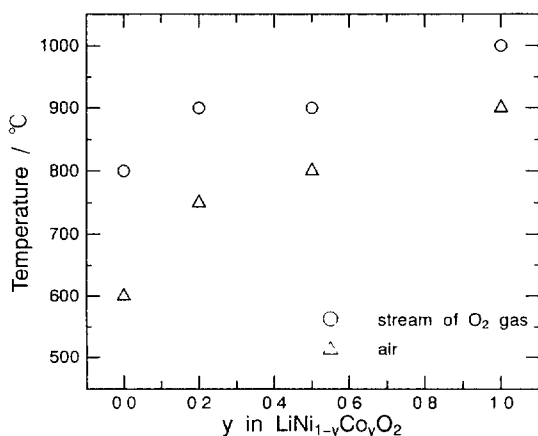


Fig. 5. The upper limit temperature for maintaining stoichiometry ( $\text{Li}/(\text{Ni} \cdot \text{Co}) = 1.0$ ) with Co content of  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ .

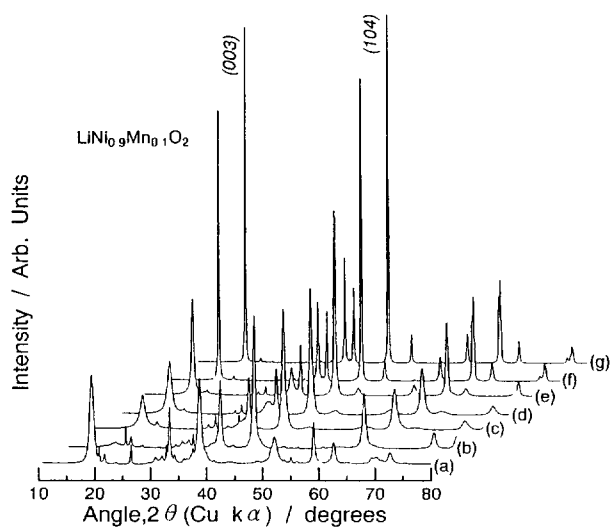


Fig. 6 X-ray diffraction patterns of reaction products prepared by mixing  $\text{Ni}(\text{OH})_2$ ,  $\gamma\text{-MnOOH}$  and  $\text{LiOH} \cdot \text{H}_2\text{O}$  at (a) 150 °C, (b) 300 °C, (c) 450 °C, (d) 500 °C, (e) 600 °C, (f) 750 °C, and (g) 800 °C in air. The atomic ratio of  $\text{Li}:\text{Ni}:\text{Mn}$  was 1.0:0.9:0.1.

The effect of replacement of Ni with Mn was not observed in this study. We are now exploring this result.

### 3.2. Electrochemical results and discussion

Fig. 7 shows variations of charge/discharge capacity and coulombic efficiency at the first cycle with a Co content of  $\text{Li}(\text{Ni} \cdot \text{Co})\text{O}_2$  produced under a stream of oxygen gas. As shown in this figure, the charge capacity decreased and the coulombic efficiency increased with increase in Co content. Because the charge capacity of  $\text{LiCoO}_2$  is smaller than that of  $\text{LiNiO}_2$  in the range of 3.0–4.0 V, the charge capacity was decreased. We considered that the relation between coulombic efficiency and Co content would be related with Ni vacancy. It was found out from the relation between Co content and irreversible capacity (charge capacity–discharge capacity) that  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  has the largest capacity.

Fig. 8 shows the result of charge/discharge cycling tests using  $\text{LiNiO}_2$  and  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  synthesized at 750 and at 900 °C, respectively. It was clarified from the tests that the

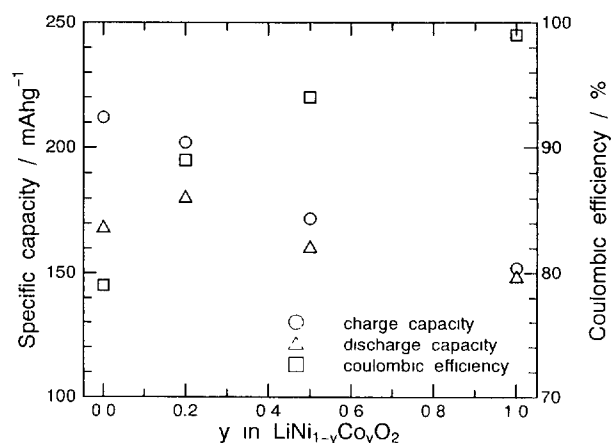


Fig. 7. Charge/discharge performance and coulombic efficiency at first cycle with Co content of  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ ,  $y = 0.0$  and  $y = 0.2$  synthesized at 750 °C,  $y = 0.5$  synthesized at 800 °C and  $y = 1.0$  synthesized at 900 °C in an oxygen atmosphere.

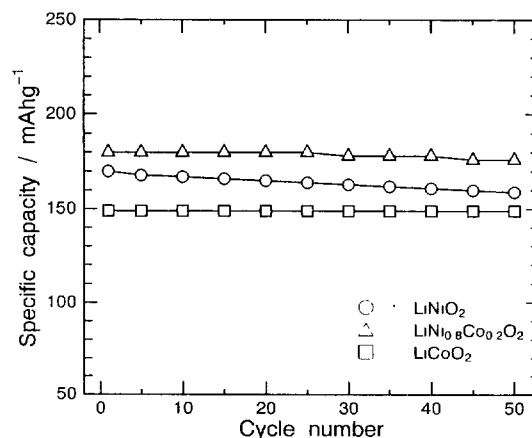


Fig. 8. Charge/discharge cycling performance using  $\text{LiNiO}_2$  and  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  synthesized at 750 °C and  $\text{LiCoO}_2$  synthesized at 900 °C in an oxygen atmosphere

discharge capacity fading with increase in cycle number was suppressed by replacement of a part of Ni with Co. We considered that the capacity fading was suppressed by the development of the layered structure wherein formation of Ni vacancy was suppressed by replacement with Co.

$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  prepared under a stream of oxygen gas showed a small irreversible capacity at the first cycle and higher cycle specific discharge capacity of  $\sim 180 \text{ mAh g}^{-1}$ .

#### 4. Conclusions

It was clarified that the suppression of the Ni vacancy formation in NiO was very important for: (i) the synthesis of  $\text{LiNiO}_2$  wherein the layer structure containing less Ni vacancy developed well; (ii) the addition of Co had a sup-

pressive effect on the Ni vacancy formation in NiO; (iii) the irreversible capacity of first cycle was reduced, and (iv) a stable charge/discharge cycle can be established depending on the suppressive degree of Ni vacancy formation.

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