

Synthesis and properties of LiNiO_2 as cathode material for secondary batteries

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Abstract

The optimum preparation condition and electrochemical properties of LiNiO_2 as the cathode material for lithium secondary batteries were investigated. LiNiO_2 samples were prepared from $\text{Li}(\text{OH})_2 \cdot \text{H}_2\text{O}$ and $\text{Ni}(\text{OH})_2$ in the range from 500 to 900 °C. The compound prepared in an oxygen atmosphere at 700 °C exhibited the highest discharge capacity of 200 mAh/g in the voltage range from 3.0 to 4.3 V. The structure and charge-transfer resistance of the $\text{Li}_{1-x}\text{NiO}_2$ compound were examined at each state-of-charge by X-ray diffractometry and a.c. impedance spectroscopy. The charge-transfer resistances were low in the range of $0.15 < x < 0.75$, which was related to the expansion of the interlayer distance between NiO_2 layers.

Keywords: Secondary lithium batteries; Synthesis; Cathodes; Lithium; Nickel

1. Introduction

Transition metal oxides, such as LiCoO_2 [1], LiNiO_2 [2], and LiMn_2O_4 [3], have been proposed as cathode materials for 4 V secondary batteries. Although LiCoO_2 has been practically utilized as the cathode material for lithium-ion batteries, LiNiO_2 is more attractive because of its lower cost and the possibility of a higher discharge capacity. However, this compound shows structural and compositional varieties depending on their preparation conditions [4–7]. Stoichiometric LiNiO_2 is difficult to obtain, because a high-temperature treatment of LiNiO_2 leads to the decomposition from LiNiO_2 to $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ ($x > 0$) which has a partially disordered cation distribution at the lithium sites. The stoichiometry of LiNiO_2 affects the electrochemical properties. So, it is necessary to prepare LiNiO_2 under optimum conditions in order to have high performances.

The optimum preparation condition of LiNiO_2 has been investigated, and the results including its properties are discussed in this paper.

2. Experimental

LiNiO_2 samples were prepared by heating a mixture of $\text{LiOH} \cdot \text{H}_2\text{O}$ and $\text{Ni}(\text{OH})_2$ ($\text{Li}/\text{Ni} = 1.1/1$ in molar ratio) in the range from 500 to 900 °C for 5 h in air

or oxygen. The products were examined by X-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation. The total nickel content was determined by EDTA titration and the nickel oxidation state by reduction to Ni(II) with excess ferrous sulfate and back titration with standard potassium dichromate.

Electrochemical tests were carried out using three-electrode cells. The cathode was made by pressing a mixture of 80 wt.% (w/o) LiNiO_2 , 17 w/o acetylene black, and 3 w/o polytetrafluoroethylene (PTFE) binder on to a stainless-steel net. The 1.0 cm \times 1.0 cm cathode with about 40 mg of active materials was used. Lithium metal was used as both reference and counter electrodes. The electrolyte used was a 1.0 M solution of LiClO_4 in a 1:1 mixture of propylene carbonate (PC) and 1,2-dimethoxyethane (DME) by volume or a 1.0 M solution of LiClO_4 in PC. Cycling tests were carried out by two modes. One was constant-current cycling between 3.0 and 4.3 V. The other consisted of constant-capacity charging (90–200 mAh/g based on the sample weight) followed by constant-current discharge to 3.0 V. The current density of 1 mA/cm² was employed. Open-circuit voltages (OCV) as a function of composition were obtained by the constant-current charge of 1 mA/cm² and equilibration on open circuit for 11 h. The a.c. impedance of the cathode was measured for each OCV value obtained above by a frequency response analyzer (Solartron 1174) interfaced with a potentiostat/

galvanostat (Solartron 1186). The combined system potentiostatically controlled the cell voltage and supplied a 10 mV r.m.s. perturbation sweeping the frequency from 100 kHz to 0.2 mHz. Furthermore, the cathodes which were charged to various states-of-charge were rinsed with DME and dried, then examined by X-ray diffractometry (XRD).

3. Results and discussion

Fig. 1 shows the XRD patterns of samples prepared between 500 and 900 °C for 5 h in air. The diffraction peaks became higher and sharper by preparing above 600 °C, indicating that the reaction was accelerated and crystallization proceeded. Samples prepared above 600 °C showed the XRD pattern of LiNiO_2 ($R\bar{3}m$). However, the intensity of the (003) peak decreased and the lattice parameters c and a increased slightly with increasing temperature. The XRD patterns of samples prepared in oxygen are shown in Fig. 2. Similarly to the samples prepared in air, the crystallization of the samples prepared over 600 °C proceeded fully. The intensities of (003) peaks for the samples prepared in oxygen above 700 °C were higher than those in air.

Fig. 3 shows the average oxidation state of nickel determined by chemical analysis. The oxidation state of nickel greatly differed under different preparation conditions. The oxidation state increased by forming LiNiO_2 in the range of 500 to 600 °C. The decrease of the oxidation state of nickel corresponded to the increase of the lattice parameters, which indicated the

decomposition of LiNiO_2 to $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ ($x > 0$) at higher temperatures [6]. The oxidation state for the compound prepared in oxygen was much higher and closer to the value of the stoichiometric compound (3.0) than that in air. This indicates that the decomposition from LiNiO_2 to $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ was suppressed in an oxygen atmosphere.

Charge/discharge tests were carried out in the range of 3.0 to 4.3 V at a current density of 1 mA/cm². Fig. 4 shows the initial charge/discharge curves of LiNiO_2 prepared at 700 °C in oxygen. The OCV of a freshly prepared cathode was 3.45 V. The charge voltage increased gradually with charge and a plateau appeared at 4.2 V. Fig. 5 shows the relationship between the initial charge/discharge capacity and the oxidation state of nickel for LiNiO_2 except for the samples prepared at 500 °C because of low discharge capacity. The discharge capacity was 197 mAh/g at the oxidation state of 3.06 (at 700 °C in oxygen), 173 mAh/g at 2.91 (at 700 °C in air), and 147 mAh/g at 2.85 (at 800 °C in air). Thus, the closer to 3.0 the oxidation state the higher the discharge capacity was. The initial discharge capacity of the sample prepared at 700 °C in oxygen was the highest. The individual compounds had a difference of about 40 mAh/g between the charge and discharge capacity. Subsequent cycling did not show any difference. When the cathode was discharged to a lower voltage, a voltage plateau between 2.0 and 1.5 V appeared. This plateau involved about 0.15 Li/mol, and corresponded to the formation of LiNiO_2 .

Since the initial discharge capacity of the LiNiO_2 compound prepared at 700 °C in oxygen was the highest,

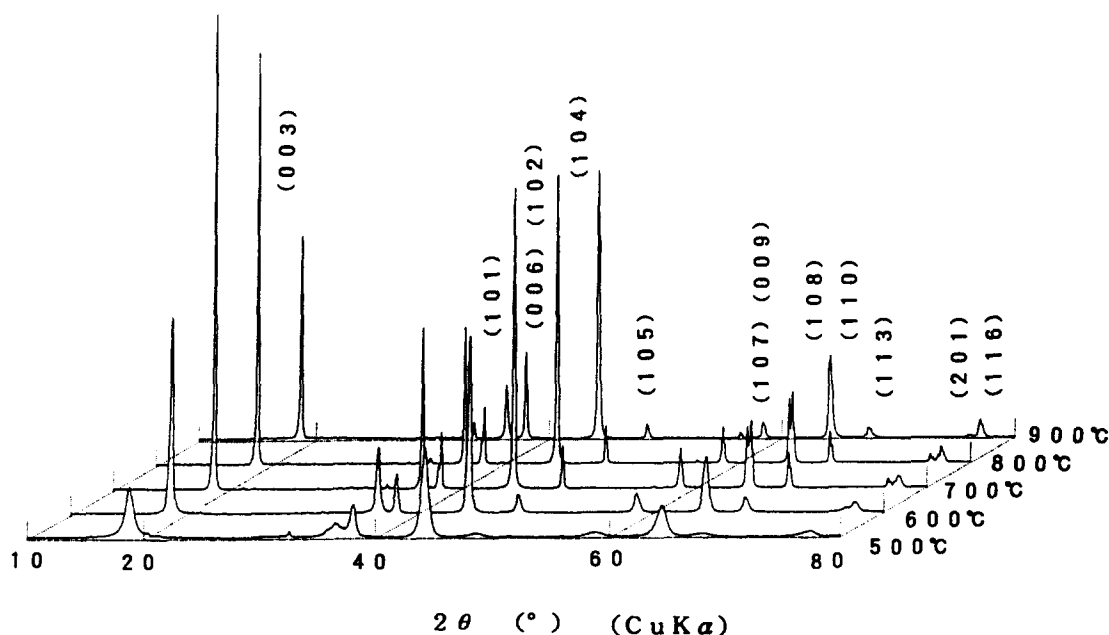


Fig. 1. X-ray diffraction patterns of LiNiO_2 prepared by heating a mixture of $\text{LiOH} \cdot \text{H}_2\text{O}$ and $\text{Ni}(\text{OH})_2$ in the range from 500 to 900 °C for 5 h in air.

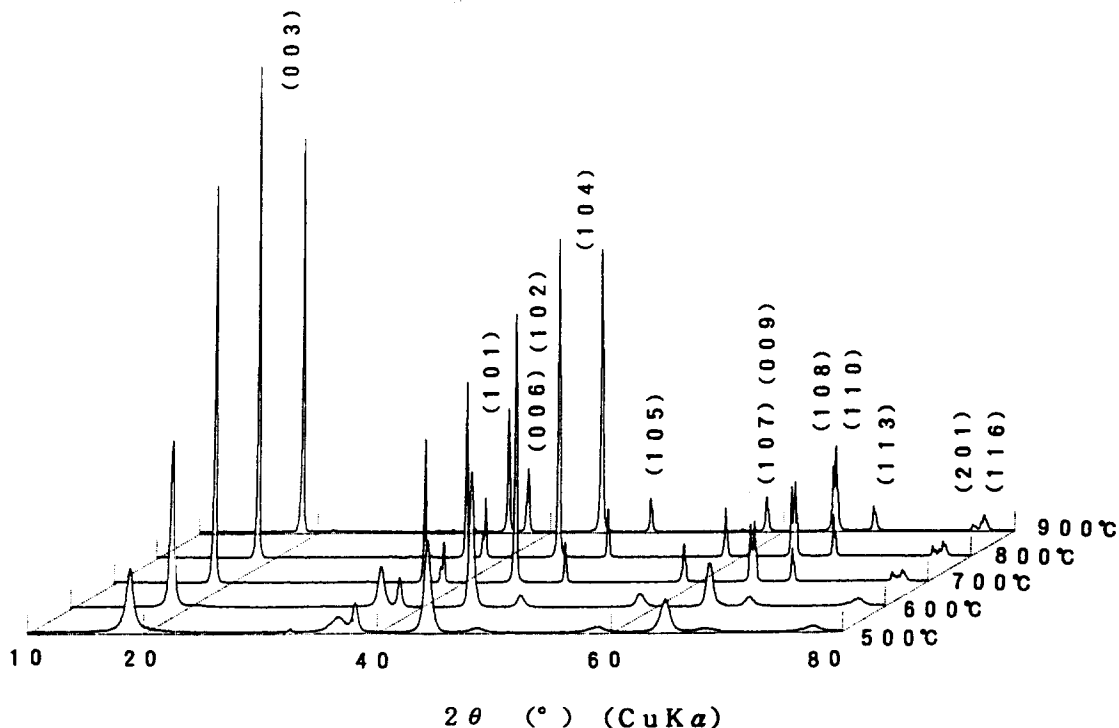


Fig. 2. X-ray diffraction patterns of LiNiO_2 prepared by heating a mixture of $\text{LiOH}\cdot\text{H}_2\text{O}$ and $\text{Ni}(\text{OH})_2$ in the range from 500 to 900 °C for 5 h in oxygen.

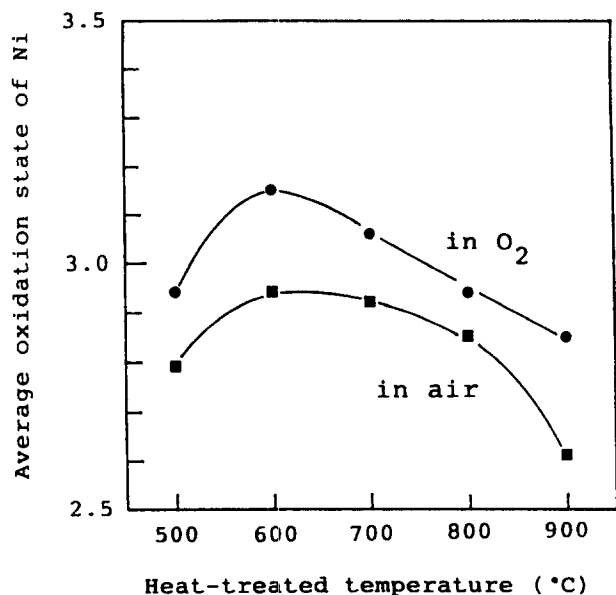


Fig. 3. Average oxidation state of nickel vs. temperature when heat-treating LiNiO_2 .

the results on this sample are reported hereafter. OCV obtained by the intermittent charge are shown in Fig. 6. In Fig. 6, the x value is calculated from the cathode mass and the charge transfer. The characteristic OCV was observed at about 3.65, 4.00, and 4.18 V, respectively. It is considered that the decrease of OCV for $x > 0.9$ would be due to the reaction of the cathode with the electrolyte. In order to follow a change in the crystal

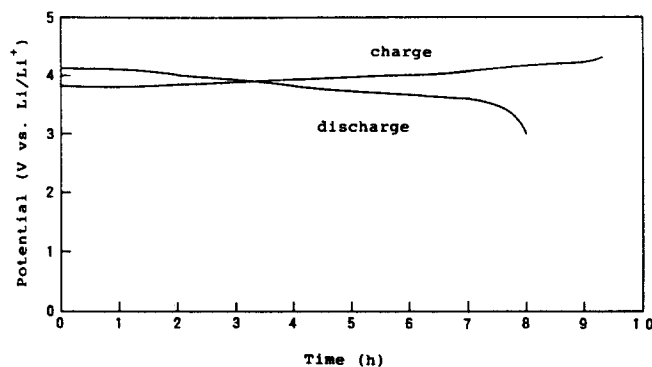


Fig. 4. Charge and discharge curves of LiNiO_2 in 1 M $\text{LiClO}_4/\text{PC} + \text{DME}$. Charge/discharge limits 4.3/3.0 V at a rate of 1 mA/cm². Active mass of LiNiO_2 was 40.6 mg.

structure of LiNiO_2 during charge, X-ray examinations were carried out. Fig. 7 shows the lattice parameters as a function of the x value in $\text{Li}_{1-x}\text{NiO}_2$. The lattice parameters (c and a) were indicated for a hexagonal phase. The OCV curve and XRD data showed four distinct regions during charge [4,8]. For $0 < x < 0.25$ in $\text{Li}_{1-x}\text{NiO}_2$, the structure was the original hexagonal one. The lattice parameter c decreased slightly with increasing x . For $0.25 < x < 0.55$, the structure became a monoclinic phase. The lattice parameter c increased with the x value. For $0.55 < x < 0.75$, the structure became a hexagonal phase again. For $x > 0.75$, another hexagonal phase of which the lattice parameter c was very small appeared.

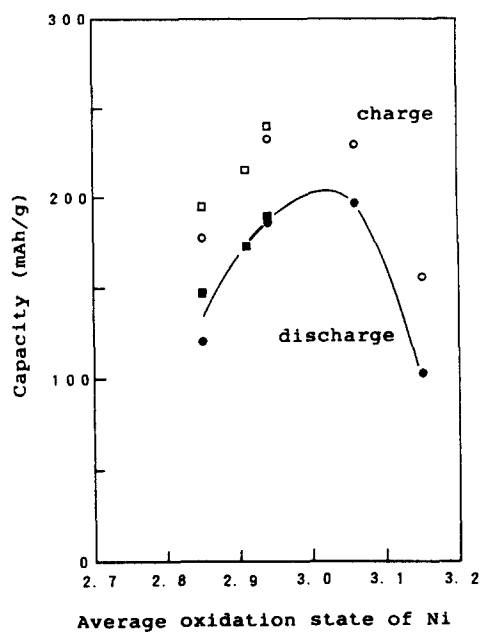


Fig. 5. Relationship between initial charge/discharge capacity and average oxidation state of nickel for LiNiO_2 : (\square), (\blacksquare) charge and discharge capacity of LiNiO_2 prepared in air; (\circ), (\bullet) charge and discharge capacity of LiNiO_2 prepared in oxygen.

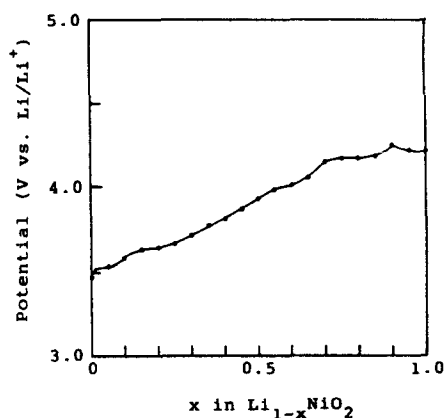


Fig. 6. Open-circuit voltage curve of $\text{Li}_{1-x}\text{NiO}_2$ in 1 M LiClO_4/PC .

A.c. impedance of the cathode was examined for various x values. Fig. 8 shows the complex impedance diagrams for various x values. The complex impedance diagrams exhibited two semicircles in the frequency range of 100 kHz to 0.01 Hz and a line inclined at approximately 45° to the real axis in the range of 0.01 to 0.001 Hz. It is considered that the semicircle in the high frequency range is attributable to a surface-layer impedance at the cathode/electrolyte interface and the other semicircle corresponds to a charge-transfer impedance, and the line part is related to a Warburg impedance for diffusional transport of electroactive species. Charge-transfer resistances obtained from the semicircles are shown in Fig. 9. The charge-transfer resistances were very high in the ranges of $x < 0.15$ and $x > 0.8$. On the contrary, the charge-transfer resistances were from 10

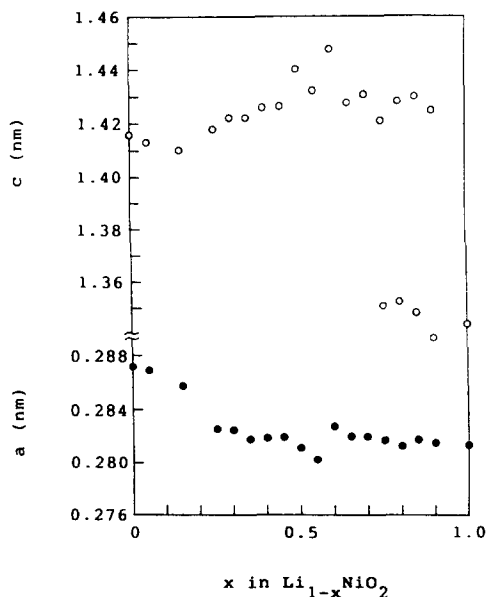


Fig. 7. Lattice parameters of $\text{Li}_{1-x}\text{NiO}_2$ as a function of x during initial charge. Hexagonal lattice parameters are indicated.

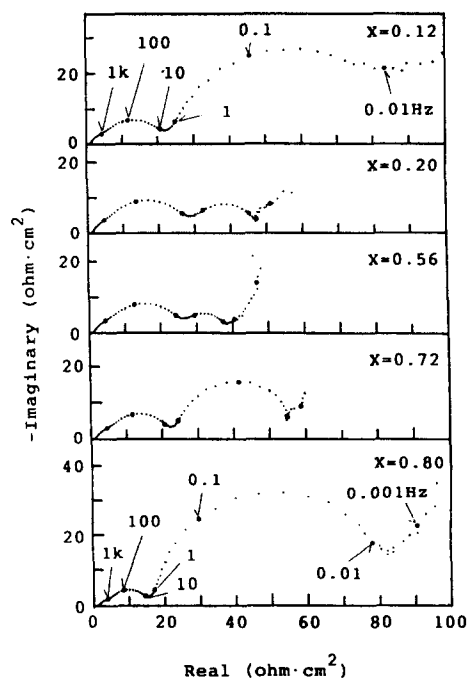


Fig. 8. Complex impedance diagrams of $\text{Li}_{1-x}\text{NiO}_2$ at various x values in 1 M $\text{LiClO}_4/\text{PC}+\text{DME}$.

to $30 \Omega \text{ cm}^2$ in the range of $0.15 < x < 0.75$. Since the lattice parameter c increased in this region as shown in Fig. 7, the interlayer distance between NiO_2 layers expanded by the extraction of lithium ion from the LiNiO_2 crystal. It is considered that the charge-transfer resistance decreased because the expansion of the interlayer distance made the transfer of lithium ions in the interlayer to be easy.

Fig. 10 shows the cycle characteristics of LiNiO_2 prepared at 700°C in oxygen under a constant-charge

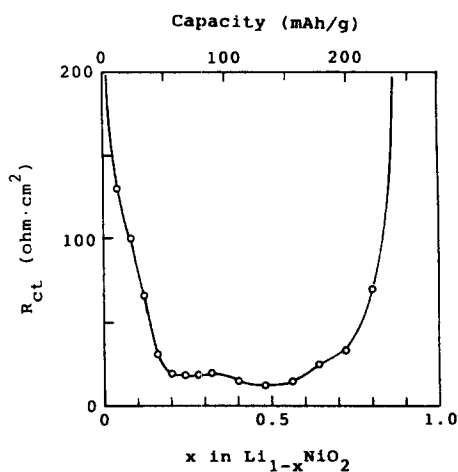


Fig. 9. Charge-transfer resistances of $\text{Li}_{1-x}\text{NiO}_2$ as a function of x in 1 M $\text{LiClO}_4/\text{PC}+\text{DME}$.

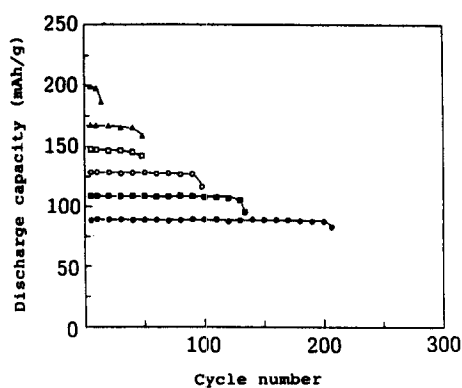


Fig. 10. Cycle characteristics of LiNiO_2 under a constant-charge capacity at a rate of $1.0 \text{ mA}/\text{cm}^2$ in 1 M $\text{LiClO}_4/\text{PC}+\text{DME}$.

capacity at a rate of $1.0 \text{ mA}/\text{cm}^2$. The cycle life was 200 cycles at a charge capacity of $90 \text{ mAh}/\text{g}$, 98 cycles at $130 \text{ mAh}/\text{g}$, and 12 cycles at $200 \text{ mAh}/\text{g}$. The cell capacity is expected to increase for practical use.

4. Conclusions

The synthesis and electrochemical properties of LiNiO_2 have been investigated in this paper. The structure and composition of the compound depended on their preparation conditions. The compound which had the composition close to the stoichiometric LiNiO_2 could be prepared under optimum conditions. This compound had the discharge capacity of $200 \text{ mAh}/\text{g}$ in the voltage range of 3.0 to 4.3 V.

The structure and a.c. impedance of $\text{Li}_{1-x}\text{NiO}_2$ were examined during charge. It has been found that the charge-transfer resistance was related to the structural transformation of $\text{Li}_{1-x}\text{NiO}_2$. The transfer resistances were low in the range of $0.15 < x < 0.75$.

Acknowledgement

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