

Synthesis and properties of gallium-doped LiNiO_2 as the cathode material for lithium secondary batteries

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Abstract

Gallium-doping to LiNiO_2 was investigated, and we found that it is effective to improve the cycling behavior of LiNiO_2 . The obtained specimen is single phase with hexagonal structure without any other foreign matters such as LiGaO_2 by X-ray diffraction measurement. The crystal structure during charging process is stabilized by gallium doping. Hexagonal structure is retained all over the charging state without monoclinic phase and without two hexagonal phase regions which are observed in undoped LiNiO_2 . Consequently, the crystal lattice parameters change continuously and gradually. The gallium-doped LiNiO_2 shows superior rechargeable capacity of 190 mAh/g and retention of more than 95% after 100 cycles in the cycling test between 3.0 and 4.3 V at room temperature. In the cycling test with higher charging voltage (4.4 or 4.5 V), the rechargeable capacity reaches more than 200 mAh/g without significant degradation of cycling behavior. It also demonstrates excellent over-charge resistance. © 1997 Elsevier Science S.A.

Keywords: Lithium secondary batteries; Cathodes: Lithium; Nickel oxide; Gallium; Crystal structure

1. Introduction

LiNiO_2 is a more attractive material than LiCoO_2 because of its low cost and possibility of higher rechargeable capacity. However, the cycling behavior at high capacity (> 150 mAh/g) is insufficient [1–3]. During the charging process, LiNiO_2 shows sequential change in crystal structure from the hexagonal phase to the monoclinic phase, hexagonal phase again, then two hexagonal phases, finally a single hexagonal phase. At the two-phase region, the second hexagonal phase with short *c*-lattice parameter appears, therefore the sudden shrinkage of the crystal lattice occurs [1,4]. It seems to be related to the deformation of the NiO_2 layer in the LiNiO_2 crystal lattice, and such deformation may result in an irreversible structure change. The two hexagonal phases appear at the deeply charged state having a small amount of lithium ion. The hexagonal phase with shorter *c*-lattice parameter in the two hexagonal phases must have a very low Li^+ concentration, because its *c*-lattice parameter is as short as that of the final hexagonal phase which have very low Li^+ concentration. It is supposed that Li^+ rearrangement occurs where the local Li^+ concentration becomes below a certain thresh-

old, so that the energy of local area reduces, the phase separates into two stable states with smaller and larger amounts of lithium ion than the average concentration. It is expected that the phase separation would be inhibited by a uniform Li^+ distribution and a restriction of Li^+ rearrangement at a deeply charged state. To achieve this condition, we attempted a uniform substitution of Ni^{3+} by the trivalent ion of which the valence does not fluctuate. Li^+ de-intercalation requires a valence change of nickel ion from 3+ to 4+, therefore Li^+ would remain around the substituted ion and distribute uniformly at deeply charged state. Furthermore, the Li^+ rearrangement would be restricted by restraining Li^+ around the substituted ion. We selected the gallium ion as a dopant which substitutes the nickel ion, because it forms a trivalent Ga^{3+} ion, and its ionic radius (0.76 Å) is close to that of the Ni^{3+} ion (0.74 Å).

In this paper, the preparation, the crystal structure change during the charging process, and the cycling behavior of the gallium-doped LiNiO_2 are described.

2. Experimental

Lithium nitrate, basic nickel carbonate and gallium compounds were mixed in a basic aqueous solution and dried

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under vacuum with stirring. Gallium oxide, gallium hydroxide and gallium nitrate were used as the gallium compounds. The molar ratio of $\text{Li}/(\text{Ga} + \text{Ni})$ was 1.05, and that of $\text{Ga}/(\text{Ga} + \text{Ni})$ ($=y$; Ga content) was varied from 0 to 0.05. Then the resultant powder mixtures were fired at 640–720 °C for 5–15 h in O_2 atmosphere. The obtained specimens were examined by powder X-ray diffraction (XRD) method using $\text{Cu K}\alpha$ radiation.

Electrochemical tests were carried out using a plate-type cell. The cathode was prepared by coating the paste, obtained by kneading the mixture of LiNiO_2 , acetylene black, 1-methyl-2-pyrrolidone including poly(vinylidene difluoride) onto a stainless-steel mesh. The anode was lithium metal and the electrolyte was an 1 M solution of LiPF_6 in ethylene carbonate (EC)–dimethyl carbonate (DMC)–ethylmethyl carbonate (EMC) mixture. The change in crystal structure of the specimens during charging process was examined by XRD measurement of the charged cathode in Ar atmosphere. The charge/discharge characteristics of the specimens were evaluated by cycling tests between 3.0 and 4.3 V in a current density of 36 mA/g at room temperature. The cell was charged galvanostatically up to 4.3 V followed by potentiostatic charging for 8 h and then discharged galvanostatically to 3 V. The over-charge resistance was evaluated by cycling test with higher charging voltage, i.e., 4.4 and 4.5 V, respectively. The pseudo open-circuit voltage (pseudo-OCV) was measured by stepwise charge/discharge with 2 h rest.

3. Results and discussion

3.1. Preparation

No impurity phase was detected in the specimens prepared using gallium nitrate as the starting material. In contrast, the specimens using gallium oxide or gallium hydroxide included

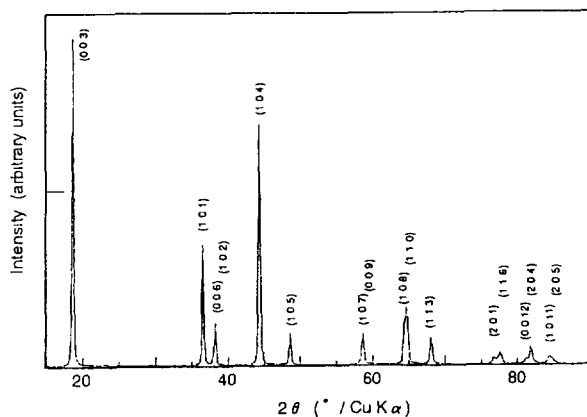


Fig. 1. XRD pattern of the specimen prepared from LiNO_3 , NiCO_3 and $\text{Ga}(\text{NO}_3)_3$, as raw materials which is assigned to single structure (Ga content $y=0.02$).

the impurity phase of LiGaO_2 . The specimens are supposed to include less gallium in the crystal structure of LiNiO_2 than the specimens prepared using gallium nitrate, probably due to low reactivity of starting gallium compounds. Fig. 1 shows the XRD pattern of the specimen prepared using gallium nitrate with Ga content of 0.02 fired at 660 °C for 15 h. It is assigned to a hexagonal structure ($R\bar{3}m$) with lattice parameters of $a=2.88$ Å and $c=14.20$ Å. The obtained lattice parameters are essentially the same as previously reported those of LiNiO_2 [1]. It is considered that gallium substitution of nickel gives no detectable change in lattice parameters because of their similar size in trivalent state.

The specimens prepared using gallium nitrate were further evaluated in the following section.

3.2. Crystal structure change during charging process

XRD patterns at (003) reflection of the specimens corresponding to various charged states are shown in Fig. 2. Though the two hexagonal phases appear in the specimen of $y=0.005$, the gap of the interlayer distance between them (~ 0.18 Å) is shorter than that of LiNiO_2 (~ 0.3 Å) [1]. The specimen of $y=0.02$ retains hexagonal structure all over the charging process, i.e., without the monoclinic phase and

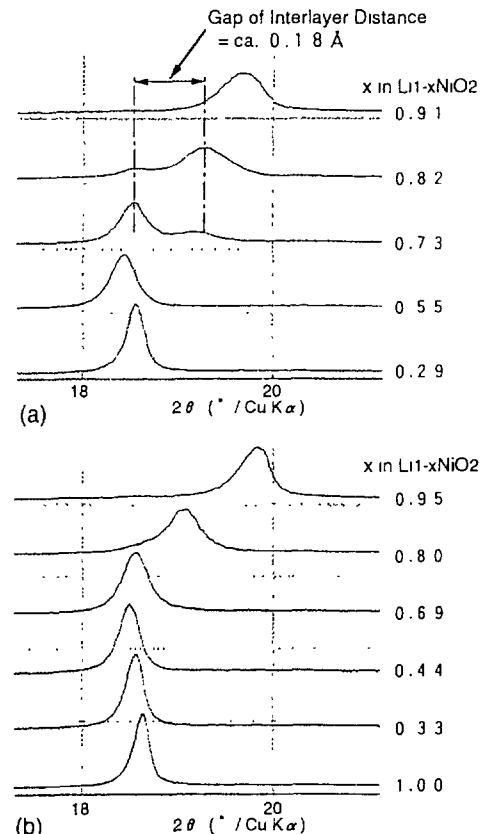


Fig. 2. XRD patterns at (003) reflection of gallium-doped LiNiO_2 during charging process (a) Ga content $y=0.005$, and (b) Ga content $y=0.02$

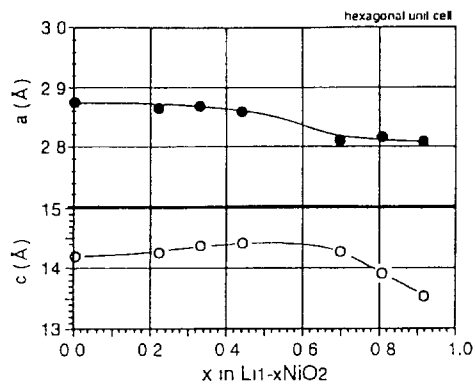


Fig. 3 Change in lattice parameters during charging process in gallium-doped LiNiO_2 (Ga content $y=0.02$).

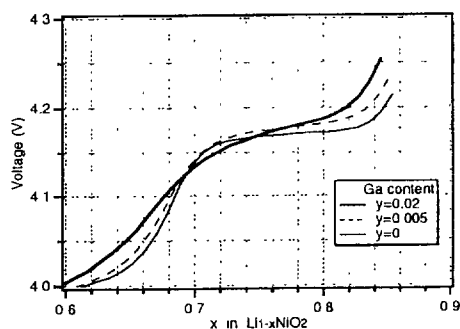


Fig. 4. Pseudo-OCV curves of gallium-doped LiNiO_2 , measured by stepwise charge/discharge with 2 h rest

without the two-hexagonal-phase region. Fig. 3 shows the change in lattice parameters in the specimen of $y=0.02$. The a -lattice parameter of the specimen changes is the same as that of undoped LiNiO_2 . However, the c -lattice parameter changes continuously and gradually even at the region beyond $x=0.7$ in $\text{Li}_{1-x}\text{NiO}_2$ in contrast to the discontinuous change in the undoped LiNiO_2 . It is noteworthy that the gallium doping allows the existence of the hexagonal phase with intermediate c -lattice parameter instead of the two hexagonal phases observed in the undoped LiNiO_2 . We have confirmed that the occupation rate of nickel or gallium in the lithium layer is very low (at most 1%) by Rietveld analysis. Although the location of doped gallium is not evident, we guess the gallium distribution to be uniform in LiNiO_2 and Li^+ is restricted around gallium not to transfer to two hexagonal phases.

Fig. 4 shows the pseudo-OCV curves of the specimens. As the Ga content increases, the shape of the curve becomes smooth. $\text{Li}_{1-x}\text{NiO}_2$ ($0.72 < x < 0.82$) in the specimen of $y=0.02$ would be stabilized, because the plateau region disappears. This is consistent with above-mentioned disappearance of two-hexagonal-phase region.

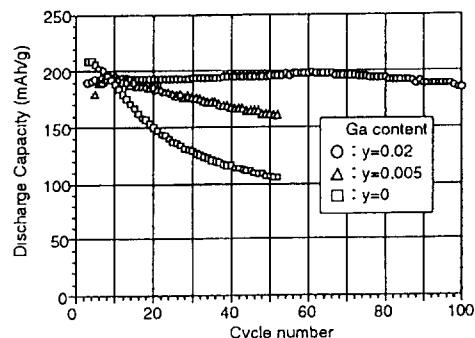


Fig. 5. Cycle characteristics of gallium-doped LiNiO_2 ; current density 36 mA/g, charge: 4.3 V, and discharge: 3.0 V.

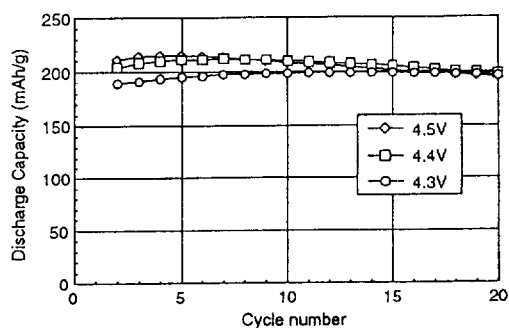


Fig. 6. Cycle characteristics of gallium-doped LiNiO_2 , Ga content $y=0.02$; current density 36 mA/g; charge: 4.3–4.5 V, and discharge: 3.0 V.

It is concluded that the crystal structure of LiNiO_2 during charging process is stabilized by gallium doping.

3.3. Cycling behavior

The cycle characteristics obtained from the cycling test between 3.0 and 4.3 V are given in Fig. 5. With the increase in gallium content, the cycling behavior is obviously improved. Especially the specimen with a Ga content of $y=0.02$ shows high rechargeable capacity of ~ 190 mAh/g and retention of more than 95% after 100 cycles. In the cycling test between 3.0 and 4.4 or 4.5 V, as shown in Fig. 6, the rechargeable capacity reaches ~ 210 mAh/g, and more than 200 mAh/g are retained after 20 cycles. Thus, the gallium-doped LiNiO_2 also demonstrates an excellent over-charge resistance.

4. Conclusions

The gallium-doping to LiNiO_2 stabilizes the crystal structure during the charging process, i.e., single hexagonal struc-

ture is retained all over the charging state without monoclinic phase and without two-hexagonal-phase region. Consequently, the crystal lattice parameters change continuously and gradually improving the cycling behavior at high capacity (~ 190 mAh/g). The gallium-doped LiNiO_2 also demonstrates an excellent over-charge resistance. The thermal stability of the specimen is now under investigation.

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