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Phase transitions during charging and discharging and electrochemical performances of LiNiO₂ doped with gallium

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LiNiO₂ and LiNi_{0.975}Ga_{0.025}O₂ samples were synthesized by the combustion method. The starting materials, in desired proportions, were dissolved in distilled water and mixed with urea by a magnetic stirrer. The mixture was calcined at 750 °C for 36 h in an O₂ stream after preheating at 400 °C for 30 min in air. The phase transitions during charging and discharging and electrochemical performances of the synthesized samples were then investigated. The dQ/|dV| vs. voltage curves, where Q is the charge capacity and V is the voltage, for the charge and discharge of LiNiO₂ and LiNi_{0.975}Ga_{0.025}O₂ at n (number of cycles) = 1 and n = 2 exhibit four peaks, respectively, indicating four phase transitions from a hexagonal structure (H1) to a monoclinic structure (M), from the M to a second hexagonal structure (H2), from the H2 to H2 and a third hexagonal structure (H3), and from the H2 + H3 to H3 or vice versa. LiNi_{0.975}Ga_{0.025}O₂ had a larger first discharge capacity of 166 mA h/g than LiNiO₂. It showed a cycling performance, which is not bad, with a discharge capacity degradation rate of 0.76 mA h/g/cycle from n = 1 to n = 50. LiNiO₂ had a smaller first discharge capacity of 158 mA h/g but a better cycling performance than LiNi_{0.975}Ga_{0.025}O₂ prepared by the combustion method were compared with those of the sample prepared by the solid-state reaction method.

Key words: $LiNi_{1,y}M_yO_2$ (M = Ni or Ga), Combustion method, Phase transitions, Discharge capacity, Cycling performance.

Introduction

Lithium-ion batteries are one of the most favorite types of rechargeable batteries for portable electronic goods [1-9]. LiMn₂O₄ [10-15], LiCoO₂ [16-18], and LiNiO₂ [19-21] have been intensively so that they may be applied to the cathode materials of lithium secondary batteries. LiMn₂O₄ is relatively inexpensive and does not cause environmental contamination, but its cycling performance is unsatisfactory. LiCoO₂ has a large diffusivity and a high operating voltage, and its synthesis is easy. However, it contains an high-priced element, Co. LiNiO₂ has drawn interest as a prospective cathode material since it has a large discharge capacity [22] and is inexpensive and environmentally-friendly. On the other hand, its synthesis is very difficult compared with LiCoO₂ and LiMn₂O₄.

 $Li_{1-x}Ni_{1+x}O_2$ is known to form rather than the stoichiometric LiNiO₂ during synthesis since high-temperature treatment leads to a decomposition of

LiNiO₂ into Li_{1-x}Ni_{1+x}O₂ with partial Ni distribution at Li sites (cation mixing) [23]. This hinders the formation of the ideally layered structure and prevents the lithium ions from undergoing the easy movement, which is necessary for intercalation and deintercalation during cycling. This gives rise to a small discharge capacity and poor cycling performance.

Co [24], Al [25, 26], Ti [27], Ga [22], Mn [28] and Fe [29, 30] were substituted for nickel synthesizing LiNiO₂ in oxygen in order to improve its electrochemical properties. LiNi_{1-y}Al_yO₂ ($0.1 \le y \le 0.50$) specimens were synthesized with a co-precipitation method and their electrochemical properties were examined by Guildmard et al. [25]. They showed that all the phase transitions observed for the LiNiO₂ system were restrained by aluminum substitution. Chang et al. [27] synthesized $Li_xNi_{1-y}Ti_yO_2$ (0.1 \le y \le 0.5) using a solid state reaction and perceived partial disordering between the transition metal (Ni and Ti) layer and lithium by Rietveld refinement. They came to the conclusion, by considering the ionic radius and the Ni-O bond length, that the Ni(II) ions were partially stabilized in the lithium sites. Galliumdoping into LiNiO₂ was investigated by Nishida et al. [22]. They found that it was effective to improve the cycling behavior of LiNiO₂. The obtained specimen

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contained a single phase with a hexagonal structure without any other foreign matters as analyzed by X-ray diffraction measurement. The crystal structure during the charging process was stabilized by gallium doping. The hexagonal structure was retained all over the charging state without a monoclinic phase and without the two hexagonal phase regions which are observed in undoped LiNiO₂. Consequently, the crystal lattice parameters changed continuously and gradually.

 $LiNiO_2$ synthesized by the solid-state reaction method has neither a high discharge capacity nor good cycling performance, possibly because it has poor crystallinity and non-uniform particle size. On the other hand, in the combustion method, the starting materials are liquid and thus homogeneous mixing of the starting materials is possible. This may lead to good crystallinity and uniform particle size.

The range of substituted fraction, y, in LiNi_{1-y}M_yO₂ of many researches was $0.0 \le y \le 0.9$. Results showed that charge and discharge capacities decreased rapidly when y is equal to or larger than 0.025, except when Co was substituted for Ni. Among the LiNi_{1-y}Ga_yO₂ samples synthesized by milling and solid-state reaction method in our previous works [31, 32], a specimen with a composition of LiNi_{0.975} Ga_{0.025}O₂, in which a small amount of Ga was substituted for Ni, showed relatively good electrochemical properties.

In this work, a composition of LiNi_{0.975}Ga_{0.025}O₂ was selected and excess lithium was added to compensate the Li ion evaporated during high temperature synthesis. LiNiO₂ and LiNi_{0.975}Ga_{0.025}O₂ specimens were synthesized by a combustion method with an excess lithium amount z = 0.04 in Li₁₊₂Ni_{1-y}M_yO₂. The phase transitions during charging and discharging and electrochemical performances of the synthesized samples were then investigated. The electrochemical properties of LiNi_{0.975}Ga_{0.025}O₂ prepared by the combustion method were compared with those of the sample prepared by the solid-state reaction method.

Materials and Methods

LiNO₃, Ni(NO₃)₂·6H₂O, and GaNO₃·xH₂O purchased from Aldrich Chemical were used as starting materials.

Lithium was added excessively to make up for the evaporated lithium during synthesis. The excess lithium amount z in $\text{Li}_{1+z}\text{Ni}_{1-y}\text{M}_y\text{O}_2$ was 0.04. The starting materials, in the desired proportions, were dissolved in distilled water and mixed with urea by a magnetic stirrer. The mole ratio of urea to nitrate was 3.6. The mixture was heated to 400 °C in air and that temperature was maintained for 30 min. During that time, the mixture formed ash by a combustion reaction. The ash was then pelletized and calcined at 750 °C for 36 h in an O₂ stream. The heating and cooling rates were about 100 °C/h. These preparation conditions are the optimum ones to synthesize LiNiO₂ by the combustion method

studied in our previous work [33].

The phases of the synthesized samples were identified by X-ray powder diffraction analysis (Rigaku III/A diffractometer) with Cu K α radiation, a scanning rate of 6 °/min, and a range of diffraction angles (2 θ) of 10 ° ≤ 2 θ ≤ 80 °.

The electrochemical cells were made up of LiNi_{1-y} M_yO₂ as a positive electrode, Li foil as a negative electrode, and an electrolyte (Purelyte, Samsung General Chemicals Co., Ltd.) prepared by dissolving 1 M LiPF₆ in a 1 : 1 (volume ratio) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The positive electrode were made up of synthesized materials, acetylene black, and polyvinylidene fluoride (PVDF) binder dissolved in 1-methyl-2-pyrrolidinone (NMP) with a weight ratio of 85 : 10 : 5. A Whatman glass-filter was employed as a separator. The coin-type (2016) cells were assembled in an argon-filled dry box. All of the electrochemical tests were carried out at room temperature with a potentiostatic/galvanostatic system. The assembled cells were cycled between 2.7 and 4.4 V at the rate of 0.1 C.

Results and Discussion

Fig. 1 shows the XRD pattern of $\text{LiNi}_{0.975}\text{Ga}_{0.025}\text{O}_2$ synthesized with an excess lithium amount z in $\text{Li}_{1+z}\text{Ni}_{1-y}$ $M_y\text{O}_2$ equal to 0.04. This sample possesses the α -NaFeO₂ structure of the rhombohedral system (space group; $R\overline{3}m$) with no evidence of any impurities.

According to Ohzuku et al. [34], electrochemically reactive LiNiO₂ showed a larger integrated intensity ratio of the 003 peak to the 104 peak (I_{003}/I_{104}) and a clear split of the 108 and 110 peaks in its XRD patterns. The degree of cation mixing, which is the displacements of nickel and lithium ions, is low if the value of I_{003}/I_{104} is large and the 108 and 110 peaks are split clearly. The value of ($I_{006} + I_{102}$)/ I_{101} is called the R-factor, and is known to decrease as the unit cell volume of Li_yNi_{2-y}O₂ decreases. The R-factor increases



Fig. 1. XRD pattern of $LiNi_{0.975}Ga_{0.025}O_2$ synthesized with an excess lithium amount z = 0.04.

	a (Å)	c (Å)	c/a	Unit cell volume (Å ³)	I_{003}/I_{104}	$\frac{\text{R-factor}}{((I_{006}+I_{102})/I_{101})}$
LiNiO ₂	2.884	14.212	4.928	102.367	1.238	0.526
$L11N1_{0.975}Ga_{0.025}O_2$	2.882	14.212	4.931	102.244	1.232	0.532

Table 1. Values of unit cell volume, I₀₀₃/I₁₀₄, and R-factor for LiNiO₂ and LiNi_{0.975}Ga_{0.025}O₂.



Fig. 2. Curves of voltage vs. x in $Li_xNi_{0.975}Ga_{0.025}O_2$ at 0.1 C rate for the first charge-discharge of $LiNi_{0.975}Ga_{0.025}O_2$.



Fig. 3. Voltage vs. discharge capacity curves at 0.1 C rate at the first cycle for $LiNiO_2$ and $LiNi_{0.975}Ga_{0.025}O_2$.

as the y in $Li_yNi_{2-y}O_2$ decreases for y near 1. This indicates that the R-factor increases as the degree of cation mixing becomes larger [19].

Table 1 presents the values of unit cell volume, I_{003}/I_{104} , and R-factor for LiNi_{0.975}Ga_{0.025}O₂ and LiNiO₂. The values of these parameters for LiNiO₂ were given in our previous work [35]. The unit cell volume of LiNi_{0.975}Ga_{0.025}O₂ is smaller than that of LiNiO₂. LiNi_{0.975}Ga_{0.025}O₂ has a larger I_{003}/I_{104} and a larger R-factor than LiNiO₂. When I_{003}/I_{104} is smaller than 1.2, cation mixing occurs. On the other hand, when I_{003}/I_{104} is larger than 1.2, the composition of the sample is completely stoichiometric [23, 36]. The values of I_{003}/I_{104} for LiNiO₂ (1.238) and LiNi_{0.975}Ga_{0.025}O₂ (1.252) are larger than 1.2. This indicates that LiNiO₂ and LiNi_{0.975}Ga_{0.025}O₂ have the stoichiometric composition.

The curves of voltage vs. x in Li_xNi_{0.975}Ga_{0.025}O₂ at 0.1



Fig. 4. Curves of voltage vs. x in $Li_xNi_{0.975}Ga_{0.025}O_2$ at 0.1 C rate for the first and second charge-discharge cycles of $LiNi_{0.975}Ga_{0.025}O_2$.



Fig. 5. Curves of dQ/|dV| vs V for the first and second chargedischarge cycles of (a) LiNiO₂ (b) LiNi_{0.975}Ga_{0.025}O₂.

C rate for the first charge-discharge of $LiNi_{0.975}Ga_{0.025}O_2$ are shown in Fig. 2. Long plateaus in the charge and

discharge curves correspond to large charge and discharge capacities, respectively. Quite a large difference in x of the first charge and discharge curves reveals quite a larger first charge capacity than the first discharge capacity. Quite a large difference between the first charge capacity and the first discharge capacity is known to be due to the layer formed at the interface between the electrode and electrolyte [37]. When the voltage vs. x curves for $\text{Li}_x\text{Ni}_{0.975}\text{Ga}_{0.025}\text{O}_2$ are observed in detail, the charge and discharge curves exhibit several plateaus. This indicates that phase transitions occur at several different voltages in the electrode fabricated with $\text{LiNi}_{0.975}\text{Ga}_{0.025}\text{O}_2$.

The voltage vs. discharge capacity curves at 0.1 C rate at the number of cycle, n, of one for LiNiO_2 and $\text{LiNi}_{0.975}\text{Ga}_{0.025}\text{O}_2$ are shown in Fig. 3. The curves exhibit several plateaus, indicating that phase transitions occur at several different voltages in these electrodes. $\text{LiNi}_{0.975}\text{Ga}_{0.025}\text{O}_2$ (166 mA h/g) has a larger first discharge capacity than LiNiO_2 (158 mA h/g).

The curves of voltage vs. x in $Li_xNi_{0.975}Ga_{0.025}O_2$ at 0.1 C rate for the first and second charge-discharge cycles are shown in Fig. 4. The second charge capacity is much smaller than the first charge capacity and slightly larger than the second discharge capacity. The second charge and discharge curves also exhibit several plateaus, indicating that phase transitions occur at several different voltages in these electrodes.

Fig. 5 shows the curves of dQ/|dV| vs. V for the first and second charge-discharge cycles of LiNiO₂ and LiNi_{0.975}Ga_{0.025}O₂. Here, Q is the charge capacity and V is the voltage. The area surrounded by the charging and discharging curves is proportional to the sum of the charge and discharge capacities. The areas for the first cycle are larger than those for the second cycle. The dQ/|dV| vs. voltage curves for the charge and discharge of LiNiO₂ and LiNi_{0.975}Ga_{0.025}O₂ at n = 1 and n = 2exhibit four peaks, respectively, indicating that phase transitions occur at four different voltages in the electrodes fabricated with these samples. A peak in the dQ/|dV| vs. voltage curve corresponds to a plateau in the voltage vs. x in Li_xNiO₂ or Li_xNi_{0.975}Ga_{0.025}O₂ curve, where two phases co-exist [38]. Arai et al. [39] reported that during charging and discharging, LiNiO₂ goes through three phase transitions; the phase transitions from a hexagonal structure (H1) to a monoclinic structure (M), from the monoclinic structure (M) to a second hexagonal structure (H2), and from the second hexagonal structure (H2) to a third hexagonal structure (H3) or vice versa. Ohzuku et al. [34] reported that, during charging and discharging, LiNiO₂ goes through four phase transitions; the phase transitions from H1 to M, from the M to H2, from the H2 to hexagonal structures H2+H3, and from the H2 + H3 to H3 or vice versa. The four peaks in the dQ/|dV| vs. voltage curves for the charge and discharge of LiNiO₂ and LiNi_{0.975}Ga_{0.025}O₂ at n = 1 and n = 2 show the phase transitions from H1 to M, from the M to H2, from the H2 to hexagonal



Fig. 6. Variation of discharge capacity with the number of cycles, n, for LiNiO₂ and LiNi_{0.975}Ga_{0.025}O₂ from n = 1 to n = 50.



Fig. 7. Variations of discharge capacity with the number of cycles for the LiNi_{0.975}Ga_{0.025}O₂ samples synthesized by the combustion method and by the solid-state reaction method from n = 1 to n = 20.

structures H2 + H3, and from the H2 + H3 to H3 or vice versa. The dQ/|dV| vs. voltage curves of $Li_{1+z}NiO_2$ (z = 0.08, 0.10, 0.12, and 0.15) for charging and discharging showed four peaks [40], revealing four phase transitions from H1 to M, from the M to H2, from the H2 to H2 + H3, and from the H2 + H3 to H3 or vice versa. Song et al. [41] reported that -dx/|dV| vs. V curves of $LiNi_{1-y}Ti_yO_2$ (y = 0.012 and 0.025) for charging and discharging also showed four peaks.

Fig. 6 shows the variation of discharge capacity with the number of cycles, n, for LiNiO₂ and LiNi_{0.975}Ga_{0.025}O₂ from n = 1 to n = 50. LiNi_{0.975}Ga_{0.025}O₂ has a higher first discharge capacity (166 mA h/g) than LiNiO₂ (158 mA h/g). It shows a cycling performance, which is not bad, with a discharge capacity degradation rate of 0.76 mA h/g/ cycle. LiNiO₂ has a smaller first discharge capacity but a better cycling performance than LiNi_{0.975}Ga_{0.025}O₂ with a discharge capacity degradation rate of 0.45 mA h/g/cycle.

 $LiNi_{0.975}Ga_{0.025}O_2$ with a larger first discharge capacity than $LiNiO_2$ has a higher discharge capacity degradation

rate than LiNiO2. A larger first discharge capacity corresponds to a larger amount of intercalation of Li, which is related to the wider change in the value of x in Li_xNiO₂ or Li_xNi_{0.975}Ga_{0.025}O₂. The larger change in the value of x will cause larger expansion and contraction of the LiNiO₂ phase with the α -NaFeO₂ structure due to intercalation and deintercalation. This will make the structure strained and distorted. With cycling, the interstitial sites and thus the α -NaFeO₂ structure will be destroyed. This decreases the fraction of the phase with the α -NaFeO₂ structure, leading to capacity fading of the sample with cycling. For the samples with smaller discharge capacity, the expansion and contraction due to intercalation and deintercalation can be within the limit of elasticity of the samples, and the lattice destruction can thus be small. The discharge capacity can accordingly decrease slowly with cycling (i.e., the capacity fading rate can be low).

Fig. 7 shows the variations of discharge capacity with the number of cycles for the LiNi_{0.975}Ga_{0.025}O₂ samples synthesized by the combustion method and by the solid-state reaction method from n = 1 to n = 20. To synthesize the sample by the solid-state reaction method, a mixture with a composition of LiNi_{0.975}Ga_{0.025}O₂, using starting materials LiOH·H₂O (Kojundo Chemical Lab. Co., Ltd, purity 99%), Ni(OH)₂ (Kojundo Chemical Lab. Co., Ltd, purity 99.9%), Ga₂O₃ (Aldrich Chemical, purity 99%), was prepared by wet SPEX milling under distilled acetone for 1 h, and dried in a shaking incubator with 50 rpm at 50 °C for 48 h. The mixture was then preheated at 450 °C for 5 h in air, pressed into pellets, and calcined at 750 °C for 30 h under an oxygen stream. The sample synthesized by the combustion method has a larger first discharge capacity (166 mA h/g) than that synthesized by the solid-state reaction method (162 mA h/g), with a smaller discharge capacity degradation rate of 1.59 mA h/g/cycle than that of the sample synthesized by the solid-state reaction method (2.97 mA h/g/cycle). The LiNi_{0.975}Ga_{0.025}O₂ sample synthesized by the combustion method has a discharge capacity degradation rate of 1.23 mA h/g/cycle from the fourth cycle to the 20th cycle. The larger first discharge capacity and better cycling performance of the LiNi_{0.975}Ga_{0.025}O₂ synthesized using the combustion method are believed to result from the better crystallinity and higher uniformity of the particle size of the sample synthesized using the combustion method than that synthesized using the solid-state reaction method.

Conclusions

LiNiO₂ and LiNi_{0.975}Ga_{0.025}O₂ samples were synthesized by a combustion method. The dQ/|dV| vs. voltage curves, where Q is the charge capacity and V is the voltage, for the charge and discharge of LiNiO₂ and LiNi_{0.975}Ga_{0.025}O₂ at n = 1 and n = 2 exhibit four peaks, respectively, indicating four phase transitions from a hexagonal structure (H1) to a monoclinic structure (M), from the M to a second hexagonal structure (H2), from the H2 to H2 and a third hexagonal structure (H3), and from the H2 + H3 to H3 or vice versa. LiNi_{0.975}Ga_{0.025}O₂ had a larger first discharge capacity of 166 mA h/g than LiNiO₂. It showed a cycling performance, which is not bad, with a discharge capacity degradation rate of 0.76 mA h/g/cycle from n = 1 to n = 50. LiNiO₂ had a smaller first discharge capacity of 158 mA h/g but a better cycling performance than LiNi_{0.975}Ga_{0.025}O₂ with a discharge capacity degradation rate of 0.45 mA h/g/cycle from n = 1 to n = 50. LiNi_{0.975}Ga_{0.025}O₂ with a larger first discharge capacity than LiNiO₂ has a higher discharge capacity degradation rate due to larger expansion and contraction of the LiNiO₂ phase with the α -NaFeO₂ structure according to intercalation and deintercalation. LiNi_{0.975}Ga_{0.025}O₂ prepared by the combustion method had better electrochemical properties than that prepared by the solid-state reaction method.

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