

## Electrochemical properties of $\text{Li}_{1+x}(\text{Ni}_{1-y}\text{Ga}_y)\text{O}_2$ cathode material synthesized by emulsion method

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To investigate the effect of Li excess and Ni substitution with Ga, powder was prepared by emulsion method and calcined at various temperatures for various times. The optimum condition for the synthesis of  $\text{Li}_{1+x}\text{NiO}_2$  was to be calcined at 750 °C for 24 hrs in the oxygen stream. The amount of lithium excess was determined as  $x = 0.12$  in  $\text{Li}_{1+x}\text{NiO}_2$  composition. The optimum condition for the synthesis of  $\text{LiNi}_{1-y}\text{Ga}_y\text{O}_2$  was to be calcined at 700 °C for 36 hrs in the oxygen stream. The amount of Ga substitution was decided as  $y = 0.01$  in  $\text{LiNi}_{1-y}\text{Ga}_y\text{O}_2$  composition. From the results of the amount of lithium excess and Ga substitution,  $\text{Li}_{1.12}\text{Ni}_{0.99}\text{Ga}_{0.01}\text{O}_2$  composition was selected in this experiment. The emulsion-derived powder of this composition was synthesized at 700 °C for 36 hrs. The initial and final discharge capacities after 20 cycles were 158 and 121 mAh/g, respectively. The fading rate in discharge capacity after 20 cycles was 23%.

**Key words:**  $\text{LiNiO}_2$ , Lithium excess, Emulsion Method, Gallium doping, Electrochemical properties.

### Introduction

$\text{LiNiO}_2$  is one of promising cathode materials for lithium ion secondary battery because of its high capacity and relatively excellent economic and environmental pollution characteristics compared with  $\text{LiCoO}_2$  [1, 2]. However,  $\text{LiNiO}_2$  is known to exhibit the unstable crystal structure due to the cation mixing and severe capacity fading during the charge-discharge cycle. To improve the electrochemical properties of  $\text{LiNiO}_2$ , several cations have been added into  $\text{LiNiO}_2$  to substitute for Ni [3, 4].

It has been reported that  $\text{Ni}^{2+}$  occupied 7% of the Li site in  $\text{LiNiO}_2$  crystal structure [5] and Ga-doped  $\text{LiNiO}_2$  showed superior rechargeable capacity and retention of more than 95% after 100 cycles [6]. Therefore in this experiment, the effect of Li excess and Ga substitution of Ni in  $\text{LiNiO}_2$  was studied.  $\text{Li}_{1+x}\text{NiO}_2$  ( $0 \leq x \leq 0.16$ ) and  $\text{LiNi}_{1-y}\text{Ga}_y\text{O}_2$  ( $0 \leq y \leq 0.10$ ) compositions were chosen to investigate the effect of the lithium excess and Ga substitution. From the results of these experiments, finally  $\text{Li}_{1+x}\text{Ni}_{1-y}\text{Ga}_y\text{O}_2$  composition was studied to investigate the electrochemical properties.

The emulsion method was adopted to prepare the powder of  $\text{Li}_{1+x}\text{Ni}_{1-y}\text{Ga}_y\text{O}_2$  composition. This method is well known as being very effective in the homogeneous

synthesis of multi-component system materials because the organic phase divides the precursor solution into colloids of water-in oil type by high speed rotation. All of these colloids, i.e., emulsions, are spherical with uniform composition which suggests that the crystalline solid of the multi-component system could be synthesized easily at the proper calcination temperature by the simple decomposition and reaction of the emulsion-derived powder [7-9]. This emulsion method will be more preferable for the synthesis of  $\text{Li}_{1+x}\text{Ni}_{1-y}\text{Ga}_y\text{O}_2$  powders than any other process.

### Experimental Procedure

$\text{LiOH} \cdot \text{H}_2\text{O}$  (99.95%, Aldrich Chemical Company, Inc.),  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (99.99%, High Purity Chemicals, Japan), and  $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  (99.9%, Aldrich, USA) were chosen as starting materials and dissolved into distilled water. The homogeneous precursor solution (0.5 mol/L for the  $\text{Li}_{1+x}\text{Ni}_{1-y}\text{Ga}_y\text{O}_2$  composition) was made by mixing of each aqueous solution on a magnetic stirrer for 24 hrs. The water-in-oil type emulsion of  $\text{Li}_{1+x}\text{Ni}_{1-y}\text{Ga}_y\text{O}_2$  composition was prepared by rotating the mixture of precursor solution and organic phase in the ratio of 2 : 1 at 4000 rpm for 5 min. The emulsion was sprayed into the kerosene heated to 170 °C and dried at 120 °C in the oven to evaporate the water and kerosene included in the emulsion. As-dried powders were calcined at various temperatures for various times in an oxygen stream with heating and cooling rates of 1 °C/min.

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The calcined powders were examined by an X-ray diffractometer (XRD, Rigaku, D/MAX-111A) and scanning electron microscope (SEM, JEOL JSM-6400). The electrochemical properties were measured at room temperature with a half cell of Li metal/electrolyte 1M LiPF<sub>6</sub>-ethylene carbonate (EC) and dimethyl carbonate (DMC) (1 : 1 in volume)/cathode material. The positive materials consisted of Li<sub>1+x</sub>Ni<sub>1-y</sub>Ga<sub>y</sub>O<sub>2</sub> powder, acetylene black and PTFE at the ratio of 88 : 10 : 2 by weight. Lithium foil and glass microfibre filter were used for the anode and separator, respectively. The cells were automatically charged and discharged in the range of between 2.7 and 4.2 V at 9.5 mAh/g for 20 cycles.

## Results and Discussion

In the previous work, LiNiO<sub>2</sub> powder calcined at 750 °C for 24 hrs showed the highest rechargeable capacity and retention of capacity with cycle [10]. This condition was adopted to synthesize LiNiO<sub>2</sub> with lithium excess for the investigation of the optimum amount of Li excess. Li<sub>1+x</sub>NiO<sub>2</sub> (0.00 ≤ x ≤ 0.16) composition was chosen. The emulsion-derived powder was calcined at 750 °C for 24 hrs.

XRD patterns of these calcined powders are shown in Fig. 1. All the observed XRD peaks of the calcined powders are identified as the single LiNiO<sub>2</sub> layered crystal structure only. From the intensities of these XRD spectrums, the intensity ratios of (003) to (104) peaks ( $I_{003}/I_{104}$  ratio) were calculated and shown in Fig. 2. The value of  $I_{003}/I_{104}$  is generally used to examine the crystallinity of layered structure [11, 12]. The value of  $I_{003}/I_{104}$  increased from 1.24 to 1.52 until x = 0.12 and then decreased to 1.40 above x = 0.12.

The highest  $I_{003}/I_{104}$  value, 1.52 was obtained at x = 0.12 in Li<sub>1+x</sub>NiO<sub>2</sub>. It is considered that the crystallinity of this composition was well developed compared with other compositions. In the work of the oxygen pressure effect on the synthesis of LiNiO<sub>2</sub>, LiNiO<sub>2</sub> single phase was formed under the oxygen gas pressure except air atmosphere but the Ni<sup>2+</sup> content which occupied Li<sup>+</sup> site of LiNiO<sub>2</sub> was in the range of 9.0 ~ 7.0% [5]. Addition of excess Li to LiNiO<sub>2</sub>

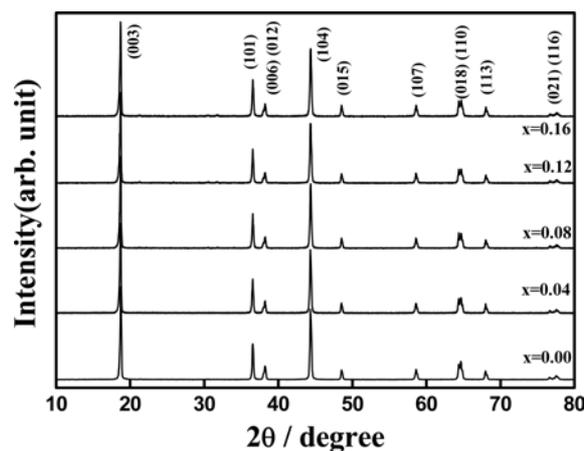


Fig. 1. XRD patterns of Li<sub>1+x</sub>NiO<sub>2</sub> powders synthesized at 750 °C for 24 hrs.

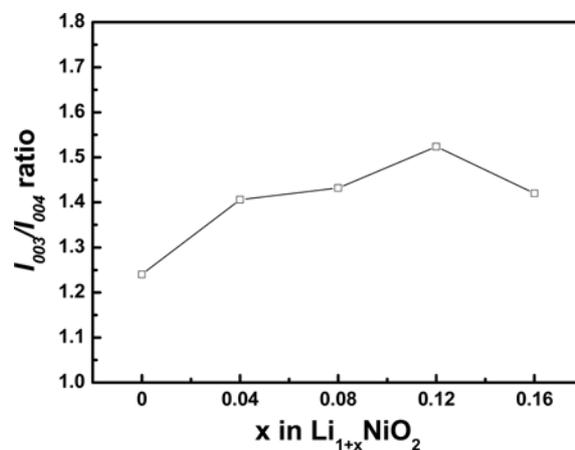


Fig. 2.  $I_{003}/I_{104}$  ratio of Li<sub>1+x</sub>NiO<sub>2</sub> powders synthesized at 750 °C for 24 hrs.

increased  $I_{003}/I_{104}$  to the highest value of 1.52 at x = 0.12 in the Li<sub>1+x</sub>NiO<sub>2</sub>. This is considered that addition of excess Li to LiNiO<sub>2</sub> decreased cation mixing of Li<sup>+</sup> with Ni<sup>2+</sup> in the LiNiO<sub>2</sub> crystal structure because LiNiO<sub>2</sub> has 9.0 ~ 7.0% of cation mixing even though the stoichiometric LiNiO<sub>2</sub> composition.

Lattice parameter of the synthesized Li<sub>1+x</sub>NiO<sub>2</sub> powders was calculated from XRD patterns and shown in Fig. 3. In Fig. 3, lattice parameter of a axis decreased and that of c axis increased with increasing

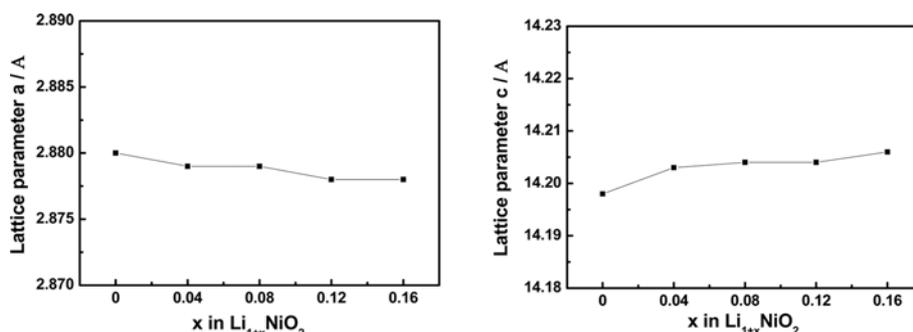


Fig. 3. Lattice parameter changes with increasing Li excess in Li<sub>1+x</sub>NiO<sub>2</sub>.

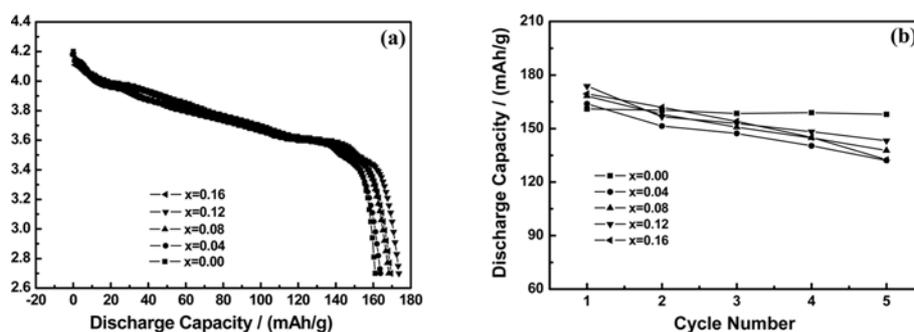


Fig. 4. First discharge capacities (a) and capacity changes with cycle (b) of the powders with lithium excess.

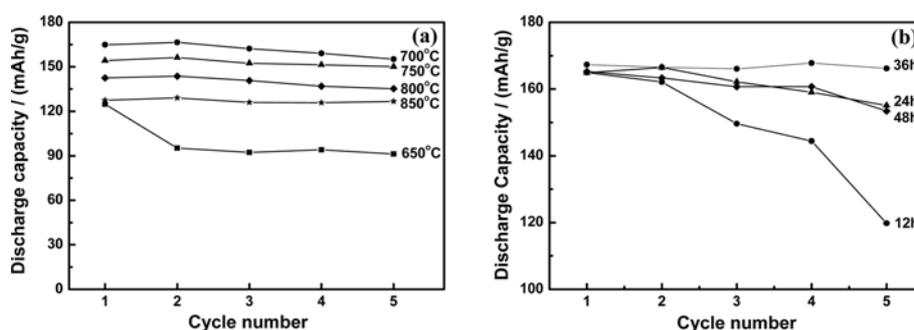


Fig. 5. The discharge capacities of powders calcined at various (a) temperatures and (b) times.

the amount of Li excess. In the research of the oxygen pressure effect on the synthesis of  $\text{LiNiO}_2$  [5], the degree of cation mixing in Li site of  $\text{LiNiO}_2$  lowered as the oxygen pressure increased and was determined to be related to the change of lattice parameter. Lower degree of cation mixing decreased lattice parameter of a axis and increased that of c axis. However, lattice parameter was not so different on the amount of Li excess.

As discussed above, Li excess in  $\text{Li}_{1+x}\text{NiO}_2$  increased  $I_{003}/I_{104}$  ratio and changed the lattice parameter. However the lattice parameter change with lithium excess is not so different. It is considered that lattice parameter change is from the decrease of the cation mixing in  $\text{LiNiO}_2$  because lattice parameter of a axis decreased and that of c axis increased with decreasing cation mixing as reported in the previous work [5].

The first through fifth cycle discharge capacities of  $\text{Li}_{1+x}\text{NiO}_2$  calcined powder with addition of Li excess are shown in Fig. 4. The first discharge capacity increased to the maximum value of 174 mAh/g at  $x = 0.12$  and then decreased above  $x = 0.12$  in  $\text{Li}_{1+x}\text{NiO}_2$  as shown in Fig. 4(a). However, the cyclic rechargeable capacity of the compositions with Li excess became lower than those of  $\text{LiNiO}_2$  without Li excess. From the higher  $I_{003}/I_{104}$  and first discharge capacity of the compositions with lithium excess, it is considered that the excess lithium developed the crystal structure by decreasing the degree of cation mixing in Li site with  $\text{Ni}^{2+}$ , but excess lithium also hindered the intercalation-deintercalation of  $\text{Li}^+$  in cyclic charge-discharge process.

The composition substituted a part of Ni with Ga was

fixed as  $\text{LiNi}_{0.99}\text{Ga}_{0.01}\text{O}_2$  because this composition showed the highest electrochemical properties in  $\text{LiNi}_{1-y}\text{Ga}_y\text{O}_2$  [13]. The emulsion-derived powder of this composition was calcined at various temperatures and times. The first through fifth cycle discharge capacities of these calcined powders are shown in Fig. 5. In Fig. 5(a), the powder calcined at 700 °C for 24 hrs shows the highest discharge and rechargeable capacity. To investigate the optimum holding time, emulsion-derived powder was calcined at 700 °C for various times. The discharge capacities of powders calcined for various times are shown in Fig. 5(b). It is seen that the powder calcined for 36 hrs has the highest discharge and rechargeable capacity.

From the results of the above experiment, the amount of lithium excess and Ga are fixed as  $x = 0.12$  and

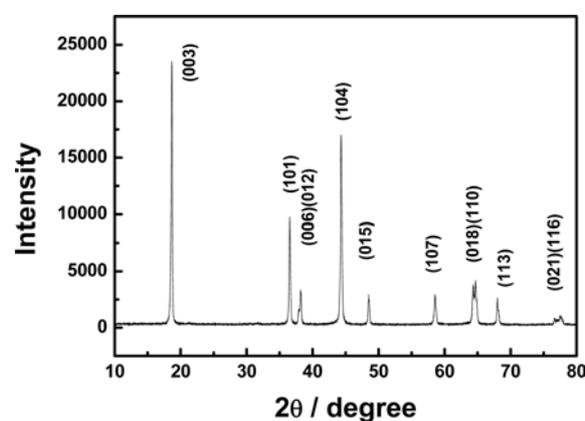


Fig. 6. XRD pattern of  $\text{Li}_{1.12}\text{Ni}_{0.99}\text{Ga}_{0.01}\text{O}_2$  powder calcined at 700 °C for 36 h.

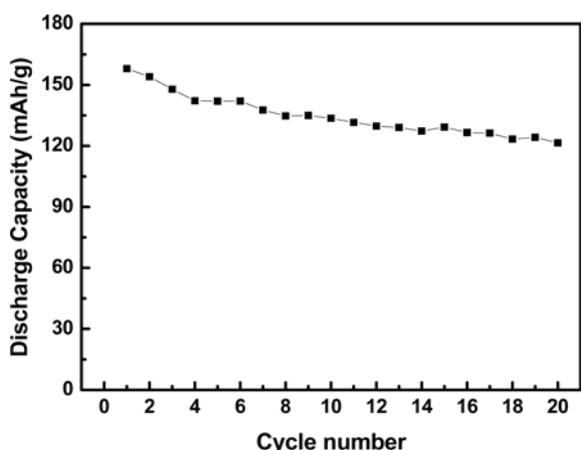


Fig. 7. The rechargeable capacity changes of  $\text{Li}_{1.12}\text{Ni}_{0.99}\text{Ga}_{0.01}\text{O}_2$  with increasing charge-discharge cycle.

$y = 0.01$  at  $\text{Li}_{1+x}\text{Ni}_{1-y}\text{Ga}_y\text{O}_2$  in the following experiment because this composition has higher  $I_{003}/I_{104}$  and first discharge capacity than any other composition. The powder of  $\text{Li}_{1.12}\text{Ni}_{0.99}\text{Ga}_{0.01}\text{O}_2$  was prepared by emulsion method and calcined at  $700^\circ\text{C}$  for 36 hrs. Fig. 6 shows the XRD pattern of this synthesized powder. This XRD peak was identified as a single  $\text{LiNiO}_2$  layered structure only.

Fig. 7 shows the cyclic rechargeable capacity of  $\text{Li}_{1.12}\text{Ni}_{0.99}\text{Ga}_{0.01}\text{O}_2$ . The first discharge capacity and retention of cyclic capacity of this composition during 20 cycles was 158 mAh/g and 77%. However the retention of cyclic capacity was 77%, lower than 93.4% of  $\text{LiNi}_{0.99}\text{Ga}_{0.01}\text{O}_2$  without lithium excess. Addition of Li excess in  $\text{Li}_{1.12}\text{Ni}_{0.99}\text{Ga}_{0.01}\text{O}_2$  decreased the cyclic rechargeable capacity.

### Conclusions

$\text{Li}_{1+x}\text{Ni}_{1-y}\text{Ga}_y\text{O}_2$  ( $0 \leq x \leq 0.16$ ,  $0 \leq y \leq 0.10$ ) were synthesized to investigate the effect of lithium excess and Ga substitution.

1. Addition of Li excess to  $\text{Li}_{1+x}\text{NiO}_2$  increased first discharge capacity but decreased cyclic rechargeable capacity.

2. The composition,  $\text{LiNi}_{1-y}\text{Ga}_y\text{O}_2$  substituted by Ga showed the higher first discharge and cyclic rechargeable capacity.

3. The composition with Li excess and Ga substitution,  $\text{Li}_{1.12}\text{Ni}_{0.99}\text{Ga}_{0.01}\text{O}_2$  showed lower first discharge capacity and cyclic rechargeable capacity than the composition without Li excess.

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