

Electrochemical properties of $\text{LiNi}_{1-y}\text{Ga}_y\text{O}_2$ cathode materials synthesized by emulsion method

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Gallium doped LiNiO_2 , $\text{LiNi}_{1-y}\text{Ga}_y\text{O}_2$, was synthesized using the emulsion method. The emulsion-derived powder was calcined at a temperature range of 650 to 850 °C for 1248 hrs. A single phase of $\text{LiNi}_{1-y}\text{Ga}_y\text{O}_2$ was obtained at 650 °C. 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 an oxygen stream. The composition of $\text{LiNi}_{0.990}\text{Ga}_{0.010}\text{O}_2$ showed the largest discharge capacity. The initial and final discharge capacities after 20 cycles were 167.3 mAh/g and 156.2 mAh/g, respectively. The fading rate was only 6.6% after 20 cycles of charge-discharge.

Key words: Cathode material, $\text{LiNi}_{1-y}\text{Ga}_y\text{O}_2$, Emulsion method, Charge-discharge

Introduction

LiMO_2 system compounds, where M is Ni, Co, Mn, have been intensively investigated over the past two decades as cathode materials for rechargeable lithium ion secondary batteries [1-4]. Among these compounds, LiNiO_2 is one of the most promising cathode materials due to its high energy density, low cost, and relatively good environmental characteristics compared with LiCoO_2 compound [5, 6]. However, the unstable structure of LiNiO_2 , which has a nonstoichiometric composition of $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$, leads to severe capacity fading. This phenomenon is the result of cation mixing of Ni^{2+} at Li and Ni^{3+} in LiNiO_2 during charge-discharge. In order to improve the above problem, several cations have been added to the LiNiO_2 system to substitute for Ni [7, 8]. In this experiment, Gallium (Ga) was chosen as the substituent of Ni to form a composition of $\text{LiNi}_{1-y}\text{Ga}_y\text{O}_2$ ($y = 0.0 \sim 0.1$), and the effect of Ga substitution for Ni, phase transition with synthesis condition, and electrochemical properties were then investigated.

Experimental Procedure

The $\text{LiNi}_{1-y}\text{Ga}_y\text{O}_2$ system was synthesized using the emulsion method. 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. $\text{LiOH} \cdot \text{H}_2\text{O}$ (99.95%, Aldrich Chemical Company, Inc. U.S.A), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.9%, High Purity Chemicals, Japan), and $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (99.9%, Aldrich Chemical Company, Inc. U.S.A) were chosen as starting materials. These materials were dissolved in distilled water and mixed with a magnetic stirrer for 24 hrs to prepare a homogeneous precursor solution (0.5 mol/l for the $\text{LiNi}_{1-y}\text{Ga}_y\text{O}_2$ composition). The organic phase for emulsifying was prepared with the same composition and using the same process as that previously reported [9, 10]. The precursor solution and organic phase were mixed at the ratio of 2 : 1 and emulsified to a water-in-oil type emulsion at a rotational speed of 4000 rpm for 5 minutes. The emulsion was sprayed into the kerosene heated to 170 °C and dried at 120 °C in the oven. As-dried powders were calcined at various temperatures with the heating/cooling rate of 1 °C /min. The crystal phase of the calcined powder was examined using an X-ray diffractometer (XRD: Rigaku, D/MAX-111A). The shape of the resultant particles and the microstructure were observed with a scanning electron microscope (SEM: JEOL JSM6400). The electrochemical properties of the samples were tested at room temperature for 20 cycles with a half cell fabricated as Li metal/electrolyte 1 M LiPF_6 /ethylene carbonate (EC) and dimethyl carbonate (DMC) (1 : 1 in volume)/positive material. The positive electrode consisted of $\text{LiNi}_{1-y}\text{Ga}_y\text{O}_2$ powder as the cathode material, acetylene black as the conductor, and (PTFE) as the binder at the ratio of 88 : 10 : 2 by weight. Lithium foil and a glass micro-fiber filter (GF/A, Whatman) were used for the anode and separator, respectively. The cells were automatically charged and discharged between 2.7 V and 4.2 V at 9.5 mA/g.

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Results and Discussion

Among the $\text{LiNi}_{1-y}\text{Ga}_y\text{O}_2$ ($0.00 \leq y \leq 0.100$) compositions, $\text{LiNi}_{0.990}\text{Ga}_{0.010}\text{O}_2$ was selected to investigate the particle shape and optimum calcination temperature with time. The XRD pattern and SEM photograph of the as-dried powder of the $\text{LiNi}_{0.990}\text{Ga}_{0.010}\text{O}_2$ composition are shown in Fig. 1. The XRD pattern was identified as being composed of the crystal phases of $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$ and LiNO_3 . While these phases formed during drying differ from the starting materials, the Ga compound is not shown in this figure. This means that these crystal phases were formed during drying by the reaction of various component ions such as Li^+ , Ni^{2+} , and NO_3^- which were dissolved in the water. The SEM image of as-dried powder shows an agglomerated shape with nano-sized particles.

Fig. 2 shows the XRD patterns, the intensity ratios of (103) to (104) peak (I_{103}/I_{104} ratios) and the cyclic discharge capacities of the $\text{LiNi}_{0.990}\text{Ga}_{0.010}\text{O}_2$ powder synthesized at $650 \sim 850^\circ\text{C}$ for 24 hrs under a stream of oxygen gas. Fig. 2(a) shows that a Li_2CO_3 phase was not formed during the calcination of the emulsion-derived powder due to the reaction between Li^+ and the organic phase, and remained as an unreacted phase. All the powders calcined above 650°C exhibited a single

phase of the layered structure. The analysis of these XRD patterns indicated that the $\text{LiNi}_{0.990}\text{Ga}_{0.010}\text{O}_2$ single phase could be synthesized above 650°C . Fig. 2(b) shows that the I_{103}/I_{104} ratios increased to a maximum value of 1.326 at 700°C and then decreased with increasing temperature. It has been reported that the I_{103}/I_{104} ratios can be used as a reliable quantitative criterion for cation mixing and a higher value of this ratio indicates less cation mixing (becomes a near stoichiometric composition) [11]. Fig. 2(c) shows that the first discharge capacity increased to the maximum

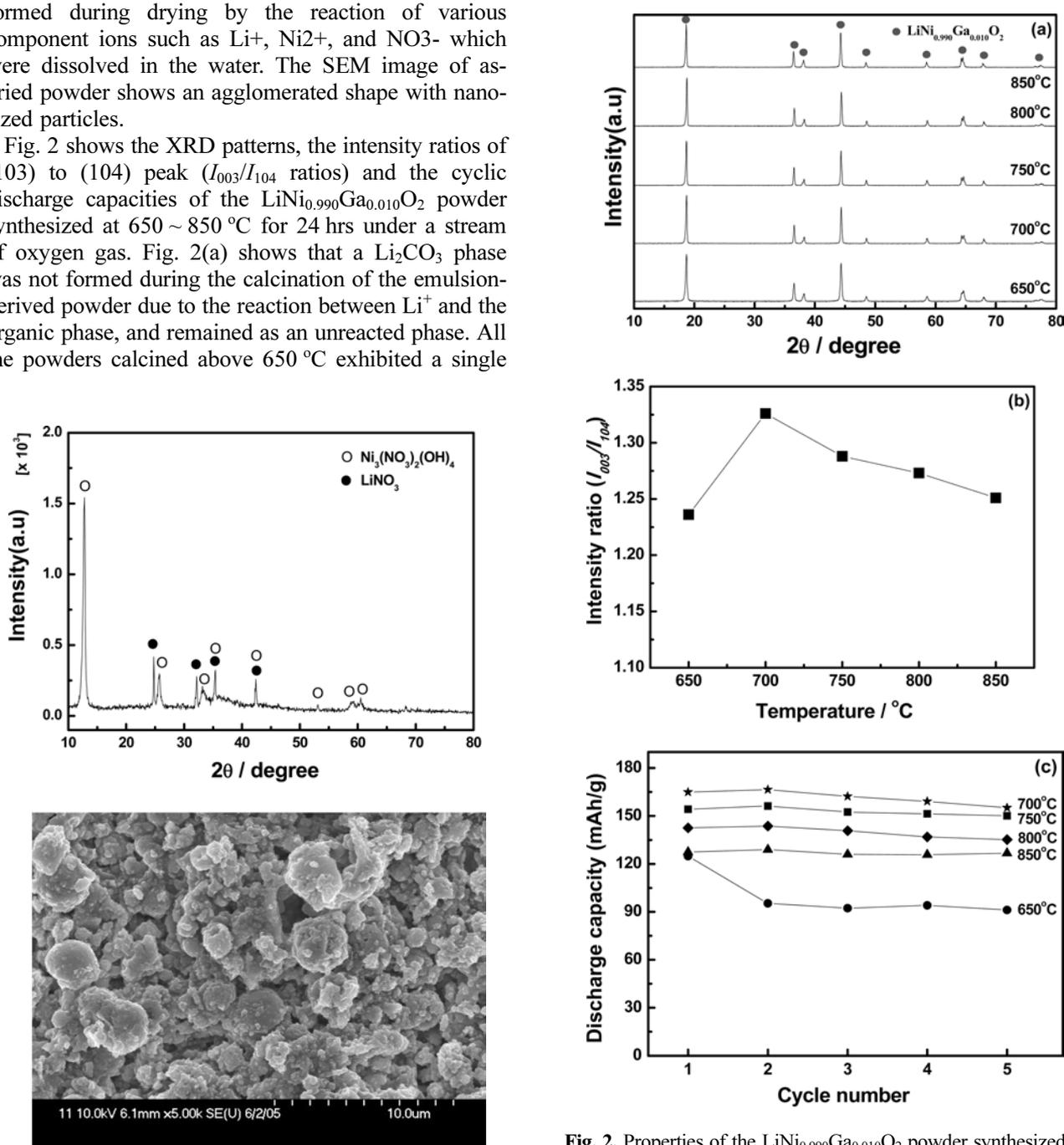


Fig. 1. XRD pattern and SEM image of as-dried powder

Fig. 2. Properties of the $\text{LiNi}_{0.990}\text{Ga}_{0.010}\text{O}_2$ powder synthesized at $650 \sim 850^\circ\text{C}$ for 24 hrs: (a) XRD patterns, (b) I_{103}/I_{104} ratios, and (c) cycle discharge capacities.

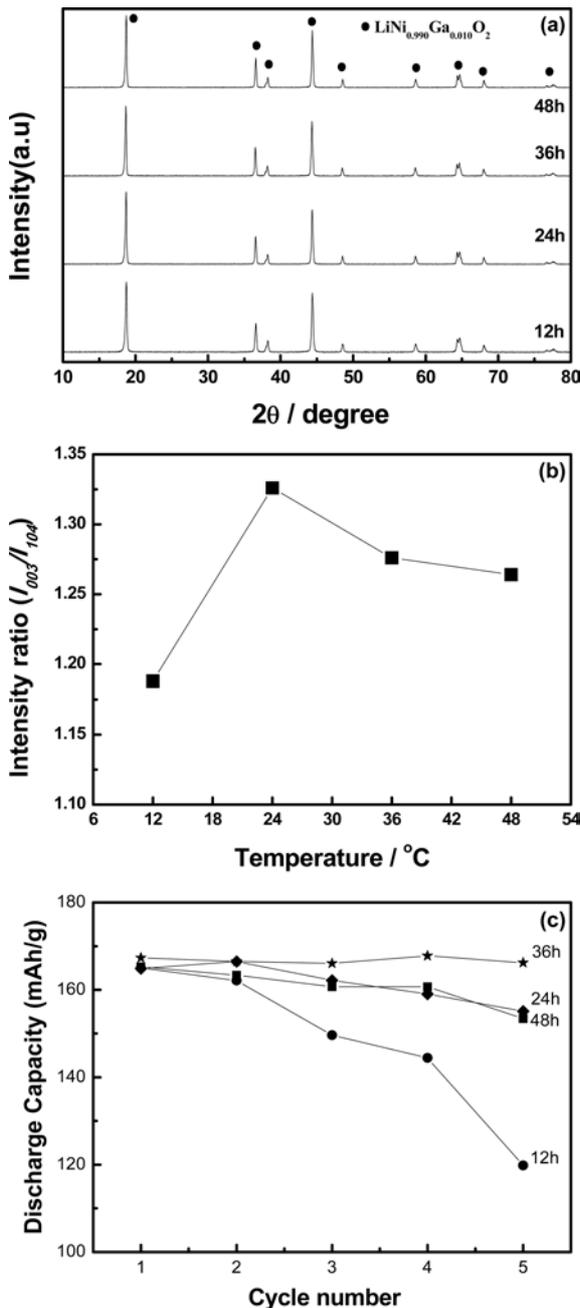


Fig. 3. XRD patterns (a), intensity ratio (b), and cyclic discharge capacities (c) of $\text{LiNi}_{0.990}\text{Ga}_{0.010}\text{O}_2$ synthesized powder for various times at 700°C .

value of 164.88 mAh/g at 700°C and then decreased with increasing temperature. The lowest discharge capacity at 650°C was due to the poorly developed crystal. The decreasing discharge capacity above 750°C was caused by the decomposition of $\text{LiNi}_{0.990}\text{Ga}_{0.010}\text{O}_2$ to $\text{Li}_{1-x}\text{Ni}_x\text{Ni}_{0.990-x}\text{Ga}_{0.010}\text{O}_2$ with disordered cation distribution [12, 13].

To determine the optimum synthesis time, $\text{LiNi}_{0.990}\text{Ga}_{0.010}\text{O}_2$ powders were varied with time at 700°C . The XRD results, I_{003}/I_{104} ratios, and discharge capacities of the powders synthesized at 700°C for 12~48hrs are

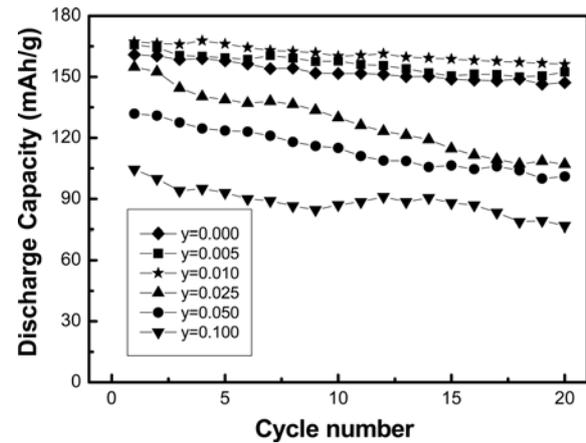


Fig. 4. Discharge capacity of $\text{LiNi}_{1-y}\text{Ga}_y\text{O}_2$ powder (700°C , 36hrs) with cycle number.

Table 1. Discharge capacities and fading rates of $\text{LiNi}_{1-y}\text{Ga}_y\text{O}_2$.

Parameter	Value					
Value of y in $\text{LiNi}_{1-y}\text{Ga}_y\text{O}_2$	0.100	0.050	0.025	0.010	0.005	0.000
1 st discharge capacity (mAh/g)	104.47	131.90	154.84	167.30	165.81	160.91
Final discharge capacity (mAh/g)	76.73	101.00	107.05	156.23	152.41	147.13
Fading rate (%)	26.55	23.43	30.86	6.62	8.08	8.56

shown in Fig. 3. All XRD patterns show that the single phase of $\text{LiNi}_{0.990}\text{Ga}_{0.010}\text{O}_2$ was synthesized irrespective of the holding times (Fig. 3(a)). The highest value of I_{003}/I_{104} ratios, 1.326, was obtained at 24 hrs as shown in Fig. 3(b), but the highest discharge capacity was obtained in 36hrs. From the above results, it was determined that the optimum condition to synthesize $\text{LiNi}_{0.990}\text{Ga}_{0.010}\text{O}_2$ was heating at 700°C for 36 hrs. Therefore, the complete experimental range of compositions, $\text{LiNi}_{1-y}\text{Ga}_y\text{O}_2$ ($y=0.000, 0.005, 0.010, 0.025, 0.050, 0.100$), were synthesized at this condition. The XRD patterns of powders with varying Ga amounts show the single layered structure without any relation (not shown). The cyclic charge-discharge properties of $\text{LiNi}_{1-y}\text{Ga}_y\text{O}_2$ powder synthesized at 700°C for 36hrs were measured for 20 cycles and are shown in Fig. 4. The first discharge capacity and fading rate according to the cycles of the charge-discharge test are listed in Table 1. The composition of $\text{LiNi}_{0.990}\text{Ga}_{0.010}\text{O}_2$ shows the highest initial discharge capacity of 167.30 mAh/g and the lowest fading rate of only 6.62% in the $\text{LiNi}_{1-y}\text{Ga}_y\text{O}_2$ (0.000y0.100) system. Also, $\text{LiNi}_{0.990}\text{Ga}_{0.010}\text{O}_2$ shows a relatively high initial discharge capacity and low fading rate (165.81 mAh/g and 8.08%) compared with LiNiO_2 . The electrochemical property was improved by substituting the 0.010 fraction of Ni

ion with Ga ion in LiNiO_2 . The substitution of nickel ion with gallium ion in LiNiO_2 increases the crystal structure stability but also renders Li^+ difficult to intercalate into the crystal structure because of the fixed valance of gallium ion.

Conclusions

The cathode material, $\text{LiNi}_{1-y}\text{Ga}_y\text{O}_2$, was synthesized using the emulsion method and formed at various temperatures and times in an oxygen stream. The most suitable synthesized condition was heating at $700\text{ }^\circ\text{C}$ for 36hrs. The discharge capacity of $\text{LiNi}_{1-y}\text{Ga}_y\text{O}_2$ increased until $y=0.010$ and decreased above $y=0.025$. $\text{LiNi}_{0.990}\text{Ga}_{0.010}\text{O}_2$ showed the highest initial discharge capacity and improved cycle life. The initial and final discharge capacities after 20 cycles were 167.30 mAh/g and 156.23 mAh/g , respectively. The fading rate was only 6.62% after 20 cycles of charge-discharge.

Acknowledgments

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