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Electrochemical properties of $LiNiO_2$ cathode material synthesized by the emulsion method

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Abstract

$LiNiO_2$ powder, cathode material of Li secondary battery, was prepared by the emulsion method. Shape, crystal phase and electrochemical properties of the powders heated to various temperatures for various times were investigated by SEM, XRD and a charge–discharge tester. Single phase $LiNiO_2$ could be synthesized at 700 °C for 24 h, i.e. at a lower temperature compared with other processes. The optimum heating temperature and time for $LiNiO_2$ synthesis were 750 °C and 24 h in an oxygen stream. The powder calcined at 750 °C for 24 h has the highest $I_{0\,0\,3}/I_{1\,0\,4}$ value and the first largest discharge capacity (161 mAh g^{-1} at the 1st cycle and 147 mAh g^{-1} at the 20th cycle).

Keywords: Lithium ion secondary battery; $LiNiO_2$; Cathode material; Emulsion method; Electrochemical property

1. Introduction

Various kinds of $LiMO_2$ (M = Ni, Co) type compounds and $LiMn_2O_4$ have been studied intensively as cathode electrode materials of secondary batteries over the past two decades [1–4]. Of these, $LiNiO_2$ is one of the most promising cathode materials because it has high operating voltage, high discharge capacity, high energy density, low production cost and low environmental pollution compared to $LiCoO_2$ cathode material [5,6]. However, there are some problems involved in applying $LiNiO_2$ as cathode electrode material. One of these is the difficulty in the synthesis because of the high vapor pressure of lithium oxide and the presence of Ni^{2+} at Li and Ni^{3+} site in $LiNiO_2$, leading to the nonstoichiometric composition $Li_{1-x}Ni_{1+x}O_2$.

Among the several methods reported to synthesize $LiNiO_2$, the solid-state reaction method [7,8] and solution methods such as coprecipitation [9], sol–gel [10] and ultrasonic spray pyrolysis [11] need some steps of precalcination, grinding and calcination to yield single phase $LiNiO_2$.

The emulsion method is a useful process to synthesize multi-component material systems [12,13]. In this method, an organic phase consisted of surfactant, solvent and emulsifying agent divides precursor solution of starting materials into water-in-oil type emulsion by high-speed agitation. Each emulsion has spherical shape with colloidal size and same composition. It is considered that the emulsion could be decomposed and crystalline solid could be synthesized easily by calcination at proper temperature. This emulsion method is more preferable for the synthesis of layered $LiNiO_2$ powders than any other process. In this work, we investigated optimum conditions for the synthesis of $LiNiO_2$ by emulsion method and electrochemical properties of $LiNiO_2$ such as phase transition, discharge capacity and cycle life, etc.

2. Experimental procedure

The starting materials used for the synthesis of $LiNiO_2$ were $LiOH{\cdot}H_2O$ (99.95%, Aldrich Chemical Company, Inc. USA) and $Ni(NO_3)_2{\cdot}6H_2O$ (99.99%, High Purity Chemicals, Japan). These materials were dissolved into distilled water and mixed on the magnetic stirrer for 24 h to prepare precursor solution with the concentration 0.5 mol L^{-1} for $LiNiO_2$ composition. Organic phase for emulsifying was prepared from mixing of span 80 (5 (v%/v%)), kerosene (92 (v%/v%)) and paraffin oil (3 (v%/v%)) on the magnetic stirrer for 24 h.

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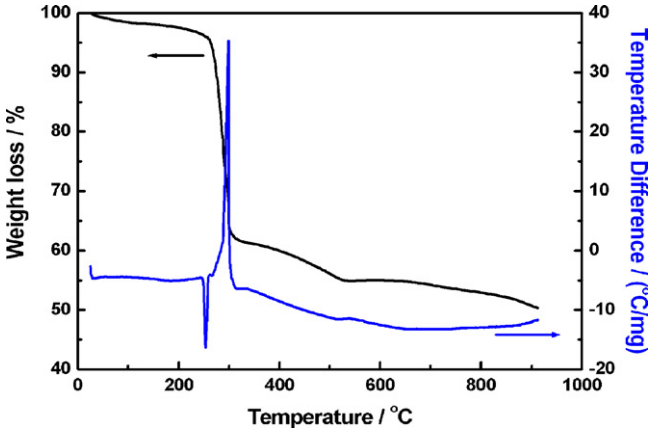

Fig. 1. DT-TGA curves of the as-dried powder.

The precursor solution and organic phase were mixed in the ratio of 2:1 and rotated at the speed of 4000 rpm for 5 min to be water-in-oil type emulsion. To evaporate the water included in the emulsion rapidly, the prepared emulsion was sprayed into the petroleum heated at 170 °C. The powder was filtered from petroleum and dried at 120 °C in the oven. Thermal analysis of the emulsion-derived powder was carried out with a heating rate of 10 °C min^{-1} using DT-TGA apparatus.

The emulsion-derived powder was calcined under flowing oxygen gas at the temperature range of 650 ~ 850 °C for various times with heating and cooling rate of 100 °C h^{-1}. The crystal phase of the calcined powder was examined using X-ray diffractometer (XRD: Rigaku, D/MAX-111A) with Cu Kα radiation operated at 40 kV, 40 mA and scanning speed of 4° min^{-1}. The shape of the particles and microstructure was observed with a scanning electron microscope (SEM: JEOL JSM-6400). The electrochemical properties of samples were tested at room temperature for 20 cycles with half cell fabricated as Li metal/electrolyte 1M $LiPF_6$-ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume)/positive material. The positive electrode consisted of $LiNiO_2$ powder as cathode material, acetylene black as conductor and PTFE as binder at the ratio of 88:10:2 by weight. Lithium foil and glass micro-fiber filter (GF/A, Whatman) were implemented as an anode and separator, respectively. The cells were automatically charged and discharged between 2.7 and 4.2 V at 9.5 mA g^{-1}.

3. Results and discussion

Fig. 1 shows the DT-TGA curves of as-dried powder. There are two peaks in the DTA curve and abrupt weight loss is observed at the peak temperatures. The endothermic peak at 253 °C is due to the decomposition of nickel nitrate and exothermic peak at 298 °C came from oxidation of organic phases, which were used to emulsify the homogeneous mixed solution.

The SEM photograph and XRD pattern of the as-dried powder are shown in Fig. 2. This powder has a porous spherical shape agglomerated with small particles because this powder was dried rapidly by spraying the emulsion into the petroleum heated at 170 °C. This XRD pattern of the as-dried powder was identified only as $Ni_4(NO_3)_2{\cdot}(OH)_4$ crystal without the peaks for lithium salt. This means that $Ni_4(NO_3)_2{\cdot}(OH)_4$ was precipitated due to the solubility in water in spite of the rapid drying, but lithium salt was kept as amorphous state during drying the emulsion.

From DT-TGA curves, all the endothermic and exothermic reactions occurred under 400 °C in air. The crystal phase and powder shape were examined with SEM and XRD after heating the as-dried powder at 400 °C and are shown in Fig. 3. SEM photograph shows powder shape agglomerated with fine particles under100 nm. XRD pattern was identified as $Li_{1-x}Ni_{1+x}O_2$, NiO, Li_2CO_3 and an unknown peak. It is considered that NiO was formed from the decomposition of $Ni_4(NO_3)_2{\cdot}(OH)_4$ which is precipitated in the process of drying emulsion, Li_2CO_3 was made from the reaction between Li_2O and carbon decomposed from $Li(OH){\cdot}H_2O$ and organic phase, and a little of $Li_{1-x}Ni_{1+x}O_2$ was formed from the reaction between NiO and Li_2O while heating the as-dried powder at 400 °C. These events suggest that $LiNiO_2$ should be synthesized through the solid-state reaction between NiO and Li_2CO_3 during calcination.

The as-dried powder was calcined at the various temperatures of 650 ~ 850 °C for 24 h to determine the

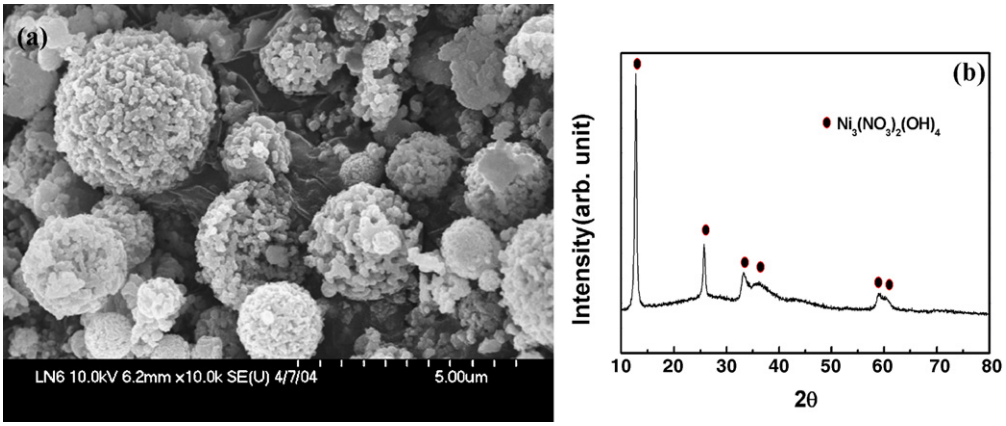

Fig. 2. SEM photograph (a) and XRD pattern (b) of the as-dried powder.

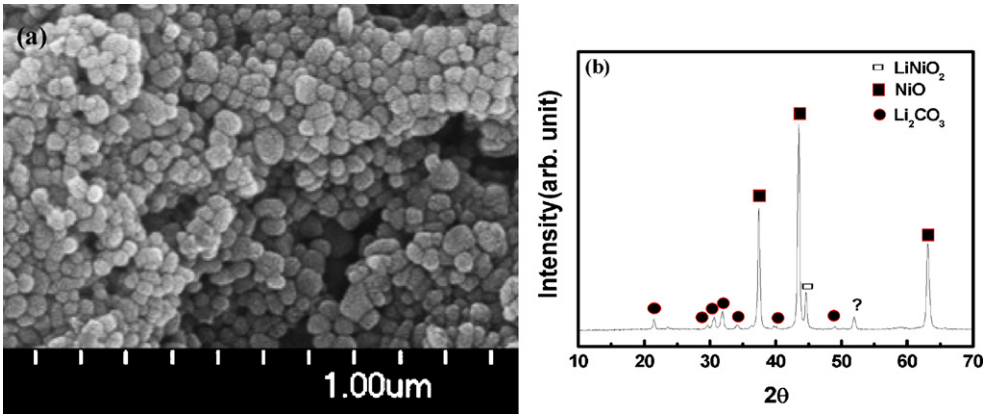

Fig. 3. SEM photograph (a) and XRD pattern (b) of the powder calcined at 400 °C.

temperature to synthesize $LiNiO_2$ single phase. Fig. 4 shows the XRD patterns of the calcined powder and intensity ratio of (0 0 3) and (1 0 4) peaks ($I_{0\,0\,3}/I_{1\,0\,4}$). All the observed XRD peaks above 700 °C are assigned to $LiNiO_2$ layered crystal structure only. However, a small quantity of Li_2CO_3 remained as an unreacted material in the powder calcined at 650 °C. This means that 650 °C is not high enough for Li_2CO_3 to react with NiO completely to form $LiNiO_2$. The calcination temperature, 700 °C which single phase could be synthesized is a lower temperature compared with other processes, such as solid-state reaction and solution method. It has been reported that the value of $I_{0\,0\,3}/I_{1\,0\,4}$ could be used as a reliable criterion for the stoichiometry of $LiNiO_2$, which indicates the degree of displacement of nickel and lithium ions [7]. The value of $I_{0\,0\,3}/I_{1\,0\,4}$ increased from 0.65 at 650 °C to 1.13 at 700 °C abruptly, showed the largest value of 1.24 at 750 °C and then decreased with the increase of the calcination temperature. Decrease of the value of $I_{0\,0\,3}/I_{1\,0\,4}$ above 750 °C could be explained with the loss of lithium from the host structure due to the high vapor pressure of lithium at a high calcination temperature [14].

The decrease of the value of $I_{0\,0\,3}/I_{1\,0\,4}$ indicates the formation of $Li_{1-x}Ni_{1+x}O_2$ from $LiNiO_2$. $Li_{1-x}Ni_{1+x}O_2$ has a disordered cation distribution which Ni occupy the lithium site partially in the layered structure and affects the electrochemical properties [15,16]. The first through fifth cycle discharge capacities of the powder calcined at various temperatures for 24 h are shown in Fig. 5. In Fig. 5(a), the first discharge capacity increased to the maximum value of 161 mA g^{-1} at 750 °C and decreased with increasing calcination temperature. Low discharge capacity below 750 °C resulted from unreacted Li_2CO_3 at 650 °C and poorly developed crystal at 700 °C. Decrease in discharge capacity above 750 °C could be explained with the decomposition of $LiNiO_2$ to $Li_{1-x}Ni_{1+x}O_2$ with disordered cation distribution at the lithium sites as described above [16]. This tendency in the variation of discharge capacity is similar to the value of $I_{0\,0\,3}/I_{1\,0\,4}$ changes. From the XRD patterns, the value of $I_{0\,0\,3}/I_{1\,0\,4}$ and discharge capacities of powders calcined at various temperatures, 750 °C is considered to be the optimum calcination temperature to synthesize $LiNiO_2$. However, all the discharge capacities except 650 °C were not as altered from a cycle number, as shown Fig. 5(b).

In this experiment, $LiNiO_2$ single phase could be synthesized and the value of $I_{0\,0\,3}/I_{1\,0\,4}$ was 1.13 at 700 °C. This temperature is lower than 750 °C which $LiNiO_2$ was prepared and the value of $I_{0\,0\,3}/I_{1\,0\,4}$ was 1.08 in the solid-state reaction method [17]. This means the powder prepared by the emulsion method has high reactivity because precursor solution was divided into water-in-oil type colloid with same composition and dried rapidly. This emulsion-derived powder

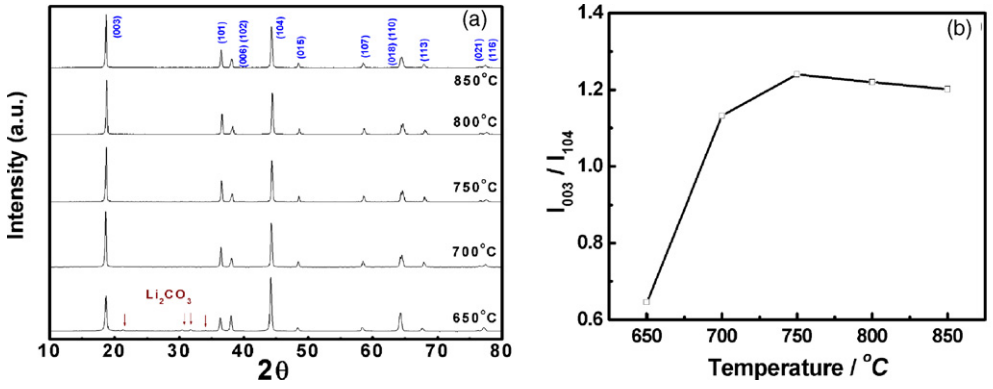

Fig. 4. XRD patterns (a) and the value of $I_{0\,0\,3}/I_{1\,0\,4}$ (b) of powders calcined at various temperatures for 24 h.

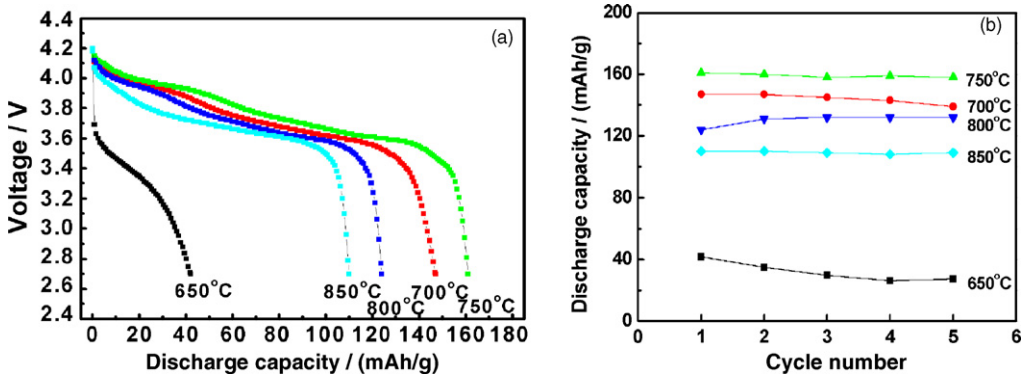

Fig. 5. First discharge capacity (a) and capacity changes with cycle (b) of the powders calcined at various temperatures for 24 h.

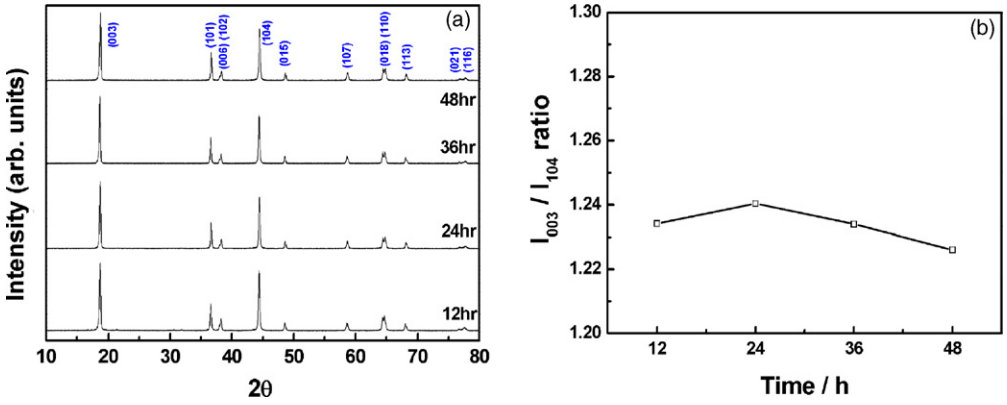

Fig. 6. XRD patterns (a) and the value of I_{003}/I_{104} (b) of the powders calcined at 750 °C for various times.

could react to be $LiNiO_2$ easily compared with other methods [7–11].

In order to determine the optimum calcination time, the as-dried powder was calcined at 750 °C for various times because the largest discharge capacity was obtained at 750 °C. Fig. 6 shows the XRD patterns and the value of I_{003}/I_{104} of the calcined powders. All the XRD patterns in Fig. 6(a) show that the single phase of $LiNiO_2$ was synthesized without any relation to holding times. All the values of I_{003}/I_{104} are above 1.22 and the highest value, 1.24 was obtained at 24 h calcination as shown in Fig. 6(b). However, the ratios were not so different on holding times. It is considered from the XRD patterns and the value of I_{003}/I_{104} that 12 h holding is not sufficient for $LiNiO_2$ crystal to grow well and more than 24 h holding makes $LiNiO_2$ to decompose into $Li_{1-x}Ni_{1+x}O_2$ as heating at high temperature [15,16]. From these results, 24 h is the optimum calcination time to synthesize $LiNiO_2$ at 750 °C.

The first through fifth cycle discharge capacities of the powder calcined for various times at 750 °C are shown in Fig. 7. The first discharge capacity increased to the maximum at 24 h and decreased with holding time as shown in Fig. 7(a). It is

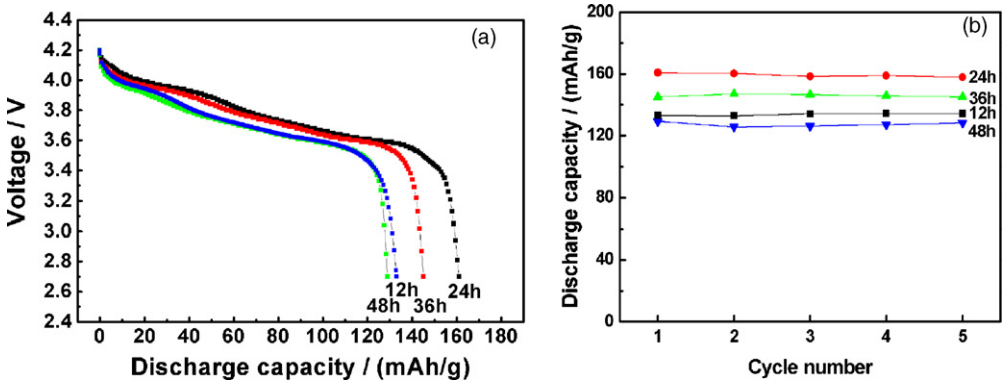

Fig. 7. First discharge capacities (a) and capacity changes with cycle (b) of the powders calcined at 750 °C for various times.

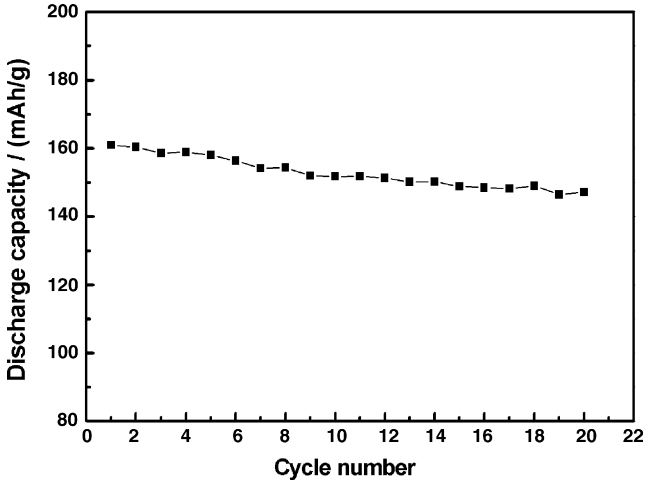

Fig. 8. Variation of discharge capacity with cycle number.

considered that $LiNiO_2$ crystal was not well-developed in heating for 12 h and $LiNiO_2$ decomposed to $Li_{1-x}Ni_{1+x}O_2$ in heating for more than 24 h. However, cyclic discharge capacities are not as different with a cycle number, as shown in Fig. 7(b).

To investigate the cycle life of the powder prepared using the emulsion method, charge–discharge capacity of $LiNiO_2$ powder synthesized at 750 °C for 24 h was measured because this condition is determined as the optimum condition in this experiment. Fig. 8 shows the variation of discharge capacity with cycle number. Discharge capacity is 161 mAh g^{-1} at the 1st and 147 mAh g^{-1} at the 20th cycle. The capacity fading from 161 mAh g^{-1} to 147 mAh g^{-1} was observed during charge–discharge cycling. The fading rate is 9% after 20th cycle. This fading is explained by substitution of Ni ion in lithium site, which results in the disturbance of diffusion of lithium ion in the charge–discharge process [16].

4. Conclusions

The cathode material, $LiNiO_2$ was prepared by the emulsion method and calcined at various temperatures and times in an oxygen atmosphere. $LiNiO_2$ single phase could be synthesized from 700 °C, which is a lower temperature compared with other processes, such as solid-state reaction and solution method. The optimum condition for the synthesis of $LiNiO_2$ cathode material was heating at 750 °C for 24 h. The powder calcined at 750 °C for 24 h has the largest first discharge capacity and also the highest value of I_{003}/I_{104}. The discharge capacity was 161 mAh g^{-1} at the 1st cycle and 147 mAh g^{-1} at the 20th cycle.

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