Synthesis and Electrochemical Properties of $LiNiO_2$ Cathode Materials by Emulsion Method

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Abstract

Powders of cathode material, $LiNiO_2$ were prepared by an emulsion method. It has been found that the optimum condition for the synthesis of $LiNiO_2$ is the heat treatment at 750℃ for 24 hr in oxygen atmosphere. The calcined powders have layered structure, and the shape of the particles is smoothly edged polyhedron. The average particle size was estimated at 0.5~1 μm from SEM photographs. For the measurements of electrochemical properties, the cells composed of Li/{1M-$LiPF_6$-(EC＋DMC)}/cathode materials were prepared. Charge-discharge tests were carried out galvanostatically in the voltage range between 2.7 V and 4.2 V. The discharge capacity of the $LiNiO_2$ electrode prepared in the optimum condition was 161 mAh/g at first, and 147mAh/g at the 20th cycle. **[Received February 9, Accepted February 17, 2005]**

Keywords : Lithium ion secondary battery, $LiNiO_2$, Cathode material, Emulsion method

1. Introduction

More than 200 materials have been evaluated for use as positive electrodes of secondary batteries$^{1-4)}$ over the past two decades. Of these, $LiNiO_2$ is a promising cathode material for lithium secondary batteries. It has a higher discharge capacity and is relatively excellent for economics and low environmental pollutions compared to commercial $LiCoO_2$$^{5,6)}$. Because of the high vapor pressure of lithium oxides and the difficulty to convert Ni^{2+} to Ni^{3+} ions, various methods for synthesis of $LiNiO_2$ have been reported. In an emulsion method, organic phase divides homogeneous mixed solution of starting materials into fine mists by high-speed agitation. All of these divided fine mists, that is, emulsion have spherical shape and homogenized composition. It is considered that these emulsions could be easily decomposed and reacted to synthesize crystalline solid by calcination at proper temperatures. This emulsion method will be more preferable for the synthesis of layered $LiNiO_2$ powders than any other processes. 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

Experimental procedure is shown in Fig. 1.
LiOH・H_2O (99.95%, Aldrich Chemical Company,

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[2] 韓国のProf. KIM Bok-Hee（金福煕）全北大学教授は日本学術振興会（JSPS）二国間交流事業にもとづき，Korea Science and Engineering Foundation（KOSEF）より指名されて名古屋工業大学セラミックス基盤工学研究センター解析設計研究部門の石澤・井田研究室に派遣され，平成16年12月20日から平成17年１月16日まで同研究室に滞在し，「酸素分圧を制御した$LiNiO_2$の結晶構造解析」を研究テーマとして粉末X線回折を用いた研究を行った。本論文はこの研究交流の背景となった論文である。

Inc.) and $Ni(NO_3)_2 \cdot 6H_2O$ (99.99%, High Purity Chemicals, Japan) were used as starting materials to prepare mixed aqueous solutions (0.5 mol/L for the $LiNiO_2$ composition). Aqueous solutions of the starting materials were mixed on the magnetic stirrer for 24 hr. Span 80 (5 v/v%) for the surfactant, kerosene (92 v/v%) for solvent and paraffin oil (3 v/v%) for emulsifying agent were also mixed on the magnetic stirrer for 24 hr to prepare organic phase. The aqueous solution and organic phase were mixed in the ratio of 2:1 and emulsified at the speed of 4000 rpm for 5 min. To evaporate water and petroleum included in the water-in-oil type emulsions, the prepared emulsions were dropped into the petroleum heated at 170℃[7] in the silicon oil bath and dried at 120℃ in the oven. Thermal analysis of the emulsion-derived powders was carried out with heating rate of 10℃ /min using DT-TGA. The crystal structures of the calcined powders were examined with an X-ray diffractometer (XRD: Rigaku, D/MAX-111A) with CuKα radiation operated at 40 kV, 40 mA and scanning speed of 4°/min. The shape of the particles and microstructure were observed with a scanning electron microscope (SEM: JEOL JSM-6400). The electrochemical properties of samples were tested at room temperature with half cell in Li metal/ electrolyte 1M $LiPF_6$-ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume)/ cathode material. The cathode materials consist of $LiNiO_2$ powder, acetylene black as conductor and PTFE as binder at the ratio of 88:10:2 by weight. Lithium foil and glass micro-fibre filters (GF/A, Whatman) were used for anode and separator, respectively. The cells were automatically charged and discharged in the range between 2.7 and 4.2 V at 9.5 mA/g.

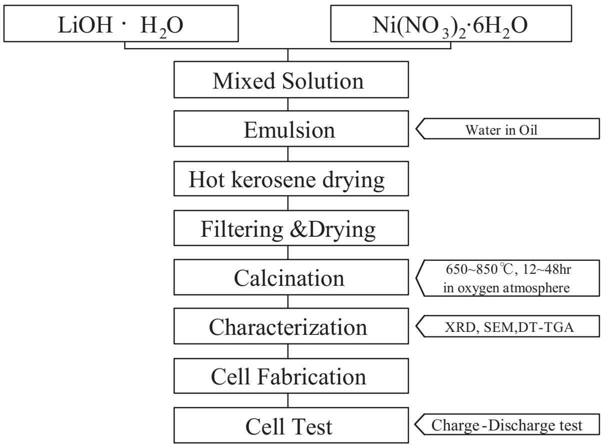

Fig. 1. Experimental procedure.

3. Results and Discussions

The XRD patterns of the $LiNiO_2$ powder synthesized at 650～850℃ for 24 hr in the oxygen atmosphere are shown in Fig. 2 (a). All the observed XRD peaks are assigned to the layered structure except some peaks observed for the powder calcined at 650℃, which can be assigned to residual Li_2CO_3 peaks. From this, it is concluded that 650℃ is not a sufficient temperature to form $LiNiO_2$.

The intensity ratio of the 003 peak to 104 peak, I_{003}/I_{104} is used to examine the cation mixing of Li^+ and Ni^{2+} in $LiNiO_2$[8]. The powder calcined at 750℃ has the highest I_{003}/I_{104}. It also shows a distinct separation between 006 and 102 peaks in the XRD pattern. These mean that the $LiNiO_2$ powder synthesized at 750℃ has better crystallinity than powders synthesized at any other temperatures.

In order to determine the optimum calcination time at 750℃, the dried powder was calcined for various heating periods. The XRD patterns of the $LiNiO_2$ powder synthesized at 750℃ for 12 hr, 24 hr, 36 hr and 48 hr in oxygen atmosphere are shown in Fig. 2 (b)

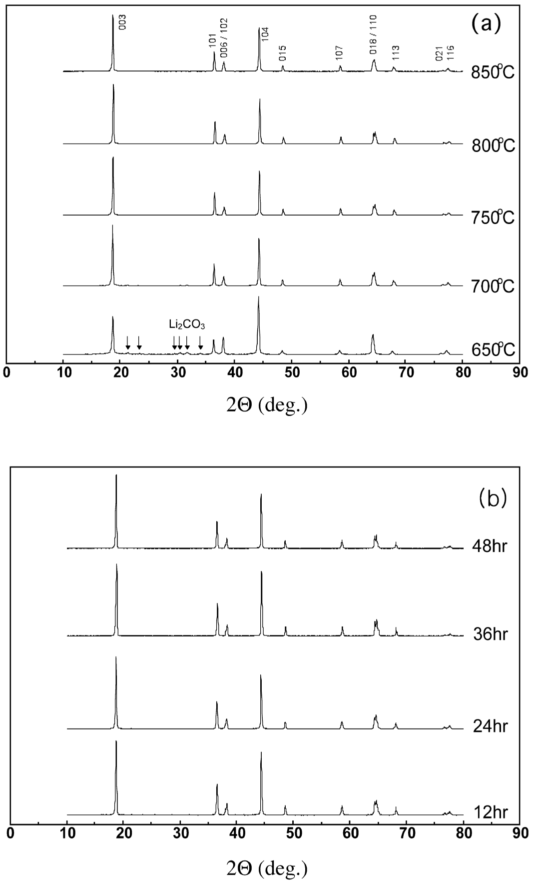

Fig. 2. XRD patterns of $LiNiO_2$ synthesized (a) at various temperatures for 24 hr and (b) at 750℃ for various heating periods.

The XRD peaks of the powders calcined at 750℃ for various heating periods show that the specimen is a single phase of $LiNiO_2$. We could not determine the optimum calcination time only from the XRD patterns. Thus, investigation of charge-discharge test was carried out for the powder calcined for various heating periods.

The SEM photographs of $LiNiO_2$ powder dried at 170℃ and calcined at 750℃ are shown in Fig. 3. The dried powder was a collection of spherical agglomerates of about 100 nm particles. The calcined powder was a collection of particles with similar shape and size. The particles appear to be smooth-edged polyhedron and the average size was approximately 0.5∼1 μm.

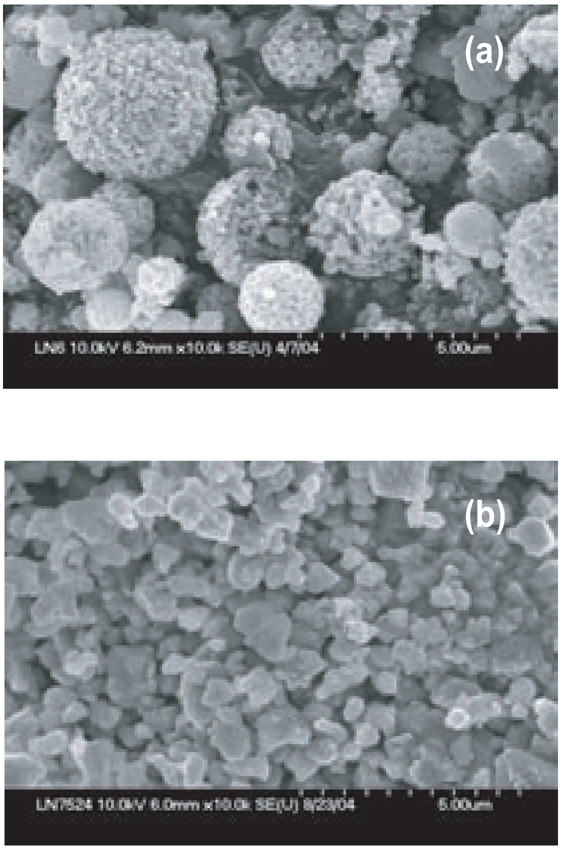

Fig. 3. SEM photographs of powder (a) dried at 170℃, (b) calcined at 750℃ for 24 hr

Fig. 4 shows the first discharge curves of $LiNiO_2$ electrode prepared for various temperatures and calcination periods in oxygen atmosphere. The curves exhibit two or three plateaus, which indicate that phase transitions occur during intercalation and de-intercalation of Li ion. The $LiNiO_2$ electrode calcined at 750℃ has the largest discharge capacity. It was expected from the highest I_{003}/I_{104} ratio of the powder synthesized at 750℃.

The $LiNiO_2$ powder synthesized at 750℃ for 24 hr has greater first discharge capacity than for any other heating periods.

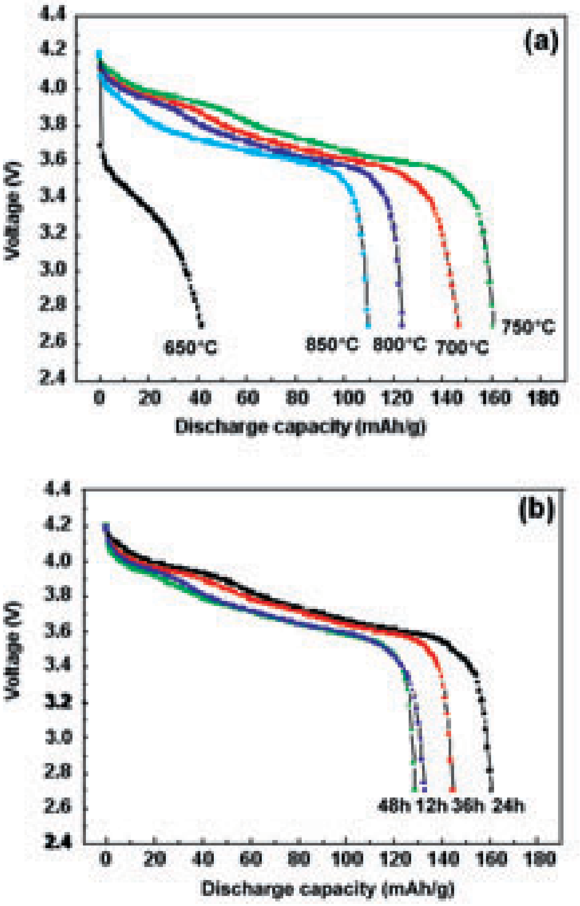

Fig. 4. First discharge capacity of $LiNO_2$ calcined (a) at various temperatures for 24 hr and (b) for various periods at 750℃.

Fig. 5 shows the discharge capacity of $LiNiO_2$ electrode during the initial 5 discharge-charge cycles. The discharge capacity change of specimens for any calcination temperature and periods is not strongly dependent on the cycle number except the specimen calcined at 650℃.

Fig. 6 shows the discharge capacity with cycle number for the $LiNiO_2$ electrode synthesized at 750℃ for 24 hr. The discharge capacity was 161mAh/g at first and 147mAh/g at the 20th cycle and the rate of decrease in discharge capacity was 9% after 20th cycle.

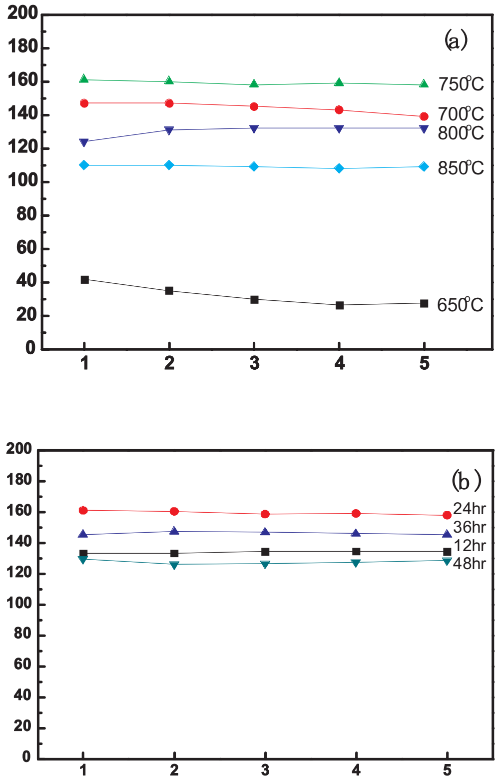

Fig. 5. Discharge capacity of $LiNiO_2$ synthesized (a) at various temperatures for 24 hr, (b) for various periods at 750℃.

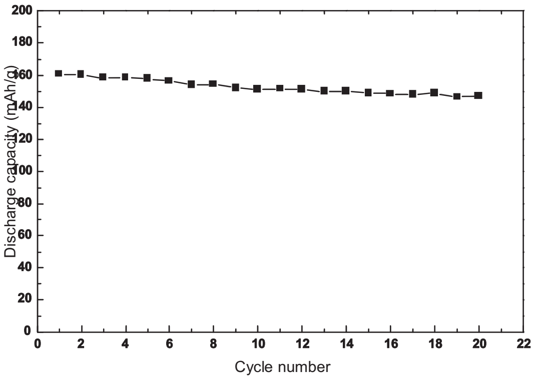

Fig. 6. Discharge capacity of $LiNiO_2$ synthesized at 750℃ for 24 hr for the initial 20 cycles.

Conclusion

The cathode material, $LiNiO_2$ was prepared by an emulsion method and calcined at various temperatures and periods in oxygen atmosphere. The optimum condition for synthesis of $LiNiO_2$ cathode material was heating at 750℃ for 24 hr. The discharge capacity was 161 mAh/g at the 1st cycle and 147 mAh/g at the 20th cycle.

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